

# Oxidation Reactions of the N-Heterocyclic Stannylenes $[o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2]\text{Sn}$ and $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_2)_2\}\text{Sn}]$ with Sulfur, Selenium, and Diphenyl Diselenide

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*Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday*

**Abstract.** The N-heterocyclic stannylenes  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_2)_2\}\text{Sn}]$  (**1**) and  $[o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2]\text{Sn}$  (**2**) were prepared in one-pot reactions from  $\text{SnCl}_2$ ,  $\text{LiN}(\text{SiMe}_3)_2$ , and the corresponding diamine, viz.  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NHSi}t\text{BuMe}_2)_2]$  and  $o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2$ , respectively. Oxidative addition reactions of **1** and **2** with  $\text{S}_8$  and  $\text{Se}_8$ , respectively, afforded the corresponding 1,3,2,4-dithiadistannenes (**(1S)**<sub>2</sub>, **(2S)**<sub>2</sub>), and 1,3,2,4-diselenadistannenes (**(1Se)**<sub>2</sub>,

**(2Se)**<sub>2</sub>). The reactions of **1** and **2** with  $\text{PhSeSePh}$  respectively furnished **1(SePh)**<sub>2</sub> and **2(SePh)**<sub>2</sub>. The crystal structures of  $o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2$ , **1**, **2**, **(1S)**<sub>2</sub>, **(2S)**<sub>2</sub>, **(1Se)**<sub>2</sub>, **(2Se)**<sub>2</sub>, **1(SePh)**<sub>2</sub>, and **2(SePh)**<sub>2</sub> were determined by single-crystal X-ray diffraction. Stannylene **2** shows a chain-like aggregation in the solid state due to intermolecular  $\text{Sn}\cdots\text{arene}$  interactions. A short intramolecular  $\text{CH}\cdots\text{Se}$  contact compatible with a hydrogen bond was observed for **(1Se)**<sub>2</sub>.

## Introduction

N-heterocyclic stannylenes are heavier analogues of the highly popular N-heterocyclic carbenes (NHCs).<sup>[1]</sup> First examples were described by *Schaeffer* and *Zuckerman* already in 1974,<sup>[2]</sup> almost simultaneous with *Lappert's* seminal paper on the first stable acyclic diaminogermynes and diaminostannylenes,<sup>[3]</sup> and long before *Arduengo's* report of the first stable NHC in 1991.<sup>[4]</sup> The first structurally characterized cyclic diaminostannylene,  $[\text{Me}_2\text{Si}(\text{N}t\text{Bu})_2]\text{Sn}$ , was published in 1978 by *Veith*.<sup>[5]</sup> Although the chemistry of N-heterocyclic stannylenes has developed remarkably since these early days,<sup>[6]</sup> it is still far away from the maturity that has been reached in the field of NHCs. For example, it has only been recently that applications of N-heterocyclic stannylenes in materials science<sup>[7]</sup> and catalysis have emerged.<sup>[8]</sup>

In continuation of our work on stable ferrocene-based NHCs,<sup>[9]</sup> we have established heavier analogues of the type  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NR})_2\}E]$  ( $E = \text{Si},^{[10]}$   $\text{Ge},^{[11]}$   $\text{Sn},^{[11b,11c]}$   $\text{Pb}^{[12]}$ ), which constitute the first N-heterocyclic tetrylenes bearing redox-active substituents.<sup>[13]</sup> We recently reported on the reactivity of several germynes of this family in oxidation

reactions with elemental sulfur, selenium, and diphenyl diselenide,<sup>[11a]</sup> and have started to extend this work in a systematic study to corresponding stannylenes and plumblylenes. We chose the hitherto unknown compound  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_2)_2\}\text{Sn}]$  (**1**) as starting point for our investigation of oxidation reactions of ferrocene-based stannylenes with sulfur, selenium, and diphenyl diselenide.

Reactions of N-heterocyclic stannylenes with these reagents have been described in the literature only very sporadically,<sup>[14]</sup> which prompted us to include  $[o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2]\text{Sn}$  (**2**) in this study.<sup>[15]</sup> These two N-heterocyclic stannylenes have two salient features in common. Firstly, both contain an aromatic backbone (based on ferrocene and benzene, respectively). Secondly, they are equipped with the same *N*-substituents, viz.  $\text{Si}t\text{BuMe}_2$ , which is the silyl analogue of the bulky tertiary alkyl group  $\text{C}t\text{BuMe}_2$ . In our previous study addressing oxidation reactions of ferrocene-based N-heterocyclic germynes of the type  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NR})_2\}\text{Ge}]$  with elemental sulfur, selenium, and diphenyl diselenide, the  $\text{C}t\text{BuMe}_2$  substituent turned out to exert a pronounced solubilising effect, which allowed a full characterization of the oxidation products by multinuclear solution NMR spectroscopy. We here report on our results obtained with  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_2)_2\}\text{Sn}]$  (**1**) and  $[o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2]\text{Sn}$  (**2**) in analogous oxidation reactions with these three reagents.

## Results and Discussion

### Compound Synthesis

The synthesis of  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_2)_2\}\text{Sn}]$  (**1**) was easily possible by reacting  $\text{SnCl}_2$  with the lithium amide  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_2)_2\}\text{Li}_2]$  previously published by us.<sup>[16]</sup> Alternatively, and more conveniently, **1** was prepared by

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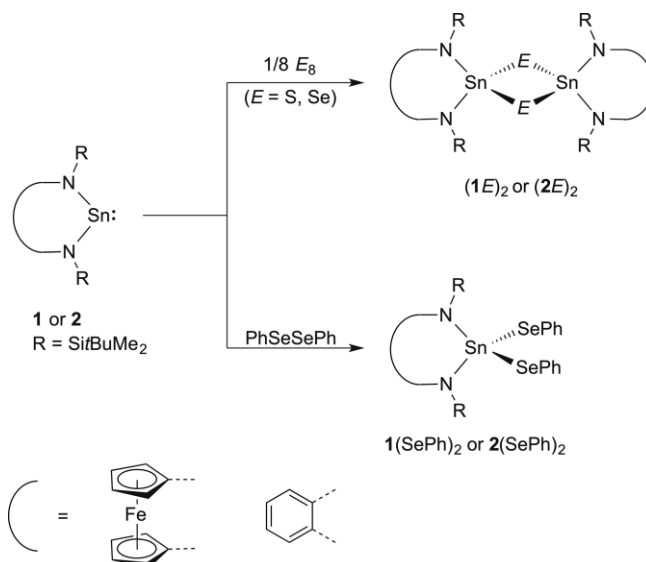
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reacting  $\text{LiN}(\text{SiMe}_3)_2$ ,  $\text{SnCl}_2$  and  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NHSi}t\text{-BuMe}_2)_2]$  in a 2:1:1 molar ratio in THF. The product was obtained in 96% yield as a crystalline solid, which was structurally characterized by X-ray diffraction (vide infra). The  $^{119}\text{Sn}$  NMR spectrum exhibits a signal at  $\delta = 550$  ppm in  $\text{C}_6\text{D}_6$ , which is close to the chemical shift values reported by us for the *tert*-butyl and trimethylsilyl homologues ( $\delta = 544$  and 589 ppm for  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-N}t\text{Bu})_2\}\text{Sn}]$  and  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_3)_2\}\text{Sn}]$ , respectively)<sup>[11b,11c]</sup> and lies in the region typical for N-heterocyclic stannylenes with strictly two-coordinate  $\text{Sn}^{\text{II}}$  according to X-ray diffraction results.<sup>[17]</sup> For comparison,  $\delta(^{119}\text{Sn}) = 456$  ppm has been reported for  $[o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2]\text{Sn}$  (**2**).<sup>[15]</sup> The synthesis of the known stannylene **2** was conveniently achieved in 89% yield by a one-pot procedure analogous to that developed for **1**.

