



*Dedicated to Prof. Ion Grosu
on the occasion of his 70th anniversary*

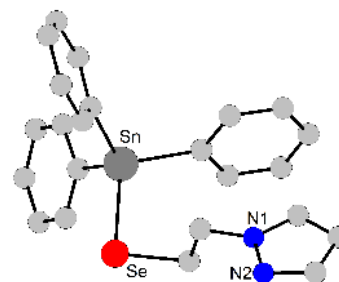
HOMOLEPTIC TRIORGANOTIN(IV) ORGANOSELENOLATES OF TYPE $R_3Sn(SeCH_2CH_2pz)$

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The homoleptic triorganotin(IV) compounds of type $R_3Sn(SeCH_2CH_2pz)$ [R = Me (**1**), ⁿBu (**2**), Bn (**3**), Ph (**4**); pz = pyrazole] were obtained by NaCl elimination in the reaction between Na[SeCH₂CH₂pz] and the appropriate triorganotin(IV) chloride. All compounds were structurally investigated in solution by multinuclear NMR (¹H, ¹³C, ⁷⁷Se, ¹¹⁹Sn) and APCI+ mass spectrometry. The NMR spectra suggested the equivalence of the three organic groups attached to tin, as well as the existence of the Se–Sn bonds in solution. The crystal and molecular structure of compound **4** was determined by single-crystal X-ray diffraction. The structure revealed a monodentate behaviour of the organoselenolato ligand, and a distorted tetrahedral coordination geometry about tin. H···N intermolecular interactions resulted in dimeric associations, while further π CH···Cg secondary bonding lead to a 3D supramolecular network.



INTRODUCTION

Organotin(IV) compounds attracted overtime a continuously increased interest due to their potential in various fields, *e.g.* biology,^{1,2} new materials,³ and organic synthesis.⁴ They proved antifungal and antibacterial properties, as well as antiproliferative activity against various types of cancer.^{5–8} Species containing both chalcogen (sulfur or selenium) and tin in the same molecule were used to design promising single-source precursors for nanoparticles or thin films of tin chalcogenides, the latter employed in narrow-gap semiconductors for photovoltaic devices.^{9–12} Organotin derivatives are used in homogenous catalysis, mainly for

transesterification reactions, and highly selective acylation of alcohols.^{13–16}

On the other hand, the organoselenium chemistry knew a tremendous development during the last years as well, based on their biological and/or catalytic properties. Various diorganodiselenides and diorganoselenides proved to be good antioxidants, apoptosis inducers, or antiproliferative agents.^{17–23} In addition, chemical species containing a pyrazole ring in their structure were used in pharmaceutical products, based on the large spectrum of biological activities induced by the pyrazole moiety, *e.g.* antibacterial, antifungal, antitumour, anti-inflammatory, or antiviral.^{24–26}

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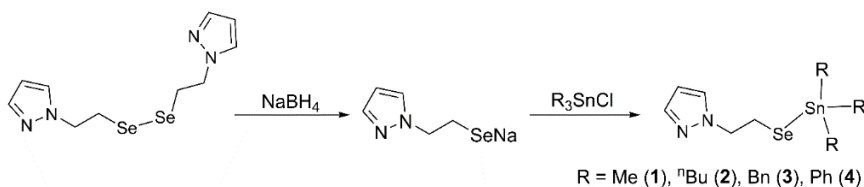
Finally, the presence of both selenium and nitrogen in the same ligand molecule, makes such species prone to coordinate easily to both *soft* and *hard* metal centers.

A huge number of tin complexes bearing ligands with S or O donor atoms were described in the literature, but the coordination ability of organoselenium ligands towards tin was much less exploited. We reported previously about the synthesis and structural characterization of various organotin(IV) compounds of type R_xSnL_{4-x} (R = alkyl or aryl groups; $x = 1 - 3$, L = mono- or bidentate ligands with chalcogen (O, S, Se) and/or N donor atoms.²⁷⁻³⁰ As a continuation of our studies, we report here about the synthesis and structural characterization of the homoleptic compounds of type $R_3Sn(SeCH_2CH_2pz)$ [R = Me (**1**), ⁿBu (**2**), Bn (**3**), Ph (**4**); pz = pyrazole]. The presence of both selenium and

the pyrazole moiety in the organoselenolato ligand is expected to significantly improve the biological activity of the organotin species.

