DOI: 10.1002/zaac.201200102

Major Distinctions in the Molecular and Supramolecular Structures of Selenium-containing Organotins, (o-MeSe-$C_6H_4CH_2$)$SnPh_{3-n}Cl_n$ (n = 0, 1, 2)

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Dedicated to Professor Klaus Jurkschat, our favorite Lehrstuhl, on the Occasion of His 60th Birthday

Keywords: Organotins; Selenium; Tin; Supramolecular chemistry; X-ray diffraction

Abstract. The synthesis and characterization of selenium-containing stannanes, (o-$MeSeC_6H_4CH_2$)$Sn(Ph)_{3-n}Cl_n$ [n = 0 (**1Se**); 1 (**2Se**); 2 (**3Se**)], is presented. The increasing Lewis acidity at tin in the series **1Se** → **2Se** → **3Se** is reflected in their respective solid state arrangements and supramolecular architecture by interactions of the type Se···Se, Sn···Se, and Cl···H–C. Overall the capacity of the selenium atom to form bidentate interactions creates geometric assemblies distinctly different to those of the oxygen and sulfur analogs.

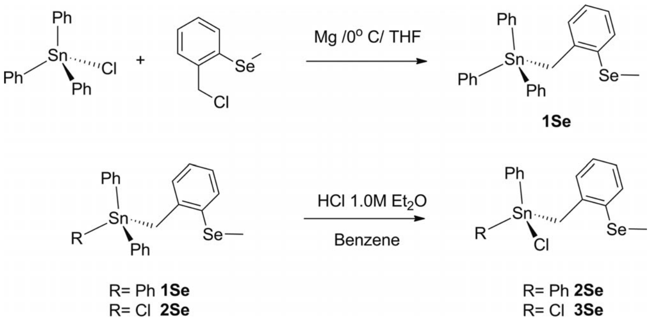
Introduction

Organotin(IV) compounds are socially useful as agrochemicals, biocides, catalysts, and stabilizers in PVC.[1] However, along with this utility there is a great concern about their toxic impact in the environment.[2] An option for reducing such bioimpact is to block the available coordination sites at the central tin atom by intramolecular coordination.[3] We have been studying such complexes using oxygen and sulfur as donating atoms,[4] and have reported very clear and strong intramolecular bonding motifs between these group 16 elements and tin in complexes of the general form (MeE-$C_6H_4CH_2$)$SnPh_{3-n}Cl_n$ (E = O, S). These interactions clearly increase as the Lewis acidity of the tin atom increases, i.e. as n changes from 0 → 1 → 2. Selenium is often structurally distinct from it lower mass group 16 analogs and, for example, features non-bonding interactions with different elements including itself,[5] and it also has significant utility as a catalyst.[6]

We now report the synthesis, spectral and structural characterization of new selenium-containing organotin compounds, where selenium has the potential for exhibiting varying strength intramolecular coordination to the central tin atom, (o-$MeSeC_6H_4CH_2$)$Sn(Ph)_{3-n}Cl_n$ [n = 0 (**1Se**); 1 (**2Se**); 2 (**3Se**)].

Results and Discussion

The title compounds are readily synthesized, purified, and characterized using the synthetic route previous described for the oxygen and sulfur analogs (Scheme 1). All spectroscopic data are in total accord with the proposed formulations.



Scheme 1.

The substitution of Sn–C bonds by Sn–Cl bonds results in an increase in the Lewis acidity of the tin,[3,4] making any potential intramolecular interactions stronger. The arrangement at the tin atom is a powerful tool for determining the formation and strength of these interactions. Without any interaction, the tin atom should be tetrahedral (bond angle 109.4°), for a tin atom with a [4+1] environment the arrangement changes from tetrahedral monocapped (TEMC)[7] to trigonal bipyramidal (TBP). For a [4+2] environment, the variable structure pathway is from the tetrahedral bicapped (TEBC) to octahedral.

The structure of the tetraorganotin compound **1Se** reflects it having a weak intramolecular Sn···Se interaction reflecting the lowest tin Lewis acidity of the series **1Se**–**3Se** (Figure 1). The Sn···Se internuclear distance is 3.984(1) Å, which is ca. 98 % of the sum of the respective van der Waals radii (ΣvdW = 4.07 Å). The [4+1] environment around tin is best represented as a monocapped tetrahedral as indicated by the following parameters: Σax = 304.4°, Σeq = 348.3°, ΣNu = 218.4°.[8] This arrangement is the same as that of the sulfur and oxygen ana-

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logs, and indeed **1Se** is isostructural with the sulfur analog showing that the volume is similar ($\mathrm{Se}_{\mathrm{vdW}}$ = 1.9 Å, $\mathrm{S}_{\mathrm{vdW}}$ = 1.80 Å, $\mathrm{O}_{\mathrm{vdW}}$ = 1.52 Å). Another parameter to assess the strength of any Sn···Se interaction is the distance of the central tin atom to the tetrahedral faces formed by the substituents; in the case of **1Se** this value is ≈ 0.7 Å for all the faces showing that the Sn···Se interaction is negligible.