The oxidation reactions of **1** and **2** with sulfur, selenium, and diphenyl diselenide are summarized in Scheme 1. The reactions with elemental sulfur were performed in toluene at room temperature and afforded the expected<sup>[18]</sup> 1,3,2,4-dithiadistannetanes  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}t\text{BuMe}_2)_2\}\text{Sn}(\mu\text{-S})_2]$  [(1S)<sub>2</sub>] and  $[\{o\text{-C}_6\text{H}_4(\text{NSi}t\text{BuMe}_2)_2\}\text{Sn}(\mu\text{-S})_2]$  [(2S)<sub>2</sub>] in high yield. The analogous 1,3,2,4-diselenadistannetanes were obtained under the same mild conditions by using red selenium ( $\text{Se}_8$ ). This metastable molecular allotrope is superior in this context to grey selenium, which is insoluble and proved to be inert towards **1** and **2** at room temperature. From a formal point of view, (1E)<sub>2</sub> and (2E)<sub>2</sub> (E = S, Se) are head-to-tail dimers of the corresponding stannanethiones or stannaneselones. Thermally stable monomeric stannanethiones and stannaneselones have been obtained so far only with extremely bulky diarylstannanes.<sup>[19]</sup> The  $^1\text{H}$  NMR signal patterns due to the protons of the two 1,1'-ferrocenylene (two singlets, each integrating for 8 H) or two *ortho*-phenylene units (two symmetrical multiplets, each integrating for 4 H) respectively present in (1E)<sub>2</sub> and (2E)<sub>2</sub> (E = S, Se) point to time-averaged molecular  $C_{2v}$  symmetry of these dimers at room temperature in solution. **1** and **2** reacted smoothly and swiftly with diphenyl diselenide at room temperature in toluene, affording **1**(SePh)<sub>2</sub> and **2**(SePh)<sub>2</sub>, respectively, in good yields.

In line with the tetracoordinate  $\text{Sn}^{\text{IV}}$  atoms present in the six oxidation products of this study, their  $^{119}\text{Sn}$  NMR signals are significantly high-field shifted to negative ppm values with respect to those of the stannylenes **1** and **2**. The  $^{119}\text{Sn}$  and  $^{77}\text{Se}$  NMR spectroscopic data for the compounds of this study are collected in Table 1. The acyclic stannylene  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$  appears to be the only diamino stannylene to date, where a complete set of  $^{119}\text{Sn}$  and  $^{77}\text{Se}$  NMR spectroscopic data is available for the corresponding oxidation products.<sup>[18a,20]</sup> These data are therefore included in Table 1 and generally compare well with those of the compounds of this study. Replacement of S by Se in the head-to-tail dimers results in a significant upfield shift of the  $^{119}\text{Sn}$  NMR signal of more than 200 ppm, in line with the heavy-atom effect of selenium.<sup>[21]</sup> Owing to the comparatively high solubilities of **1**(SePh)<sub>2</sub> and **2**(SePh)<sub>2</sub>,  $^1J(^{119}\text{Sn}^{77}\text{Se})$  coupling constants could be determined from the  $^{77}\text{Se}$  satellites present in the  $^{119}\text{Sn}$  NMR spectra. We did not observe tin satellites in the  $^{77}\text{Se}$  spectra due to



**Scheme 1.** Oxidation reactions studied in this work.

the comparatively lower abundance and spectroscopic sensitivity of  $^{77}\text{Se}$  (7.58% natural abundance, gyromagnetic ratio  $\gamma = 5.101 \times 10^7 \text{ rad}\cdot\text{T}^{-1}\cdot\text{s}^{-1}$ ) vs.  $^{117}\text{Sn}/^{119}\text{Sn}$  (7.61/8.58% natural abundance,  $\gamma = -9.5301/-9.9707 \times 10^7 \text{ rad}\cdot\text{T}^{-1}\cdot\text{s}^{-1}$ ), leading to a less favorable signal-to-noise ratio.<sup>[22]</sup> The  $^1J(^{119}\text{Sn}^{77}\text{Se})$  coupling constant values are 1744 and 1798 Hz for **1**(SePh)<sub>2</sub> and **2**(SePh)<sub>2</sub>, respectively, which is similar to the value of 1688 Hz reported for the acyclic analogue  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}(\text{SePh})_2$ <sup>[18a,20]</sup> indicating a similar degree of s-character of the tin orbital used for Sn–Se bonding in these three compounds.<sup>[23]</sup>

**Table 1.**  $^{119}\text{Sn}$  and  $^{77}\text{Se}$  NMR spectroscopic data for the tin compounds of this study. Data for  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$  and its derivatives are included for comparison.

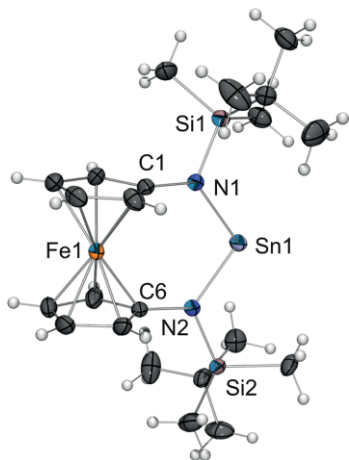
	$\delta(^{119}\text{Sn})$	$\delta(^{77}\text{Se})$	Reference
<b>1</b>	550		This work
<b>2</b>	456		[15]
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$	767		[24]
(1S) <sub>2</sub>	−211		This work
(2S) <sub>2</sub>	−18		This work
$\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{SnS}\}_2$	−105		[18a]
(1Se) <sub>2</sub>	−447	350	This work
(2Se) <sub>2</sub>	−293	491	This work
$\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{SnSe}\}_2$	−381	397 <sup>a)</sup>	[18a]
<b>1</b> (SePh) <sub>2</sub>	−140	222	This work
<b>2</b> (SePh) <sub>2</sub>	−81	206	This work
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}(\text{SePh})_2$	−183	206	[18a, 20]

a) This value is in conflict with that given earlier in reference<sup>[18b]</sup> ( $\delta = -640.1$  ppm).