RESULTS

The triorganoant(IV) compounds of type $R_3Sn(SeCH_2CH_2pz)$ [R = Me (**1**), ⁿBu (**2**), Bn (**3**), Ph (**4**); pz = pyrazole] were prepared by reacting the sodium organoselenolate $Na[SeCH_2CH_2pz]$, *in situ* obtained from $(pzCH_2CH_2)_2Se_2$ and $NaBH_4$, with the appropriate triorganotin(IV) chloride, in a 1:1 molar ratio, as depicted in Scheme 1. The alkyl substituted compounds **1** – **3** were isolated as colorless oils, while compound **4** is a microcrystalline colorless product. All compounds are soluble in common organic solvents.



Scheme 1 – Synthesis of compounds **1** – **4**.

All compounds were investigated by NMR spectroscopy (¹H, ¹³C, ⁷⁷Se, ¹¹⁹Sn, 2D experiments) in CDCl₃ solution, and mass spectrometry. For compound **4** the crystal and molecular structure was determined by single-crystal X-ray diffraction.

The molecular structure of **4** with the atom numbering scheme is shown in Fig. 1, while a selection of interatomic distances and bond angles are given in Table 1.

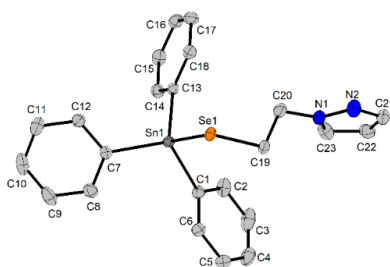


Fig. 1 – ORTEP-like representation of compound **4**, with thermal ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity.

Table 1

Interatomic distances (Å) and angles (°) for compound **4**

Sn1–C1	2.1397(1)	Sn1–Se1	2.5387(1)
Sn1–C7	2.1297(1)	N2...H19A	2.625(2)
Sn1–C13	2.1423(1)		
C1–Sn1–C7	113.33(1)	Se1–Sn1–C1	100.82(1)
C1–Sn1–C13	110.58(1)	Se1–Sn1–C7	112.48(1)
C7–Sn1–C13	108.08(1)	Se1–Sn1–C13	111.49(1)
		Sn1–Se1–C19	97.32(1)

DISCUSSION

Solution behaviour

The ^1H and ^{13}C NMR spectra of compounds **1–4** show the expected resonances for the organic groups attached to tin and selenium, respectively. For each compound, they suggest the equivalence of the three organic groups attached to tin. The aliphatic regions of both the ^1H and the ^{13}C NMR spectra of compounds **1** and **3** contain singlet resonances for the CH_3Sn and the $\text{C}_6\text{H}_4\text{CH}_2\text{Sn}$ protons, accompanied by $^{117/119}\text{Sn}$ satellites, while the spectra of the $^n\text{BuSn}$ moiety contain characteristic ^1H (multiplet) and ^{13}C (singlet) resonances, the latter accompanied by ^{119}Sn -

^{13}C satellites. The protons in the anionic $\text{pzCH}_2\text{CH}_2\text{Se}$ ligands give for all compounds multiplet resonances both in the aliphatic and the aromatic regions, with a characteristic splitting pattern determined by the proton-proton couplings. The ^1H and the ^{13}C NMR resonances of the CH_2Se moiety are accompanied by ^{77}Se - ^1H and ^{77}Se - ^{13}C satellites, respectively. The values of the ^{119}Sn - ^1H (2J) and the ^{119}Sn - ^{13}C (1J) coupling constants were used to assign the coordination geometry about tin in the complexes substituted with alkyl groups.^{31–33} We found that in compounds **1–3** the tin(IV) atoms are tetrahedrally surrounded by three alkyl groups and a $\text{pzCH}_2\text{CH}_2\text{Se}$ ligand. The values of the $^2J_{\text{SnH}}$ and the $^1J_{\text{SnC}}$ coupling constants of compounds **1–3** are given in Table 2, along with the calculated C–Sn–C angles.