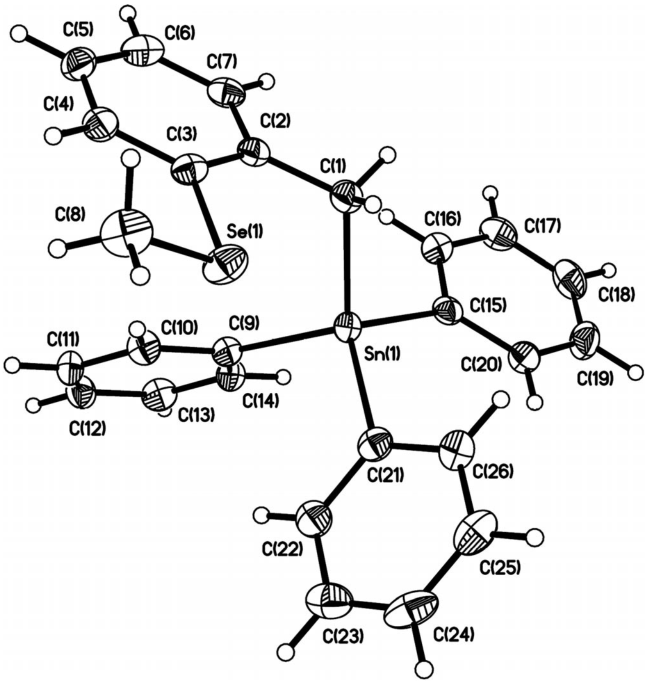

Figure 1. Molecular structure of **1Se**. The levels of probability of the ellipsoids are 50 %.

When one phenyl group is replaced by chlorine (**2Se**), the structural environment around the tin atom remains [4+1] (Figure 2). The increased Lewis acidity is reflected by a shorter internuclear Sn···Se distance of 3.312(2) Å (81 % ΣvdW) and a shorter distance of the tin atom to the face attacked by the selenium (≈ 0.4 Å) in comparison to the other three (≈ 0.8 Å). The arrangement is TEMC (Σax = 301.3°, Σeq = 350.3°, ΣNu = 240.3°) with the selenium *anti* to the chlorine (Table 1). Comparing it to the oxygen and sulfur analogs the arrangement around tin is almost the same; in addition the Sn–Cl distances are equivalent in all three compounds, 2.399(1) Å (for **2O**), 2.413(1) Å (for **2S**), and 2.402(5) Å (for **2Se**), suggesting that the strength of the interaction in the solid state for these three analogs is similar.

Replacement of two phenyl groups by chlorines (**3Se**) (Figure 3), significantly increases the tin Lewis acidity and the structure of this compound is distinctly different to that of **1Se**, **2Se**, and the oxygen and sulfur analogs **3O** and **3S**.[4] In general diorganotindichlorides often exhibit the formation of coordination oligomers and polymers by increasing their coordination to six by intermolecular Sn···Cl interactions (Table 1). In the case of **3Se** two isomers, **3Se**(**a**) and **3Se**(**b**), were found in the asymmetric unit and in both isomers tin has an environment [4+2]. However, this is not due to any intramolecular Sn···Cl interactions, but due to bridging intra- and intermolecular contacts Se···Sn···Se (Se···Sn ≈ 3.4 and 3.6 Å, respectively, Table 1), a situation not previously observed. The Se···Sn intramolecular interaction is about 83 % of ΣvdW. The arrangement at tin in both conformers is TEBC distorted, with the C–Sn–C and Cl–Sn–Cl bond angles of ca. 136° and ca. 99°, compared to the remaining angles clustering about 109° (Table 1). Each selenium atom approaches the tin atom in an *anti* position to the chlorine atoms, Cl–Sn–Se ≈ 165°, thereby generating a flattening of the corresponding tetrahedral faces. Thus, the distance from the tin atom to the face approached by the selenium atom is only ≈ 0.5 Å, whereas to the other faces it is ≈ 1.0 Å. The strength of both interactions (intra and intermolecular) can be assessed as the same after comparison of the Sn–Cl bond lengths (Table 1).