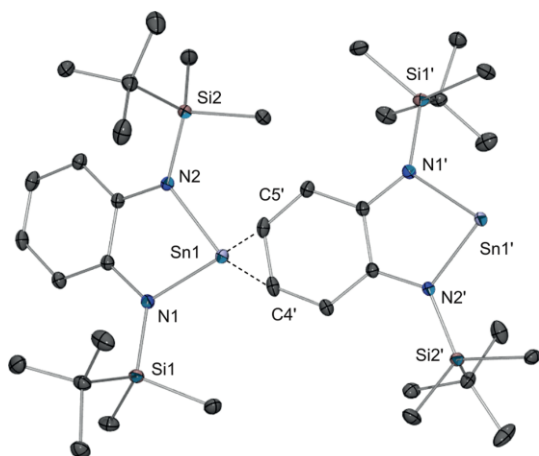
### Crystal Structures

All new compounds of this study were structurally characterized by single-crystal X-ray diffraction. The crystal structures of the known stannylene **2** and of its precursor  $o\text{-C}_6\text{H}_4(\text{NHSi}t\text{BuMe}_2)_2$  were also determined. Pertinent metric parameters of the new tin compounds and of **2** are collected in Table 2 and the corresponding molecular structures are shown

in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, Figure 7, and Figure 8 [see Figure S1, Supporting Information, for the molecular structure of  $C_6H_4(NHSi^iBuMe_2)_2$ ].



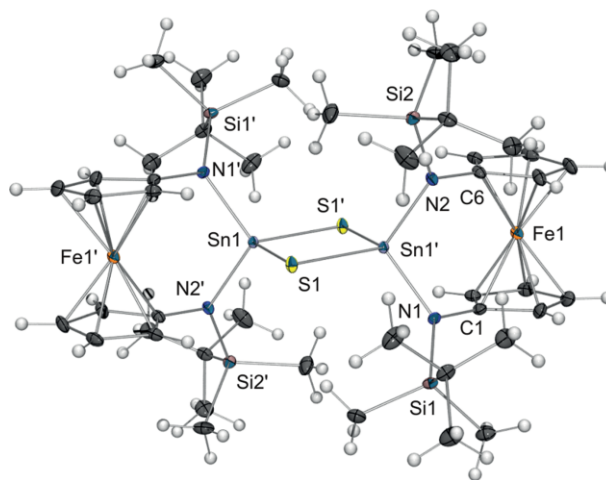
**Figure 1.** Molecular structure of **1** (ORTEP plot with 30% probability ellipsoids) in the crystal.



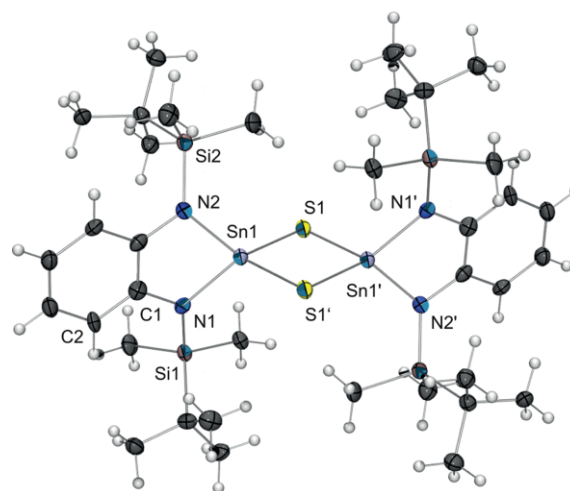
**Figure 2.** Molecular structure and aggregation of **2** (ORTEP plot with 30% probability ellipsoids) in the crystal. The two shortest intermolecular Sn...C contacts (ca. 3.12 Å) are indicated by broken lines.

The N atoms of the compounds listed in Table 2 are in a trigonal-planar bonding environment (sum of angles 357.0–360.0°). The Sn–N bonds of the N-heterocyclic stannylenes **1** and **2** are marginally longer than those of their oxidative addition products. Obviously, the decrease of the covalent radius on going from Sn<sup>II</sup> to Sn<sup>IV</sup> is approximately compensated by the effect of the increase in coordination number. This behavior is not unusual. For example, a comparison of the stannylene  $[Me_2Si(NtBu)_2]Sn$  with the corresponding tin(IV) spiro compound  $[Me_2Si(NtBu)_2]_2Sn$  reveals that the former has slightly longer Sn–N bond lengths (ca. 2.09 vs. 2.03 Å).<sup>[25]</sup> In the case of the aryl-substituted congeners  $[Me_2Si(NDipp)_2]_nSn$  ( $n = 1$ ,<sup>[26]</sup> 2<sup>[27]</sup>) (Dipp = 2,6-diisopropylphenyl) the Sn–N bond lengths of the stannylene and the tin(IV) spiro compound are essentially identical (ca. 2.06 Å).

Stannylene **2** shows a chain-like aggregation in the solid state (Figure 2) due to weak intermolecular Sn...arene interac-



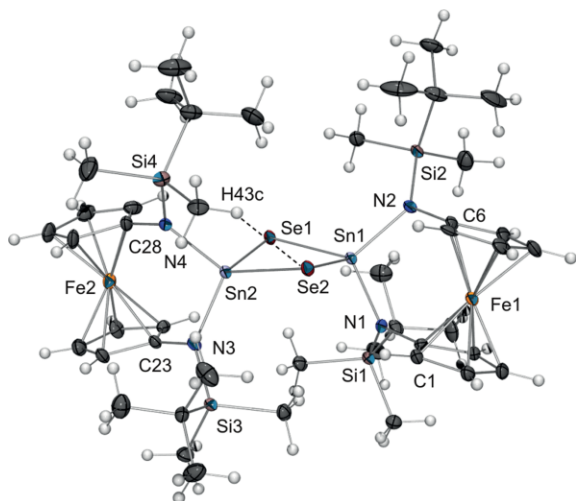
**Figure 3.** Molecular structure of  $(1S)_2$  (ORTEP plot with 30% probability ellipsoids) in the crystal.