Table 2

Values of $^2J_{^{119}\text{SnH}}$ and $^1J_{^{119}\text{SnC}}$ coupling constants, and calculated C–Sn–C angles in solution for compounds **1–3**

Compound	^1H NMR		$^{13}\text{C}\{^1\text{H}\}$ NMR	
	$^2J(^{119}\text{Sn}, ^1\text{H})$	C–Sn–C	$^1J(^{119}\text{Sn}, ^{13}\text{C})$	C–Sn–C
1	59.8	112.0 ³¹	340.1	106.6 ³²
2	–	–	317.5	104.6 ³²
3	59.1	111.6 ³¹	264.7	101.2 ³³

$$\theta = 0.0161|^2J|^2 - 1.32|^2J| + 133.4;^{31} \ ^1J = 11.40 - 875;^{32} \ ^1J = 9.990 - 746;^{33}$$

The investigation of the solution behaviour of these compounds has also the advantage of using ^{77}Se and ^{119}Sn NMR spectra, which for each compound display singlet resonances accompanied by almost equal ^{77}Se - ^{119}Sn and ^{119}Sn - ^{77}Se satellites, respectively, thus confirming that the Sn–Se bond is preserved in solution. Moreover, the NMR spectra revealed that the organoselenolato ligand interacts

with the metal center only by the chalcogen, while the nitrogen atoms in the pyrazole ring are not involved in coordination to selenium or tin, at least at room temperature.

The $^{77}\text{Se}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR chemical shifts for compounds **1–4** are summarized in Table 3. For comparison, the corresponding chemical shifts for the starting materials are given also.

Table 3

^{77}Se and ^{119}Sn NMR resonances for compounds **1–4** and the starting materials

Cpd.	$\delta_{^{77}\text{Se}}$ (ppm)	$^1J_{^{117}\text{SnSe}}/^1J_{^{119}\text{SnSe}}$ (Hz)	$\delta_{^{119}\text{Sn}}$ (ppm)	$^1J_{\text{Se}^{119}\text{Sn}}$ (Hz)	R_3SnCl	$\delta_{^{119}\text{Sn}}$ (ppm)
R_2Se_2^a	283.0	–	–	–	–	–
1	–193.3	956.2 (^{117}Sn) 993.7 (^{119}Sn)	60.1	994.2	Me_3SnCl	170.1
2	–228.5	971.6 (^{117}Sn) 1019.6 (^{119}Sn)	62.3	1018.5	Bu_3SnCl	157.4
3	–193.9	1154.4 (^{117}Sn) 1209.2 (^{119}Sn)	4.68	1206.3	Bn_3SnCl	51.1
4	–227.0	1116.7 (^{117}Sn) 1170.6 (^{119}Sn)	–68.7	1172.9	Ph_3SnCl	–45.1

^a R = pzCH_2CH_2

The NMR spectra suggest a tetrahedral coordination geometry about tin(IV), with the organoselenolato ligand as a monodentate κSe moiety.³⁴

The APCI+ mass spectra contain the base peak at m/z values corresponding to the $[\text{R}_3\text{Sn}]^+$ cation resulted by ionization, namely at 164.97234 (calcd. 164.97207), 292.11987 (calcd.

292.12075), 393.06638 (calcd. 393.06597), and 351.01956 (calcd. 351.01902), for **1**, **2**, **3**, and **4**, respectively.