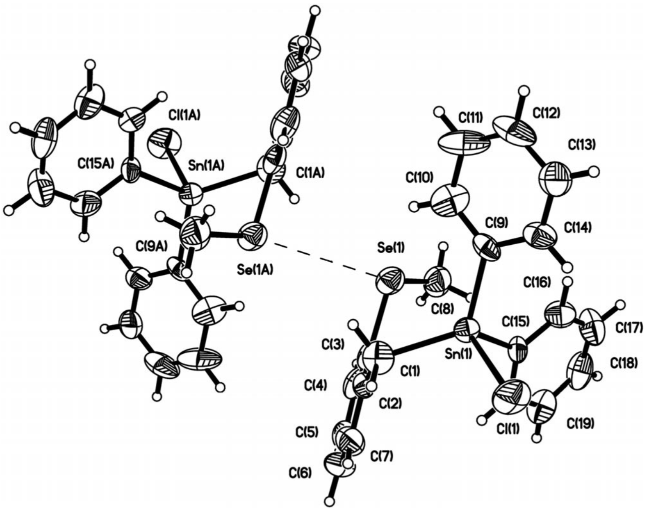

Figure 2. Molecular structure of **2Se**. The levels of probability of the ellipsoids are 30 %.

Do the Interactions Survive in Solution?

The degree to which solid-state structures reflect solution structures is always a thorny aspect of structural chemistry and in the case of organotin compounds, the use of $^{119/117}$Sn NMR can be a very useful tool. For the series of compounds reported herein we can use the ^{119}Sn chemical shifts for the series $\mathrm{Ph}_{4-n}\mathrm{SnCl}_n$ (n = 0–4)[9] as a standard set reflecting the change in Lewis acidity at the central tin atom, where no intramolecular interactions play a role. This can be done also because the ^{119}Sn δ for $(\mathrm{Ph})_4\mathrm{Sn}$ and $(\mathrm{Ph})_3\mathrm{Sn(Bn)}$ are similar (–120 and –118 ppm, respectively)[9] allowing us to disregard factors other than any intramolecular interactions when comparing the chemical shifts for **1Se**, **2Se**, and **3Se**. Apart from the possible intra- and intermolecular interactions noted above the most important variation is clearly the charge distribution around tin due to the substitution of the Ph groups by chlorine atoms.[9,10] This well-known effect is reflected in Figure 4 where the plot of ^{119}Sn δ versus the number of chlorine atoms (n) forms the familar parabolic relationship as $n = 0 \rightarrow 1 \rightarrow 2 \rightarrow 3$.

We anticipate that the ^{119}Sn δ in solution of compounds **1–3** to be modified accordingly with the strength of the interaction

Table 1. Selected bond lengths /Å and dihedral angles /° through the series.

	1Se	**2Se**	**3Se(a)**$^{a)}$	**3Se(b)**$^{a)}$
Sn–C(1)	2.183(3)	2.137(16)	2.140(11)	2.157(12)
Sn–C(9)	2.135(3)	2.091(15)	2.125(12)	2.137(8)
Sn–C(15)	2.133(3)	2.137(15)	–	–
Sn–C(21)	2.141(3)	–	–	–
Sn–Cl(1)	–	2.402(5)	2.357(3)	2.364(3)
Sn–Cl(2)	–	–	2.352(3)	2.365(3)
Se–C(3)	1.916(3)	1.909(18)	1.919(12)	1.944(12)
Se–C(8)	1.940(4)	1.941(18)	1.906(12)	1.917(7)
Se···Se$^{b)}$	–	3.737(4)	–	–
Sn···Se	3.984(1)	3.312(2)	3.426(2)	3.366(1)
Sn···Se^{c}	–	–	3.653(2)	3.682(2)
C(1)–Sn–C(9)	112.4(1)	117.7(6)	133.1(4)	139.7(4)
C(1)–Sn–C(15)	103.9(1)	119.5(6)	–	–
C(1)–Sn–C(21)	113.1(1)	–	–	–
Cl(1)–Sn–Cl(2)	–	–	95.8(1)	99.9(1)
Se···Sn–C(1)	50.9(1)	68.8(5)	61.7(3)	64.6(3)
Se···Sn–C(9)	95.3(1)	95.3(5)	88.4(3)	88.4(2)
Se···Sn–C(15)	150.9(1)	79.2(4)	–	–
Se···Sn–C(21)	74.2(1)	–	–	–
Se···Sn–Cl(1)	–	162.7(1)	82.8(1)	166.5(1)
Se···Sn–Cl(2)	–	–	164.0(1)	84.4(1)
Se···Sn–C(1)$^{d)}$	–	–	76.8(3)	77.4(3)
Se···Sn–C(9)$^{d)}$	–	–	79.3(3)	78.7(2)
Se···Sn–Cl(1) $^{d)}$	–	–	168.1(1)	75.2(1)
Se···Sn–Cl(2)$^{d)}$	–	–	72.7(1)	175.0(1)
Se···Sn-Se$^{d)}$	–	–	107.3(4)	100.0(4)
C(3)–Se–C(8)	99.8(1)	99.2(7)	100.9(6)	100.6(4)
Sn···Se–C(3)	72.9(1)	79.6(5)	80.7(4)	80.2(4)
Sn···Se–C(8)	166.2(1)	106.2(5)	133.5(4)	126.7(2)
Sn···Se–C(3)$^{c)}$	–	–	114.2(3)	115.6(4)
Sn···Se–C(8)$^{c)}$	–	–	103.4(2)	97.6(4)
Sn···Se···Sn$^{e)}$	–	–	124.0(1)	125.0(1)
C(3)–Se···Se$^{b)}$	–	91.6(4)	–	–
C(8)–Se···Se$^{b)}$	–	147.9(5)	–	–