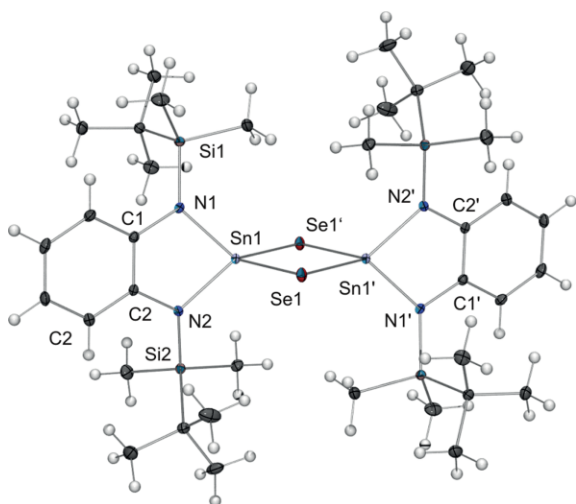
**Figure 4.** Molecular structure of  $(2S)_2$  (ORTEP plot with 30% probability ellipsoids) in the crystal.

tions indicated by Sn...C<sub>arene</sub> contacts between ca. 3.12 and 3.55 Å, which is well below the sum of the van der Waals radii of C (1.77 Å) and Sn (2.42 Å).<sup>[28]</sup> Such contacts are frequently shown by N-heterocyclic stannylenes containing aromatic backbones.<sup>[15,29]</sup> A chain-like aggregation similar to that found for **2** has been observed before in this context for stannylenes containing a naphthalene-1,8-diyl backbone.<sup>[29b,29c]</sup> In contrast, the neopentyl homologue of **2** is aggregated as a head-to-tail dimer in the solid state.<sup>[15]</sup> The ferrocene-based compounds in Table 2 exhibit rather small cyclopentadienyl ring tilt and N–C<sub>ipso</sub>–C<sub>ipso</sub>–N torsion angles, pointing to essentially unstrained and nearly eclipsed 1,3,2-diazastanna[3]ferrocenophane structures, as has been observed before by us for  $[Fe(\eta^5-C_5H_4-NR)_2]Sn$  ( $R = SiMe_3$ , *t*Bu)<sup>[11b,11c]</sup> and by Wrackmeyer et al. for the tin(IV) compounds  $[Fe(\eta^5-C_5H_4-NSiMe_3)_2]_2Sn$ <sup>[30]</sup> and  $[Fe(\eta^5-C_5H_4-NSiMe_3)_2]SnCl_2$ .<sup>[31]</sup>

The structures of  $(1S)_2$  and  $(2E)_2$  ( $E = S, Se$ ) exhibit molecular  $C_i$  symmetry with nearly diamond-shaped Sn<sub>2</sub>E<sub>2</sub> cores. In contrast, the Sn<sub>2</sub>Se<sub>2</sub> unit of  $(1Se)_2$  is nonplanar with a fold

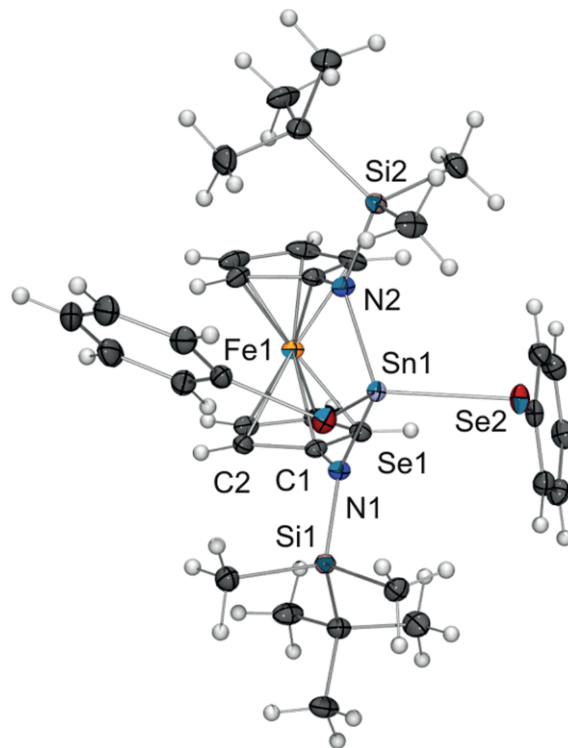


**Figure 5.** Molecular structure of  $(1\text{Se})_2$  (ORTEP plot with 30% probability ellipsoids) in the crystal. The intramolecular  $\text{CH}\cdots\text{Se}$  contact compatible with a hydrogen bond is indicated by a broken line.

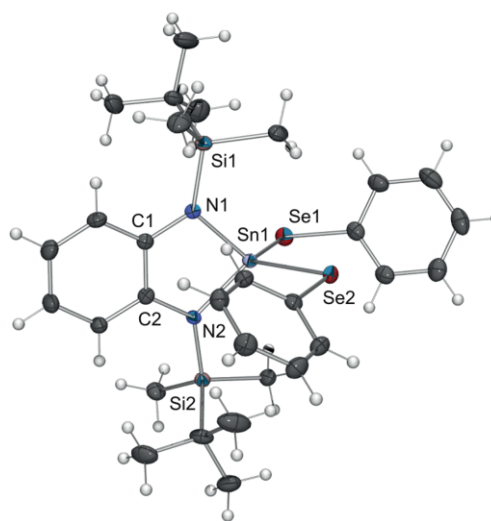


**Figure 6.** Molecular structure of  $(2\text{Se})_2$  (ORTEP plot with 30% probability ellipsoids) in the crystal.

angle between the two  $\text{SnSe}_2$  planes of  $22.4^\circ$ . This unexpected distortion may be ascribed to a rather short intramolecular  $\text{CH}\cdots\text{Se}$  contact of only ca.  $2.78 \text{ \AA}$ , compatible with hydrogen bonding (indicated by a broken line in Figure 5;  $\text{C}-\text{H}-\text{Se}$   $146^\circ$ ). The first example of a  $\text{C}-\text{H}\cdots\text{Se}$  hydrogen bond was reported in 1994 ( $\text{CH}\cdots\text{Se}$   $2.92 \text{ \AA}$ ,  $\text{C}-\text{H}-\text{Se}$   $102^\circ$ ),<sup>[32]</sup> and such hydrogen bonds are still extremely scarce.<sup>[33]</sup> Interestingly, short intramolecular  $\text{CH}\cdots\text{Se}$  contacts similar to that of  $(1\text{Se})_2$ , together with unexpected structural distortions, were recently found by us in the analogous germanium compounds  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NR})_2\}\text{Ge}(\mu\text{-Se})_2]$  ( $R = \text{CtBuMe}_2$ , 2-adamantyl).<sup>[11a]</sup> The different  $\text{Sn}-E$  bond lengths determined for  $E = \text{S}$  (average value  $2.42 \text{ \AA}$ ) and  $\text{Se}$  (average value  $2.54 \text{ \AA}$ ) are in accord with the difference of the single bond covalent radii of  $0.13 \text{ \AA}$  reported for these elements<sup>[34]</sup> and compare well with corresponding data published for closely related compounds.<sup>[14a,14-b,14c,14f,18]</sup>