Single-crystal X-ray diffraction studies

The coordination geometry about the tin atom in compound **4** is a distorted tetrahedron, with bond angles in the range $100.82(1)^\circ - 111.49(1)^\circ$, while the selenium atom has a distorted pseudo-tetrahedral coordination sphere, with the Sn1–Se1–C19 angle of $97.32(1)^\circ$. The organoselenolato group behaves as a monodentate κSe ligand, with Sn–Se interatomic distances slightly shorter than those

found in $[R_2Sn(2-SeC_5H_4N)_2]$ ($R = Me$, 2.615(3), 2.618(3), 2.595(3) and 2.585(3) Å in the two independent molecules; $R = tBu$, 2.622(2) Å).¹¹

The nitrogen atoms in the planar pyrazole ring have sp^2 hybridization. The lone pair of electrons at N2 is involved in secondary bonding with the H19A proton in the CH_2Se neighboring molecule, thus resulting in dimeric associations ($N2 \cdots H19A$ 2.625(2) Å, vs. $\Sigma r_{vdW}(N,H)$ 2.86 Å³⁵), while further $\pi CH \cdots Cg$ short contacts [$H3 \cdots Cg(C13-C18)$ and $H15 \cdots Cg(C1-C6)$] give rise to a supramolecular network. A dimeric unit in the crystal of **4** is displayed in Fig. 2 and the supramolecular network in Fig. 3.

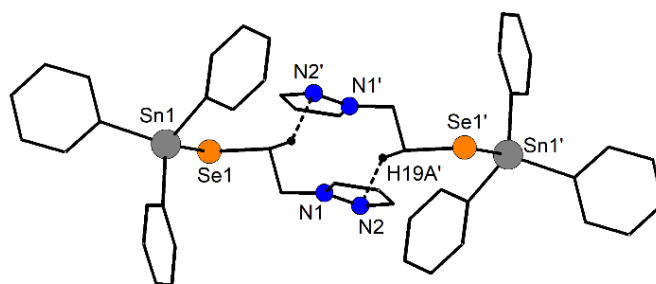


Fig. 2 – Dimeric association in the crystal of compound **4**. $N2 \cdots H19A'$ 2.625(2) Å. Symmetry equivalent positions ($-x, 1-y, 1-z$) are given by “prime”.

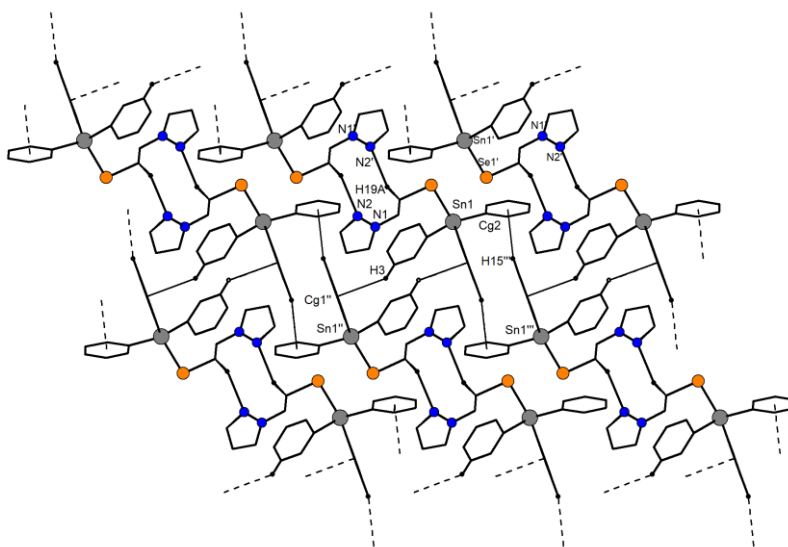


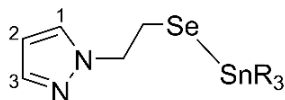
Fig. 3 – Supramolecular network (view along axis *b*) in the crystal of compound **4**. $H3 \cdots Cg1''$ 2.947 Å, $H15''' \cdots Cg2$ 2.914 Å. Symmetry equivalent positions ($1/2-x, -1/2+y, 3/2-z$) and ($3/2-x, -1/2+y, 3/2-z$) are given by *second* and *tert*, respectively