a) **3Se(a)** and **3Se(b)** refers to each one of the two conformers present in the crystal structure of **3Se**. b) Symmetry operator for the selenium atom is $-x$, $-y$, $2-z$. c) Refers to the intermolecular interaction, which is Se(b)···Sn(a) for **3Se(a)** and Se(a)^{i}···Sn(b) for **3(b)**, i = x, $-1+y$, z. d) These entries are the angles formed with the intermolecular selenium atom as described in the previous note. e) This is the angle formed by the inter and intramolecular interaction with the selenium atom, which for each conformer, a or b, is as follows: **3Se(a)**, Sn(a)–Se(a)–Sn(b), **3Se(b)**, Sn(b)–Se(b)–Sn(a)^{ii}, ii = x, $1+y$, z.

between tin and the group 16 element, showing a highfield shift as the interaction becomes stronger (Table 2). For compound **1Se**, which showed the weakest intramolecular interaction in the solid state, no change in the ^{119}Sn δ with respect to the analogous **1O** and **1S** is noted,[4] and it is deshielded with respect to the $(Ph)_4Sn$ and $(Ph)_3(Bn)Sn$ suggesting that the intramolecular interaction is lost in solution. However, in the cases of **2Se** and **3Se** the ^{119}Sn δ exhibit a highfield shift with respect to the oxygen and sulfur analogs ($Se > S > O$) possibly reflecting an impact of the intramolecular interactions in dichloromethane solution.

Unlike oxygen and sulfur, selenium has a readily accessible NMR experiment and we would expect that the ^{77}Se NMR could illustrate the various internuclear Sn···Se interactions. Our experimental results illustrate an initial deshielding of ≈ 5.3 ppm in comparison to the starting chloromethyl ligand, $ClCH_2C_6H_4SeMe$ (δ =162 ppm),[11,12] by the replacement of the chlorine by the Ph_3Sn group. Then, with the substitution of the Ph groups by the chlorine atom, there is a progressive shielding **1Se** → **2Se** → **3Se**, 167.3, 159.4, 151.8 ppm, in a constant step of ≈ 7.8 ppm.

Supramolecular Structures

As noted above, compound **1Se**, which is isostructural with its sulfur analog, can be described as a monomer, in the sense that no significant intermolecular interactions involving the heavy atoms selenium and tin are present. However, in addition to the typical interactions between aryl rings, both π stacking and edge-on, there is a chain motif generated by an intermolecular HB through the methyl group and one phenyl group (2.75 Å, HB1, Table 3). Additionally it can be noted that the selenium atom is oriented towards the aryl group in an intermolecular way that can be considered an interaction of the type $\pi(C)\cdots\sigma^*(Se–C_{Me})$.[5]

Compound **2Se** on the other hand, due to a stronger intermolecular Se···Sn interaction, presents both an intramolecular H···π interaction (HB2, 2.71 Å) and an intermolecular close contact Se···Se (Table 1), slightly smaller than ΣvdW (3.8 Å), resulting in a "dimeric" structure. This kind of Se···Se interaction was described as $n(Se)\cdots\sigma^*(Se–C_{Me})$ 3c-4e and the geometrical parameters present in **2Se** suggests that this as a weak interaction.[5] In addition to the intermolecular Se···Se contact