**Figure 7.** Molecular structure of  $1(\text{SePh})_2$  (ORTEP plot with 30% probability ellipsoids) in the crystal.



**Figure 8.** Molecular structure of  $2(\text{SePh})_2$  (ORTEP plot with 30% probability ellipsoids) in the crystal.

## Conclusions

In our previous study addressing oxidation reactions of ferrocene-based N-heterocyclic germylenes of the type  $[\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NR})_2\}\text{Ge}]$  with elemental sulfur, selenium, and diphenyl diselenide, the  $\text{CtBuMe}_2$  substituent turned out to exert a pronounced solubilising effect, in particular on the corresponding 1,3,2,4-dithiadigermetane and 1,3,2,4-diselenadigermetane. In this study we have utilized its silyl analogue  $\text{Si}t\text{BuMe}_2$ , which also lends at least satisfactory solubility to the products ob-

**Table 2.** Pertinent metric parameters /Å, ° for the structurally characterized tin compounds of this study.

	Sn–N	Sn–E	N–Sn–N	E–Sn–E	Tilt angle	N–C <sub>ipso</sub> –C <sub>ipso</sub> –N
<b>1</b>	2.058(2) 2.066(2)		105.09(10)		2.8	8.2
<b>2</b>	2.0952(14) 2.0834(14)		80.90(6)			
( <b>1S</b> ) <sub>2</sub> <sup>a)</sup>	2.033(2) 2.030(2)	2.3948(7) 2.4316(7)	108.98(9)	95.09(2)	4.3	1.7
( <b>2S</b> ) <sub>2</sub> <sup>a)</sup>	2.043(7) 2.042(7)	2.388(2) 2.446(2)	86.4(3)	94.37(7)		
( <b>1Se</b> ) <sub>2</sub> <sup>b)</sup>	2.044(8) 2.046(8) 2.052(8) 2.025(8)	2.5285(11) 2.5542(13) 2.5642(12) 2.5216(11)	106.8(3) 106.5(3)	94.92(4) 94.84(4)	3.4 3.1	1.8 0.0
( <b>2Se</b> ) <sub>2</sub> <sup>a)</sup>	2.025(2) 2.039(2)	2.5133(3) 2.5758(3)	86.22(7)	96.212(9)		
<b>1</b> (SePh) <sub>2</sub>	2.048(2) 2.043(2)	2.5414(3) 2.5423(3)	112.82(6)	104.366(10)	2.1	4.7
<b>2</b> (SePh) <sub>2</sub>	2.037(2) 2.027(2)	2.5218(3) 2.5179(3)	86.58(9)	106.451(11)		

a) Crystallographically imposed molecular  $C_i$  symmetry. b) Two independent molecules.

tained. [ $\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}^t\text{BuMe}_2)_2\}\text{Sn}$ ] (**1**) and [ $o\text{-C}_6\text{H}_4(\text{NSi}^t\text{BuMe}_2)_2\text{Sn}$ ] (**2**) were both found to react smoothly with  $\text{S}_8$ ,  $\text{Se}_8$ , and  $\text{PhSeSePh}$  under mild conditions, cleanly affording the expected products, viz. (**1E**)<sub>2</sub> and (**2E**)<sub>2</sub> ( $E = \text{S, Se}$ ) as well as **1**(SePh)<sub>2</sub> and **2**(SePh)<sub>2</sub>, in generally good yields. Previous to our study [ $\text{Me}_2\text{Si}(\text{N}^t\text{Bu})_2\text{Sn}$ ] and  $(\text{CH}_2\text{NDipp})_2\text{Sn}$  had been the only N-heterocyclic stannylenes investigated in terms of their reactivities towards elemental sulfur and selenium,<sup>[14a–14c]</sup> and to the best of our knowledge reactions of N-heterocyclic stannylenes with diphenyl diselenide had been completely absent from the literature. Our results help mitigate the surprising lack of knowledge in this area of chemistry. As a final point, we note that the short intramolecular  $\text{CH}\cdots\text{Se}$  contact compatible with a hydrogen bond, which we observed for (**1Se**)<sub>2</sub> is consistent with our recent findings concerning the occurrence of such contacts in selenium derivatives of ferrocene-based N-heterocyclic germlylenes.<sup>[11a]</sup>

## Experimental Section

All reactions involving air-sensitive compounds were performed in an inert atmosphere (argon or dinitrogen) by using Schlenk techniques or a conventional glovebox. Starting materials were procured from standard commercial sources and used as received. [ $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NHSi}^t\text{BuMe}_2)_2$ ]<sup>[35]</sup> and red selenium<sup>[36]</sup> were synthesized by following adapted versions of the published procedures. NMR spectra were recorded at ambient temperature with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHz, respectively, for <sup>1</sup>H. <sup>77</sup>Se NMR spectra were recorded with a Varian NRMS-500 spectrometer with neat dimethylselenide as external standard ( $\delta = 4$  ppm).<sup>[37]</sup> Combustion analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyzer at the Institute of Chemistry, University of Kassel, Germany.

**Synthesis of  $o\text{-C}_6\text{H}_4(\text{NHSi}^t\text{BuMe}_2)_2$ :** A hexane solution of *n*-butyllithium (11.8 mL, 1.59 M, 18.8 mmol) was added dropwise to a stirred solution of *ortho*-phenylenediamine (1.00 g, 9.3 mmol) in THF (40 mL) cooled to  $-40$  °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional hour. The solution

was again cooled to  $-40$  °C. A solution of *tert*-butyldimethylsilyl chloride (3.06 g, 20.3 mmol) in THF (15 mL) was added and the mixture allowed reaching room temperature. It was subsequently heated at a bath temperature of 80 °C for 10 h. Volatile components were removed under vacuum. The product was extracted from the residue with *n*-hexane ( $3 \times 10$  mL). The extracts were combined and their volume reduced to ca. 5 mL under vacuum. Storing of the solution at  $-40$  °C afforded the product as colorless crystals. Yield 2.65 g (84 %). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 6.99, 6.87$  (2 m,  $2 \times 2$  H,  $\text{C}_6\text{H}_4$ ), 3.05 (br., 2 H, NH), 0.95 (s, 18 H,  $\text{CMe}_3$ ), 0.16 ppm (s, 12 H,  $\text{SiMe}_2$ ). <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 138.5$  (CN), 121.2 ( $2 \times$  aryl CH), 26.6 ( $\text{CMe}_3$ ), 18.0 ( $\text{CMe}_3$ ),  $-4.0$  ppm ( $\text{SiMe}_2$ ) ppm.