EXPERIMENTAL

The diorganodiselenide $(pzCH_2CH_2)_2Se_2$ was prepared by employing the literature procedures.³⁰ The starting triorganotin halides, namely R_3SnCl ($R = Me, tBu, Bn, Ph$), as well as other necessary

reactants were commercially available and used as received. The melting point for **4** was measured on an Electrothermal 9200 apparatus. Elemental analyses were performed on a Flash EA 1112 analyzer. The APCI+ mass spectra were recorded on a Thermo Scientific LTQ-Orbitrap XL spectrometer equipped

with a standard ESI/APCI source. The ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{77}\text{Se}\{^1\text{H}\}$, and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra were recorded on a BRUKER Avance 400 instrument operating at 400.13, 100.61, 76.31, and 149.21 MHz, respectively. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts are reported in δ units (ppm) relative to the residual peak of the solvent in the ^1H NMR spectra (CHCl_3 , 7.26 ppm), and to the peak of the deuterated solvent (CDCl_3 , 77.16 ppm) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. They were assigned using 2D NMR experiments (COSY, HSQC and HMBC), and are given according to the numbering way displayed in Scheme 2. For the $^{77}\text{Se}\{^1\text{H}\}$, and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra, Me_2Se and Me_4Sn , respectively, were used as external standards. The NMR and the mass spectra were processed using the MestReNova,³⁶ and the Thermo Xcalibur³⁷ softwares, respectively.



Scheme 2 – Numbering scheme for NMR assignments.

Synthesis of $\text{Me}_3\text{Sn}(\text{SeCH}_2\text{CH}_2\text{pz})$ (1)

To a yellow solution of $(\text{pzCH}_2\text{CH}_2)_2\text{Se}_2$ (0.281 g, 0.806 mmol) in 30 mL degassed absolute ethanol, cooled on an ice bath, NaBH_4 (0.073 g, 1.929 mmol, 20% excess) was added under argon, and the reaction mixture was stirred for 1 h. After the hydrogen release had subsided, Me_3SnCl (0.321 g, 1.612 mmol) was added, and the stirring continued overnight. The next day, ethanol was evaporated, and the remaining mixture was treated with dry toluene (30 mL). The solid residue was separated by filtration, and, from the clear solution, the solvent was removed under vacuum. The title compound resulted as a colourless oil, which was subsequently washed with hexane (3×5 mL). Yield: 0.45 g (82%). Anal. calcd. for $\text{C}_8\text{H}_{16}\text{N}_2\text{SeSn}$ (MW = 337.90): C, 28.44; H, 4.77; N, 8.29%. Found: C, 28.63; H, 4.82; N, 8.33%. ^1H NMR (δ , ppm): 0.49 (s, 9H, SnCH_3 , $^2J_{119\text{SnH}}$ 59.8, $^2J_{117\text{SnH}}$ 53.2 Hz), 2.96 (t, 2H, $\text{CH}_2\text{CH}_2\text{Se}$, $^3J_{\text{HH}}$ 7.5 Hz), 4.32 (t, 2H, $\text{CH}_2\text{CH}_2\text{Se}$, $^3J_{\text{HH}}$ 7.4 Hz), 6.25 (t, 1H, pz-H_2 , $^3J_{\text{HH}}$ 2.1 Hz), 7.45 (d, 1H, pz-H_1 , $^3J_{\text{HH}}$ 2.1 Hz), 7.52 (d, 1H, pz-H_3 , $^3J_{\text{HH}}$ 1.7 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): –5.1 (SnCH_3 , $^1J_{117\text{SnC}}$ 325.4, $^1J_{119\text{SnC}}$ 340.1 Hz), 17.1 ($\text{CH}_2\text{CH}_2\text{Se}$, $^1J_{\text{SeC}}$ 15.2 Hz), 55.3 ($\text{CH}_2\text{CH}_2\text{Se}$, $^2J_{\text{SnC}}$ 11.3 Hz), 105.4 (pz-C_2), 129.5 (pz-C_1), 139.8 (pz-C_3). $^{77}\text{Se}\{^1\text{H}\}$ NMR (δ , ppm): –193.3 (s, $^1J_{117\text{SnSe}}$ 956.2, $^1J_{119\text{SnSe}}$ 993.7 Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (δ , ppm): 60.1 (s, $^1J_{\text{SnSe}}$ 994.2 Hz). APCI+ MS, m/z (%): 164.97234 (100) $[\text{M-SeCH}_2\text{CH}_2\text{pz}]^+$ (164.97207

calcd. for $\text{C}_3\text{H}_9\text{Sn}$); 233.01019 (12) $[\text{Me}_3\text{Snpz+H}]^+$ (233.00170 calcd. for $\text{C}_6\text{H}_{13}\text{N}_2\text{Sn}$).