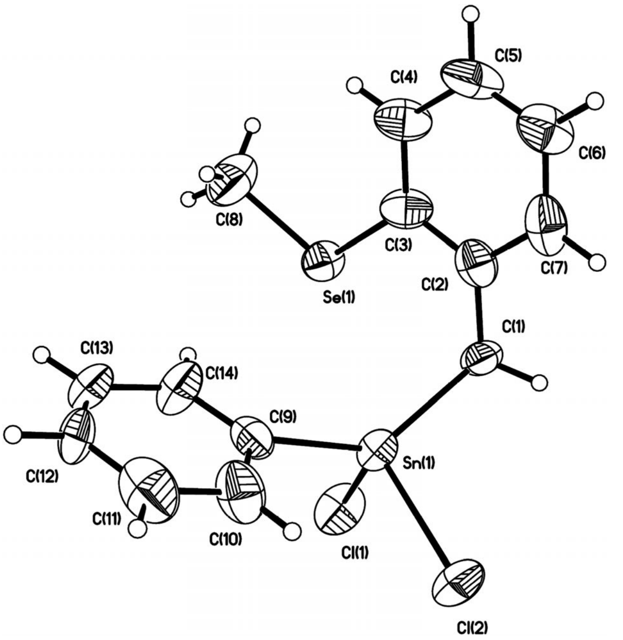

Figure 3. Molecular structure of **3Se**; the levels of probability of the ellipsoids are 50 %. Only one conformer is shown.

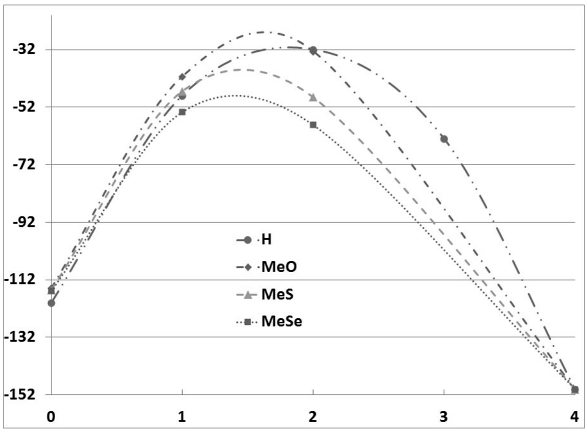

Figure 4. Comparison of the ^{119}Sn NMR spectroscopic data for compounds (o-R-$C_6H_4CH_2$)$SnPh_{3-n}Cl_n$ (R = H, MeE (E = O, S, Se)).

Table 2. ^{119}Sn NMR δ for compounds [o-(MeE)Ph]$Sn(Ph)_{3-n}$ Cl_n (E = O, S, and Se), n = 0, 1, 2.

R	RSn(Ph)$_3$	RSn(Ph)$_2$Cl	RSn(Ph)Cl$_2$
o-(MeSe)Ph	–115.8	–53.6	–58.1
o-(MeS)Ph[4]	–115.5	–46.4	–48.5
o-(MeO)Ph	–114.9	–41.4	–32.6
Ph[9]	–120	–48	–32

there is an intermolecular H···Cl (2.85 Å, HB3) and weak intermolecular H···π interactions. The latter are formed with the phenyl group R_{C9}, which is located between the methyl (HB4, 3.31 Å) and methylene group (HB5, 2.93 Å). HB3 forms a chain motif that in association with the intermolecular Se···Se contacts and/or HB3 to become a ladder (Figure 5). The ladders are additionally associated through HB4 generating the 3D structure.

In compound **3Se**, the intermolecular contact Se···Se found in **2Se** is lost, due to the formation of a further intermolecular Se···Sn interaction, probably because of the enhanced Lewis acidity of the central tin atom. This interaction forms a 1D chain (Figure 6) with the conformers **3Se**(**a**) and **3Se**(**b**) intercalated·(··a···b··)$_n$. There are intermolecular C–H···π interactions on this chain motif formed through the methyl group and the benzyl ring by both conformers (2.66 Å, HB6, and 2.89 Å, HB7, Table 3); the intramolecular contact distance from the methyl group to the phenyl ring is longer (3.534 and 3.649 Å). In addition there are intermolecular C–H···Cl interactions with an HB distance ranging from 2.775 to 2.925 Å (HB8–HB11, Table 3). These interactions generate a HB network (Figure 7).

Conclusions

Overall, the solid-state molecular structures of the title compounds **1Se**–**3Se** result in a progressive increase of the non-tetrahedral tin character, suggesting the formation of non-covalent interactions. However, in none of them, the interaction through the selenium atom is strong enough to form a TBP or octahedral arrangement; the significant change from tetrahedral arrangement can be noted by the progressive reduction in the Sn-attacking face distances of 0.7 Å → 0.4 Å → 0.5 Å.

The change in the Lewis acidity of the tin generates different coordination moieties in the crystal structure, although the 3D structure of the crystal is achieved by HB. In **1Se** the tetra-organotin is a monomer, whereas in **2Se** it is a dimer through Se···Se contacts, and for last in **3Se** a coordination polymer is formed.