**Synthesis of [ $\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NSi}^t\text{BuMe}_2)_2\}\text{Sn}$ ] (**1**):** A solution of  $\text{Li}(\text{-SiMe}_3)_2$  (412 mg, 2.46 mmol) in THF (5 mL) was added to a mixture of [ $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-NHSi}^t\text{BuMe}_2)_2$ ] (534 mg, 1.20 mmol) and  $\text{SnCl}_2$  (228 mg, 1.20 mmol) in THF (10 mL). The mixture was stirred for 10 h. Volatile components were removed under vacuum. The product was extracted from the residue with toluene ( $3 \times 5$  mL). The extracts were combined and volatile components removed under vacuum. The remaining orange brown oil solidified after several hours. Yield 634 mg (96 %). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.83, 3.79$  (2 m,  $2 \times 4$  H,  $\text{C}_5\text{H}_4$ ), 0.97 (s, 18 H,  $\text{CMe}_3$ ), 0.23 ppm (s, 12 H,  $\text{SiMe}_2$ ). <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 110.9$  (CN), 69.1, 65.7 ( $2 \times$  cyclopentadienyl CH), 27.6 ( $\text{CMe}_3$ ), 19.0 ( $\text{CMe}_3$ ),  $-0.9$  ppm ( $\text{SiMe}_2$ ). <sup>29</sup>Si NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 11.0$  ppm. <sup>119</sup>Sn NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 550$  ppm.  $\text{C}_{22}\text{H}_{38}\text{N}_2\text{FeSi}_2\text{Sn}$  (561.28): calcd. C 47.08, H 6.82, N 4.99%; found C 46.20, H 7.19, N 4.94 %.

**Synthesis of [ $o\text{-C}_6\text{H}_4(\text{NSi}^t\text{BuMe}_2)_2\text{Sn}$ ] (**2**):**  $\text{SnCl}_2$  (282 mg, 1.49 mmol) was added to a solution of  $\text{Li}(\text{SiMe}_3)_2$  (509 mg, 3.04 mmol) in THF (6 mL). The resulting bright yellow mixture was stirred for 30 min.  $o\text{-C}_6\text{H}_4(\text{NHSi}^t\text{BuMe}_2)_2$  (500 mg, 1.48 mmol) was added and stirring was continued for 4 h. Volatile components were removed under vacuum. The product was extracted from the residue with toluene ( $5 \times 2$  mL). The extracts were combined and volatile components removed under vacuum. The remaining deep yellow oil was triturated with a minimal amount of benzene in order to initiate crystallization. Yield 597 mg (89 %). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 7.32, 6.93$  (2 br.,  $2 \times 2$  H,  $\text{C}_6\text{H}_4$ ), 0.95 (s, 18 H,  $\text{CMe}_3$ ), 0.47 ppm (s, 12 H,  $\text{SiMe}_2$ ). <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 149.3$  (CN), 119.5, 118.1 ( $2 \times$  aryl CH), 27.7 ( $\text{CMe}_3$ ), 19.0 ( $\text{CMe}_3$ ), 0.2 ppm ( $\text{SiMe}_2$ ). <sup>29</sup>Si NMR ( $\text{C}_6\text{D}_6$ ):

$\delta = 10.2$  ppm.  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 456$  ppm. These data are in accord with those published by Lappert and co-workers.<sup>[15]</sup>

**Synthesis of (1E)<sub>2</sub> and (2E)<sub>2</sub> (E = S, Se) – General Procedure:** Toluene (3 mL) was added to the corresponding stannylene (0.22 mmol) and sulfur (7 mg, 0.22 mmol S) or red selenium (17 mg, 0.22 mmol Se). The mixture was stirred for 72 h. Slow evaporation of the solvent afforded the product as a crystalline solid, which was washed with *n*-hexane (5 × 1 mL) and dried under vacuum.

**(1S)<sub>2</sub>:** Yield 105 mg (80%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 4.22$  (br. s, 8 H,  $\text{C}_5\text{H}_4$ ), 3.82 (s, 8 H,  $\text{C}_5\text{H}_4$ ), 1.10 (s, 36 H,  $\text{CMe}_3$ ), 0.53 ppm (s, 24 H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 100.2$  (CN), 69.3 (br.), 66.7 (2 × cyclopentadienyl CH), 27.5 ( $\text{CMe}_3$ ), 19.7 ( $\text{CMe}_3$ ), −1.1 ppm ( $\text{SiMe}_2$ ).  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -211$  ppm.  $\text{C}_{44}\text{H}_{76}\text{N}_4\text{Fe}_2\text{S}_2\text{Si}_4\text{Sn}_2$  (1186.68): calcd. C 44.53, H 6.46, N 4.72%; found C 44.27, H 6.47, N 4.46%.

**(2S)<sub>2</sub>:** Yield 87 mg (81%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 7.30$ , 6.77 (2 m, 2 × 4 H,  $\text{C}_6\text{H}_4$ ), 0.99 (s, 36 H,  $\text{CMe}_3$ ), 0.69 ppm (s, 24 H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 141.8$  (CN), 119.5, 118.9 (2 × aryl CH), 28.2 ( $\text{CMe}_3$ ), 20.6 ( $\text{CMe}_3$ ), 0.7 ppm ( $\text{SiMe}_2$ ).  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -18$  ppm.  $\text{C}_{36}\text{H}_{68}\text{N}_4\text{S}_2\text{Si}_4\text{Sn}_2$  (970.85): C 44.54, H 7.06, N 5.77%; found C 44.35, H 6.77, N 4.77%.

**(1Se)<sub>2</sub>:** Yield 113 mg (80%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 4.20$  (br. s, 8 H,  $\text{C}_5\text{H}_4$ ), 3.82 (s, 8 H,  $\text{C}_5\text{H}_4$ ), 1.12 (s, 36 H,  $\text{CMe}_3$ ), 0.55 ppm (s, 24 H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 100.9$  (CN), 69.3 (br.), 66.6 (2 × cyclopentadienyl CH), 27.6 ( $\text{CMe}_3$ ), 19.7 ( $\text{CMe}_3$ ), −0.6 ( $\text{SiMe}_2$ ) ppm.  $^{77}\text{Se}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 350$  ppm.  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -447$  ppm.  $\text{C}_{44}\text{H}_{76}\text{N}_4\text{Fe}_2\text{Se}_2\text{Si}_4\text{Sn}_2$  (1280.47): calcd. C 41.27, H 5.98, N 4.38%; found C 41.21, H 6.25, N 4.39%.