Compounds **2** – **4** were prepared as described above for compound **1**:

$^n\text{Bu}_3\text{Sn}(\text{SeCH}_2\text{CH}_2\text{pz})$ (2), was isolated as a colourless oil from $(\text{pzCH}_2\text{CH}_2)_2\text{Se}_2$ (0.167 g, 0.479 mmol), NaBH_4 (0.043 g, 1.136 mmol), and $^n\text{Bu}_3\text{SnCl}$ (0.312 g, 0.958 mmol). Yield: 0.275 g (62%). Anal. calcd. for $\text{C}_{17}\text{H}_{34}\text{N}_2\text{SeSn}$ (MW = 464.14): C, 43.99; H, 7.38; N, 6.04%. Found: C, 44.12; H, 7.72; N, 6.31%. ^1H NMR (δ , ppm): 0.89 (t, 9H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}}$ 7.3 Hz), 1.10–1.22 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.27–1.36 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.50–1.58 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.91 (t, 2H, $\text{CH}_2\text{CH}_2\text{Se}$, $^3J_{\text{HH}}$ 7.6, $^2J_{\text{SeH}}$ 35.6 Hz), 4.29 (t, 2H, $\text{CH}_2\text{CH}_2\text{Se}$, $^3J_{\text{HH}}$ 7.5 Hz), 6.23 (t, 1H, pz-H_2 , $^3J_{\text{HH}}$ 1.8 Hz), 7.42 (d, 1H, pz-H_1 , $^3J_{\text{HH}}$ 2.1 Hz), 7.52 (br, 1H, pz-H_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 3.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $^1J_{117\text{SnC}}$ 302.4, $^1J_{119\text{SnC}}$ 317.5 Hz), 13.70 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 16.2 ($\text{CH}_2\text{CH}_2\text{Se}$, $^1J_{\text{SeC}}$ 14.6 Hz), 27.1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $^2J_{117\text{SnC}}$ 60.1, $^2J_{119\text{SnC}}$ 62.8 Hz), 28.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $^3J_{\text{SnC}}$ 21.4 Hz), 55.4 ($\text{CH}_2\text{CH}_2\text{Se}$, $^2J_{\text{SeC}}$ 9.9 Hz), 105.2 (pz-C_2), 129.3 (pz-C_1), 139.6 (pz-C_3). $^{77}\text{Se}\{^1\text{H}\}$ NMR (δ , ppm): –228.5 (s, $^1J_{117\text{SnSe}}$ 971.6 Hz, $^1J_{119\text{SnSe}}$ 1019.6 Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (δ , ppm): 62.3 (s, $^1J_{\text{SnSe}}$ 1018.5 Hz). APCI+ MS, m/z (%): 292.11987 (100) $[\text{M-SeCH}_2\text{CH}_2\text{pz+H}]^+$ (292.12075 calcd. for $\text{C}_{12}\text{H}_{28}\text{Sn}$).