The ^{119}Sn NMR spectrum suggests that the intramolecular coordination remains in solution and is stronger for compounds **2Se** and **3Se** than for the O and S analogs.

Experimental Section

General: All manipulations were performed in a nitrogen atmosphere using standard Schlenk techniques. Reagent grade tetrahydrofuran (THF) and hexanes were dried and distilled in a nitrogen atmosphere from a sodium benzophenoneketyl solution; benzene was dried and distilled from Na ribbon. Triphenyltinchloride and 1 M HCl in diethyl ether were purchased from Aldrich and used as received. 2-(Chloromethyl)phenyl methyl selenide was synthesized following the reported method and the spectroscopic data were in accord with the published data.[12] Organotin compounds (o-$MeSeC_6H_4CH_2$)$Sn(Ph)_{3-n}Cl_n$ [n = 0 (**1Se**); 1 (**2Se**); 2 (**3Se**)] were synthesized by the published procedure used for the oxygen and sulfur analogs.[4]

NMR spectra were recorded with a Bruker 300 spectrometer operating at 300.00, 111.853, 75.422, and 57.215 MHz, for ^{1}H, ^{119}Sn, ^{13}C, and ^{77}Se, respectively. Single Crystal X-ray Diffraction (SC-XRD) was collected with a Bruker APEX CCD diffractometer with Mo-K_α radiation (λ = 0.7107 Å). An absorption correction was applied to the data (SADABS) and the structures were solved by SHELXS and refined by full-matrix anisotropic least-squares against F^2 using the SHELXL program.[13]

[2-(Methylselenenyl)benzyl]triphenylstannane (1Se) Yield 62.5 %; m.p. 73–75 °C. **^{1}H NMR** ($CDCl_3$): δ = 1.84 (s, 3 H, Ar-Se-CH_3), 3.0

Table 3. HB found in the crystal structure of **1Se**–**3Se**.

HB	D–H···A$^{a)b)c)}$	(H···A) /Å	(D–H···A) /°	(H···A–R) /°
1Se				
1	$\mathrm{C8{-}H8B}\cdots R_{\mathrm{C9}}^{\mathrm{i}}$	2.75	135.0	86.5
2Se				
2	$\mathrm{C8{-}H8C}\cdots R_{\mathrm{C15}}$	2.71	164.0	75.9
3	$\mathrm{C4{-}H4}\cdots \mathrm{Cl}^{\mathrm{ii}}$	2.85	161.8	173.1
4	$\mathrm{C1}^{\mathrm{iii}}{-}\mathrm{H1B}^{\mathrm{iii}}\cdots R_{\mathrm{C9}}$	2.93	153.9	81.1
5	$\mathrm{C8}^{\mathrm{iv}}{-}\mathrm{H8B}^{\mathrm{iv}}\cdots R_{\mathrm{C9}}$	3.31	117.2	74.39
3Se				
6	$\mathrm{C8}^{1}{-}\mathrm{H8A}^{1}\cdots R_{\mathrm{C2}}^{2}$	2.66	149.2	85.9
7	$\mathrm{C8}^{2}{-}\mathrm{H8A}^{2}\cdots R_{\mathrm{C2}}^{1,\mathrm{v}}$	2.89	150.7	75.9
8	$\mathrm{C7}^{2}{-}\mathrm{H7}^{2}\cdots \mathrm{Cl1}^{1}$	2.77	166.4	108.7
9	$\mathrm{C11}^{1}{-}\mathrm{H11}^{1}\cdots \mathrm{Cl2}^{1,\mathrm{vi}}$	2.925	153.1	119.8
10	$\mathrm{C13}^{2}{-}\mathrm{H13}^{2}\cdots \mathrm{Cl1}^{2,\mathrm{vii}}$	2.864	151.0	121.1
11	$\mathrm{C4}^{2}{-}\mathrm{H4}^{2}\cdots \mathrm{Cl1}^{2,\mathrm{viii}}$	2.909	130.3	128.8

a) The symmetry operators as noted at the side of the corresponding atom in low caps roman numeral as superscript. Symmetry operators: i, x, y–1+z; ii, –1+x, y, z; iii, 1–x, –y, 2–z; iv, –x, –y, 1–z; v, x, 1+y, z; vi, 2–x, –y, –z; vii, 2–x, 1–y, 1–z; viii, –1/2+x, 3/2–y, –1/2+z. b) For **3Se** the respectively conformer to which the atom corresponds is denoted as 1 or 2 in superscript. c) The interactions to the phenyl rings are measured to the centroid, and it is denoted as R with the carbon base as the subscript.