**(2Se)<sub>2</sub>:** Yield 45 mg (38%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 7.29$ , 6.75 (2 m, 2 × 4 H,  $\text{C}_6\text{H}_4$ ), 1.01 (s, 36 H,  $\text{CMe}_3$ ), 0.75 ppm (s, 24 H,  $\text{SiMe}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 142.3$  (CN), 119.3, 118.8 (2 × aryl CH), 28.3 ( $\text{CMe}_3$ ), 20.7 ( $\text{CMe}_3$ ), 1.1 ppm ( $\text{SiMe}_2$ ).  $^{77}\text{Se}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 491$  ppm.  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -293$  ppm.  $\text{C}_{36}\text{H}_{68}\text{N}_4\text{Se}_2\text{Si}_4\text{Sn}_2$  (1064.63): C 40.61, H 6.44, N 5.26%; found C 40.54, H 6.65, N, 5.01%.

**Synthesis of 1(SePh)<sub>2</sub> and 2(SePh)<sub>2</sub> – General Procedure:** Toluene (3 mL) was added to the corresponding stannylene (0.22 mmol) and diphenyl diselenide (69 mg, 0.22 mmol). The solution was stirred for 2 h and subsequently layered with *n*-hexane (3 mL). The mother liquor was removed with a pipette from the resulting crystalline solid, which was washed with *n*-hexane (3 × 1 mL) and dried under vacuum.

**1(SePh)<sub>2</sub>:** Yield 129 mg (67%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 7.94$  (m, 4 H, aryl), 7.31 (m, 6 H, aryl), 4.05, 3.89 (2 m, 2 × 4 H,  $\text{C}_5\text{H}_4$ ), 1.00 (s, 18 H,  $\text{CMe}_3$ ), 0.63 (s, 12 H,  $\text{SiMe}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 136.6$ , 129.5, 127.7, 126.7 (4 × Ph), 104 (CN), 70.0, 67.0 (2 × cyclopentadienyl CH), 27.9 ( $\text{CMe}_3$ ), 20.6 ( $\text{CMe}_3$ ), −0.6 ppm ( $\text{SiMe}_2$ ).  $^{77}\text{Se}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 222$  ppm.  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -180$  ppm ( $^1J_{\text{SnSe}} = 1744$  Hz).  $\text{C}_{34}\text{H}_{48}\text{N}_2\text{FeSe}_2\text{Si}_2\text{Sn}$  (873.40): calcd. C 46.76, H 5.54, N 3.21%; found C 46.78, H 5.66, N 2.91%.

**2(SePh)<sub>2</sub>:** Yield 115 mg (68%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 7.48$  (m, 4 H, aryl), 7.08 (m, 2 H, aryl), 6.83 (m, 6 H, aryl), 6.68 (m, 2 H, aryl), 1.07 (s, 18 H,  $\text{CMe}_3$ ), 0.53 ppm (s, 12 H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 142.4$  (CN), 136.4, 129.1, 128.0 (3 × aryl CH), 123.5 (CSe), 117.2, 116.7 (2 × aryl CH), 28.0 ( $\text{CMe}_3$ ), 20.4 ( $\text{CMe}_3$ ), −0.8 ppm ( $\text{SiMe}_2$ ).  $^{77}\text{Se}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 206$  ppm.  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -81$  ppm ( $^1J_{\text{SnSe}} = 1798$  Hz).  $\text{C}_{30}\text{H}_{44}\text{N}_2\text{Se}_2\text{Si}_2\text{Sn}$  (765.48): C 47.07, H 5.79, N 3.66%; found: C 47.06, 5.71, N 3.17%.

**X-ray Crystallography:** For each data collection a single crystal was mounted on a micro-mount, cooled to 100(2) K, and all geometric and

**Table 3.** X-ray crystallographic details for *o*-C<sub>6</sub>H<sub>4</sub>(NHSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>, **1**, **2**, **(1S)<sub>2</sub>**, and **(2S)<sub>2</sub>**.

	<i>o</i> -C <sub>6</sub> H <sub>4</sub> (NHSi <sup>t</sup> BuMe <sub>2</sub> ) <sub>2</sub>	<b>1</b>	<b>2</b>	<b>(1S)<sub>2</sub></b>	<b>(2S)<sub>2</sub></b>
Chemical formula	C <sub>18</sub> H <sub>36</sub> N <sub>2</sub> Si <sub>2</sub>	C <sub>22</sub> H <sub>38</sub> FeN <sub>2</sub> Si <sub>2</sub> Sn	C <sub>18</sub> H <sub>34</sub> N <sub>2</sub> Si <sub>2</sub> Sn	C <sub>44</sub> H <sub>76</sub> Fe <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Si <sub>4</sub> Sn <sub>2</sub>	C <sub>36</sub> H <sub>68</sub> N <sub>4</sub> S <sub>2</sub> Si <sub>4</sub> Sn <sub>2</sub>
Formula mass	336.67	561.26	453.34	1186.64	970.80
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / Å	8.7749(8)	7.3255(5)	11.902(2)	15.3522(13)	15.1778(8)
<i>b</i> / Å	10.4556(11)	10.6869(8)	9.6783(14)	10.3361(6)	7.5081(3)
<i>c</i> / Å	12.7413(13)	16.6585(12)	20.249(7)	16.8906(15)	20.1893(11)
<i>a</i> / °	109.867(8)	81.567(6)	90	90	90
<i>β</i> / °	95.084(8)	88.999(6)	106.82(2)	106.099(7)	102.987(4)
<i>γ</i> / °	103.982(7)	85.732(6)	90	90	90
<i>V</i> / Å <sup>3</sup>	1048.0(2)	1286.44(16)	2232.8(10)	2575.1(4)	2241.9(2)
<i>Z</i>	2	2	4	2	2
<i>μ</i> / mm <sup>−1</sup>	0.170	1.638	1.254	1.719	10.972
<i>F</i> (000)	372	576	936	1216	1000
Crystal size / mm	0.29 × 0.25 × 0.22	0.15 × 0.08 × 0.04	0.34 × 0.16 × 0.06	0.13 × 0.08 × 0.03	0.34 × 0.13 × 0.09
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.6250 / 0.9714	0.6459 / 0.9285	0.6532 / 0.9272	0.4875 / 0.9166	0.0362 / 0.3694
<i>θ</i> range / °	2.164–32.575	1.236–25.498	2.101–31.458	2.108–28.000	4.124–68.968
No. of refls. measured	9662	9025	13593	13362	9169
Independent refls.	6146 [0.0286]	4765 [0.0295]	6499 [0.0223]	6150 [0.0390]	4070 [0.0557]
[ <i>R</i> <sub>int</sub> ]					
Parameters	217	293	218	272	227
Final <i>R</i> <sub>1</sub> ( <i>wR</i> <sub>2</sub> ), [ <i>I</i> > 2σ( <i>I</i> )]	0.0329 (0.0887)	0.0281 (0.0704)	0.0254 (0.0641)	0.0279 (0.0554)	0.0781 (0.2134)
Final <i>R</i> <sub>1</sub> ( <i>wR</i> <sub>2</sub> ), [all data]	0.0430 (0.0941)	0.0411 (0.0783)	0.0324 (0.0673)	0.0473 (0.0626)	0.0889 (0.2575)
Residual electron density / e <sup>−</sup> ·Å <sup>−3</sup>	−0.225 / 0.406	−0.362 / 0.076	−0.658 / 0.816	−0.368 / 0.511	−2.145 / 1.532
Goodness of fit	1.023	1.087	1.046	1.033	1.147