$\text{Bn}_3\text{Sn}(\text{SeCH}_2\text{CH}_2\text{pz})$ (3), was isolated as a colourless oil from $(\text{pzCH}_2\text{CH}_2)_2\text{Se}_2$ (0.127 g, 0.364 mmol), NaBH_4 (0.034 g, 0.898 mmol), and Bn_3SnCl (0.311 g, 0.728 mmol). Yield: 0.272 g (66%). Anal. calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{SeSn}$ (MW = 566.19): C, 55.16; H, 4.98; N, 4.95%. Found: C, 55.47; H, 5.07; N, 5.12%. ^1H NMR (δ , ppm): 2.53 (s, 2H, CH_2Sn , $^2J_{\text{SnH}}$ 59.1 Hz), 2.68 (t, 2H, $\text{CH}_2\text{CH}_2\text{Se}$, $^3J_{\text{HH}}$ 7.3, $^2J_{\text{SeH}}$ 24.1 Hz), 4.06 (t, 2H, $\text{CH}_2\text{CH}_2\text{Se}$, $^3J_{\text{HH}}$ 7.3 Hz), 6.24 (t, 1H, pz-H_2 , $^3J_{\text{HH}}$ 2.0 Hz), 6.86 (d, 6H, $\text{C}_6\text{H}_5\text{-H}_o$, $^3J_{\text{HH}}$ 7.2 Hz), 7.05 (t, 3H, $\text{C}_6\text{H}_5\text{-H}_p$, $^3J_{\text{HH}}$ 7.2 Hz), 7.15–7.22 (m, 6H, $\text{C}_6\text{H}_5\text{-H}_m$), 7.32 (d, 1H, pz-H_1 , $^3J_{\text{HH}}$ 2.1 Hz), 7.53 (d, pz-H_3 , $^3J_{\text{HH}}$ 1.8 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 16.5 ($\text{CH}_2\text{CH}_2\text{Se}$, $^1J_{\text{SeC}}$ 15.2 Hz), 22.1 (SnCH_2 , $^1J_{117\text{SnC}}$ 251.9, $^1J_{119\text{SnC}}$ 264.7 Hz), 54.94 ($\text{CH}_2\text{CH}_2\text{Se}$, $^2J_{\text{SeC}}$ 11.4 Hz), 105.2 (pz-C_2), 124.5 ($\text{C}_6\text{H}_5\text{-C}_p$), 127.8 ($\text{C}_6\text{H}_5\text{-C}_o$, $^3J_{\text{SnC}}$ 28.7 Hz), 128.9 ($\text{C}_6\text{H}_5\text{-C}_m$, $^4J_{\text{SnC}}$ 15.8 Hz), 129.6 (pz-C_1), 139.7 (pz-C_3), 139.9 ($\text{C}_6\text{H}_5\text{-C}_i$, $^2J_{\text{SnC}}$ 41.6 Hz). $^{77}\text{Se}\{^1\text{H}\}$ NMR (δ , ppm): –193.9 (s, $^1J_{117\text{SnSe}}$ 1154.4, $^1J_{119\text{SnSe}}$ 1209.2 Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (δ , ppm): 4.68 (s, $^1J_{\text{SnSe}}$ 1206.3, $^1J_{\text{SnC}}$ 266.5 Hz). APCI+ MS, m/z (%): 174.97693 (35) $[\text{pzCH}_2\text{CH}_2\text{Se}]^+$ (174.97690