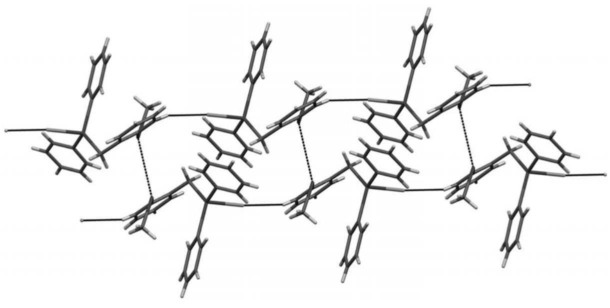

Figure 5. Ladder generated by association of the chain formed by H···Cl interactions in **2Se**, the Se···Se contacts (vertical) are displayed but the H···π interactions are omitted for clarity.

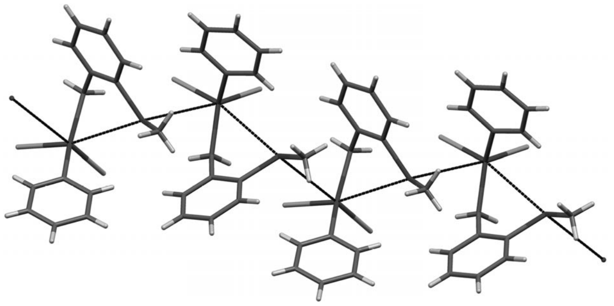

Figure 6. Motif formed by the intra and intermolecular bidentate Se–Sn interactions in **3Se**, the interactions HB6 and HB7 are omitted for clarity.

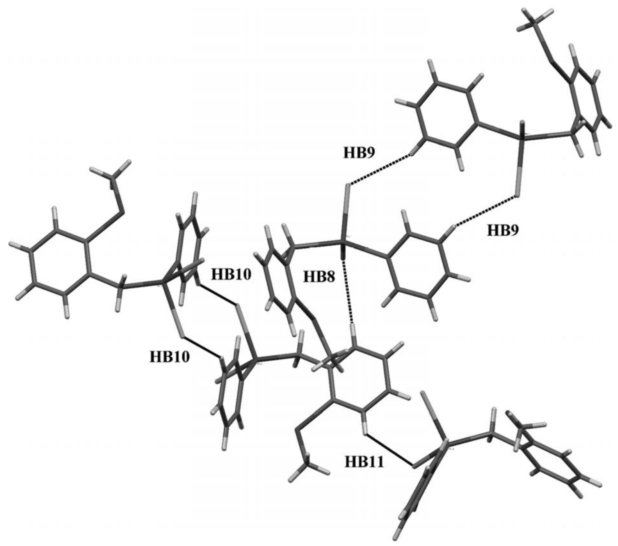

Figure 7. HB scheme for compound **3Se**, only the expanded H···Cl contacts were retained for clarity.

[s, 2 H, Ar-CH_2-Sn, $^2J(^{117/119}Sn–^1H)$ = 20.3/33.4 Hz], 7.50–6.80 (m, 19 H, Ph, Ar). **^{13}C NMR** ($CDCl_3$): δ = 7.56 (1C, CH_3-Se-Ar), 22.90 [1C, Ar-CH_2-Sn, $^2J(^{13}C–^{117/119}Sn)$ = 297.1/313.1 Hz], 125.18 (C_{ipso}-Se), 126.52, 127.85 (C_{ipso}-C), 128.46 [*meta*-Ph-Sn, $^2J(^{13}C–^{119}Sn)$ = 23.4 Hz], 128.88, 130.16 [*para*-Ph-Sn, $^2J(^{13}C–^{119}Sn)$ = 5.0 Hz], 137.07, 139.31 [*ortho*-Ph-Sn, $^2J(^{13}C–^{117/119}Sn)$ = 17.6/38.0 Hz], 141.68 [*ipso*-Ph-Sn, $^2J(^{13}C–^{117/119}Sn)$ = 434.2/455.2 Hz]. **^{77}Se NMR** ($CDCl_3$): δ = 167.30. **^{119}Sn NMR** ($CDCl_3$): δ –115.85 ppm.

SC-XRD: $C_{26}H_{24}SeSn$, Fwt = 534.1, a = 18.967(3) Å, b = 14.539(2) Å, c = 7.9937(13) Å, β = 99.051(3)°, V = 2176.9(6) Å^3, monoclinic, $P2_1/c$, Z = 4, F(000) = 1056, μ = 2.854 mm^{-1}. 12163 total reflections, 4230 unique reflections [Rint = 0.0289]. R_1 = 0.0346; wR_2 = 0.0773 for all data (number of parameters = 254); R_1 = 0.0302, wR_2 = 0.0746 for 3817 reflections [$I > 2\sigma(I)$], Goof = 1.045. T = 123(2) K.