**Table 4.** X-ray crystallographic details for (1Se)<sub>2</sub>, (2Se)<sub>2</sub>, 1(SePh)<sub>2</sub>, and 2(SePh)<sub>2</sub>.

	(1Se) <sub>2</sub>	(2Se) <sub>2</sub>	1(SePh) <sub>2</sub>	2(SePh) <sub>2</sub>
Chemical formula	C <sub>44</sub> H <sub>76</sub> Fe <sub>2</sub> N <sub>4</sub> Se <sub>2</sub> Si <sub>4</sub> Sn <sub>2</sub>	C <sub>36</sub> H <sub>68</sub> N <sub>4</sub> Se <sub>2</sub> Si <sub>4</sub> Sn <sub>2</sub>	C <sub>34</sub> H <sub>48</sub> FeN <sub>2</sub> Se <sub>2</sub> Si <sub>2</sub> Sn	C <sub>30</sub> H <sub>44</sub> N <sub>2</sub> Se <sub>2</sub> Si <sub>2</sub> Sn
Formula mass	1280.44	1064.60	873.38	765.46
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> / Å	10.3449(13)	15.1651(10)	10.1870(8)	14.8101(4)
<i>b</i> / Å	16.110(4)	7.5377(3)	12.4672(10)	11.4584(3)
<i>c</i> / Å	16.510(3)	20.3073(14)	15.6604(12)	19.2734(5)
<i>α</i> / °	82.406(16)	90	68.667(6)	90
<i>β</i> / °	87.014(12)	103.796(5)	82.283(6)	95.113(2)
<i>γ</i> / °	84.268(14)	90	75.528(6)	90
<i>V</i> / Å <sup>3</sup>	2711.6(8)	2254.4(2)	1791.8(3)	3257.68(15)
<i>Z</i>	2	2	2	4
<i>μ</i> / mm <sup>-1</sup>	2.898	2.858	3.226	3.114
<i>F</i> (000)	1288	1072	876	1536
Crystal size / mm	0.20 × 0.16 × 0.13	0.26 × 0.11 × 0.03	0.25 × 0.15 × 0.13	0.16 × 0.14 × 0.05
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.4214 / 0.6968	0.5540 / 0.8910	0.3354 / 0.6529	0.6269 / 0.8621
<i>θ</i> range / °	1.897–26.998	2.065–31.708	1.858–26.999	1.380–26.000
No. of refls. measured	18830	11817	13564	19258
Independent refls. [ <i>R</i> <sub>int</sub> ]	11384 [0.0518]	6143 [0.0245]	7689 [0.0247]	6402 [0.0190]
Parameters	543	227	389	344
Final <i>R</i> <sub>1</sub> ( <i>wR</i> <sub>2</sub> ), [ <i>I</i> > 2σ( <i>I</i> )]	0.0669 (0.1678)	0.0233 (0.0512)	0.0238 (0.0606)	0.0285 (0.0702)
Final <i>R</i> <sub>1</sub> ( <i>wR</i> <sub>2</sub> ), [all data]	0.0928 (0.1884)	0.0332 (0.0548)	0.0266 (0.0622)	0.0329 (0.0737)
Residual electron density / e <sup>-</sup> Å <sup>-3</sup>	-1.879 / 2.385	-0.394 / 1.510	-0.424 / 0.561	-0.364 / 0.842
Goodness of fit	1.127	1.045	1.052	1.093

intensity data were taken from this sample by  $\omega$ -scans with steps of 1°. Data collections were carried out using Mo-*K*<sub>α</sub> radiation ( $\lambda = 0.71073$  Å), or in case of (2S)<sub>2</sub>, with Cu-*K*<sub>α</sub> radiation ( $\lambda = 1.54186$  Å), monochromatization was done with graded multilayer mirrors. Diffraction experiments were carried out on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector [1 and 2(SePh)<sub>2</sub>] or on a Stoe StadiVari diffractometer equipped with a 4-circle goniometer and a DECTRIS Pilatus 200K detector (all other samples). The data sets were corrected for absorption (by integration, multi-scan method), Lorentz and polarization effects. The structures were solved by direct methods (SHELXT) and refined using alternating cycles of least-squares refinements against *F*<sup>2</sup> (SHELXL2014/7).<sup>[38]</sup> H atoms bonded to N atoms were refined with a distance constraint. Hydrogen atoms bonded to C atoms were included to the models in calculated positions. All protons were treated with the 1.2 fold isotropic displacement parameter of their bonding partner. Experimental details for each diffraction experiment are given in Table 3 and Table 4.

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-1971080 [*o*-C<sub>6</sub>H<sub>4</sub>(NHSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub>], CCDC-1971081 (1), CCDC-1971082 (2), CCDC-1971083 [(1S)<sub>2</sub>], CCDC-1971084 [(2S)<sub>2</sub>], CCDC-1971085 [(1Se)<sub>2</sub>], CCDC-1971086 [(2Se)<sub>2</sub>], CCDC-1971087 [1(SePh)<sub>2</sub>], and CCDC-1971088 [2(SePh)] (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

**Supporting Information** (see footnote on the first page of this article): The molecular structure of *o*-C<sub>6</sub>H<sub>4</sub>(NHSi<sup>t</sup>BuMe<sub>2</sub>)<sub>2</sub> in the crystal (Figure S1) and plots of NMR spectra (Figures S2–S33).

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