[2-(Methylselenenyl)benzyl)]diphenylchlorostannane (**2Se**). Yield 55 %; m.p. 60–62 °C. **^{1}H NMR** (C_6D_6): δ = 1.23 (s, 3 H, Ar-Se-CH_3), 2.97 [s, 2 H, Ar-CH_2-Sn, $^2J(^{119}Sn-^1H)$ = 36.0 Hz], 7.56–6.82 (m, 14 H, Ph, Ar). **^{13}C NMR** (C_6D_6): δ = 8.60 (1C, CH_3-Se-Ar), 31.78 (1C, Ar-CH_2-Sn), 126.39, 128.53, 128.87 (4C, Ph-Sn), 128.98, 129.80 (2C, Ph-Sn), 130.47, 130.81, 136.20 (4C, Ph-Sn), 140.50 (1C, *ipso*-Ph-Sn), 140.86 (1C, *ipso*-Ph-Sn). **^{77}Se NMR** ($CDCl_3$): δ = 159.47. **^{119}Sn NMR** ($CDCl_3$): δ –53.61 ppm.

SC-XRD: $C_{20}H_{19}ClSeSn$, Fwt = 492.45, a = 9.6440(19) Å, b = 21.177(4) Å, c = 9.9396(19) Å, β = 103.668(4)°, V = 1972.5(7) Å^3, monoclinic, $P2_1/n$, Z = 4, F(000) = 960, μ = 3.273 mm^{-1}. 10124 total reflections, 3661 unique reflections [Rint = 0.1070]. R_1 = 0.1797; wR_2

= 0.2188 for all data (number of parameters = 209); R_1 = 0.1191, wR_2 = 0.1985 for 2354 reflections [$I > 2\sigma(I)$], Goof = 1.221. T = 298(2) K

[2-(Methylselenenyl)benzyl)]phenyldichlorostannane (**3Se**). Yield 80 %; m.p. 88–90 °C. **^{1}H NMR** ($CDCl_3$): δ = 2.07 (s, 3 H, Ar-Se-CH_3), 3.29 (s, 2 H, Ar-CH_2-Sn), 7.46–7.11 (m, 14 H, Ph, Ar). **^{13}C NMR** ($CDCl_3$): δ = 10.84 (1C, CH_3-Se-Ar), 39.03 (1C, Ar-CH_2-Sn), 127.57, 128.39, 129.18 (2C, Ph-Sn), 129.48, 130.80, 130.97, 131.32, 134.38 (2C, Ph-Sn), 137.81, 141.42 (1C, *ipso*-Ph-Sn). **^{77}Se NMR** ($CDCl_3$): δ = 151.78. **^{119}Sn NMR** ($CDCl_3$): δ –58.10 ppm.

SC-XRD: $C_{14}H_{14}Cl_2SeSn$, Fwt = 450.8 g•mol^{-1}, a = 17.025(6) Å, b = 11.097(4) Å, c = 18.104(6) Å, β = 115.579(4)°, V = 3085.1(18) Å^3, monoclinic, $P2_1/n$, Z = 8, Z′ = 4 F(000) = 1728, μ = 4.342 mm^{-1}. 30915 total reflections, 6055 unique reflections [R_{int} = 0.0987]. R_1 = 0.1213; wR_2 = 0.2166 for all data (number of parameters = 320); R_1 = 0.0792, wR_2 = 0.1924 for 4108 reflections [$I > 2\sigma(I)$], Goof = 1.147. T = 298(2(K)

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-869513, CCDC-869514, and CCDC-869515 (**1Se**–**3S**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgement

We thank the Robert Welch Foundation of Houston, Texas, for support of this research through grant # AH–0546.

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[7] TEMC refers to an environment, in which the four covalent-bonded substituents are in an arrangement closer for a tetrahedral arrangement than for a TBP. In other words, it has less than 50 % of TBP character. The same applies to TEBC but now in contrast to a octahedral arrangement.

[8] For tetrahedral or TBP arrangements Σax refers to the sum of the angles formed by the substituents with the atom *anti* to the nucleophile, Σeq is the sum of the angles formed by the substituents pushed by the nucleophile and ΣNu is the summatory of the angles generated by the nucleophile (Se) with the substituents in the attacked face. For tetrahedral the parameters are Σax = Σeq = 328.2° and ΣNu = 211.6°, whereas for TBP they are Σax = 270, Σeq = 360° and ΣNu = 270°.

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Received: March 05, 2012

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Major Distinctions in the Molecular and Supramolecular Structures of Selenium-containing Organotins, (o-MeSe-$C_6H_4CH_2$)$SnPh_{3-n}Cl_n$ (n = 0, 1, 2)