calcd. for $C_5H_7N_2Se$, 393.06638 (100) $[Sn(CH_2C_6H_5)_3]^+$ (393.06597, calcd. for $C_{21}H_{21}Sn$). **Ph₃Sn(SeCH₂CH₂pz) (4)**, was isolated as a colourless solid, from $(pzCH_2CH_2)_2Se_2$ (0.125 g, 0.358 mmol), $NaBH_4$ (0.032 g, 0.861 mmol), and Ph_3SnCl (0.276 g, 0.716 mmol). Yield: 0.266 g (71%). M.p. 52°C. Anal. calcd. for $C_{23}H_{22}N_2SeSn$ (MW = 524.10): C, 52.71; H, 4.23; N, 5.35%. Found: C, 52.67; H, 4.44; N, 5.42%. 1H NMR (δ , ppm): 2.92 (t, 2H, CH_2CH_2Se , $^3J_{HH}$ 7.7, $^2J_{SeH}$ 34.00 Hz), 4.12 (t, 2H, CH_2CH_2Se , $^3J_{HH}$ 7.5 Hz), 6.13 (t, 1H, *pz*- H_2 , $^3J_{HH}$ 2.1 Hz), 6.96 (d, 1H, *pz*- H_1 , $^3J_{HH}$ 2.2 Hz), 7.39–7.50 (m, 10H, *pz*- H_3 + C_6H_4 - H_{m+p}), 7.58–7.74 (m, 6H, C_6H_4 - H_o). $^{13}C\{^1H\}$ NMR (δ , ppm): 18.1 (CH_2CH_2Se , $^1J_{SeC}$ 15.2 Hz), 54.8 (CH_2CH_2Se , $^2J_{SeC}$ 11.2 Hz), 105.2 (*pz*- C_2), 129.2 (C_6H_4 - C_m + *pz*- C_1 , $^3J_{SnC}$ 56.6 Hz), 130.0 (C_6H_4 - C_p , $^4J_{SnC}$ 12.6 Hz), 136.8 (C_6H_4 - C_o , $^2J_{SnC}$ 42.7 Hz), 139.6 (*pz*- C_3). $^{77}Se\{^1H\}$ NMR (δ , ppm): –227.0 (s, $^1J_{117SnSe}$ 1116.7, $^1J_{119SnSe}$ 1170.6 Hz). $^{119}Sn\{^1H\}$ NMR (δ , ppm) –68.7 (s, $^1J_{SnSe}$ 1172.9 Hz). APCI+ MS, *m/z* (%): 351.01956 (100) $[Sn(C_6H_5)_3]^+$ (351.01902 calcd. for $C_{18}H_{15}Sn$).

Crystal structure determination

Suitable crystals for single-crystal X-ray diffraction were obtained for **4** from a mixture of $CHCl_3$ and *n*-hexane in a 1:4 ratio (v:v). Details of the crystal structure determination and refinement are given in Table 4. Data were collected on a Bruker D-8 Venture diffractometer, using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) from a $I\mu S$ 3.0 microfocus source with multilayer optics, at 100 K. The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the Bruker APEX3 Software Package was used.³⁸ Intermolecular secondary bonding interactions were found with PLATON.^{39,40} The drawings were created with the Diamond program.⁴¹

Table 4

X-ray crystal data and structure refinement for $Ph_3Sn(SeCH_2CH_2pz)$ (**4**)

Empirical formula	$C_{23}H_{22}N_2SeSn$
Formula weight	524.10
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	
<i>a</i> (Å)	10.6529(3)
<i>b</i> (Å)	8.9222(2)
<i>c</i> (Å)	22.0846(6)
<i>α</i> (°)	90
<i>β</i> (°)	95.343(1)
<i>γ</i> (°)	90
Volume (Å ³)	2089.96(9)
<i>Z</i>	4
<i>D_c</i> (g/cm ³)	1.666
Absorption coefficient (mm ⁻¹)	2.974
<i>F</i> (000)	1032
Crystal size, mm	0.163 × 0.217 × 0.295
θ range for data collections (°)	2.05 to 28.35
Reflections collected	55313
Independent reflections	4831 [R(int) = 0.045]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5207/ 0 / 244
Goodness-of-fit on <i>F</i> ²	1.052
Final <i>R</i> indices [<i>F</i> ² > 2σ(<i>F</i> ²)]	R1 = 0.0185, wR2 = 0.0432
<i>R</i> indices (all data)	R1 = 0.0217, wR2 = 0.0440
Largest diff. peak and hole, eÅ ⁻³	0.570 and –0.511

CONCLUSIONS

The homoleptic triorganotin(IV) compounds of type $R_3Sn(SeCH_2CH_2pz)$ [*R* = Me (**1**), ⁿBu (**2**), Bn

(**3**), Ph (**4**); *pz* = pyrazole] were isolated as colorless oils (the aliphatic derivatives) or as a solid (the phenyl substituted derivative). For the aliphatic compounds **1** – **3** we assigned a distorted tetrahedral

coordination geometry in solution, based on the $^2J(^{119}\text{Sn}, ^1\text{H})$ or the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants in their NMR spectra recorded at room temperature. The existence of Se–Sn bonds in solution was confirmed for all compounds by their ^{119}Sn and ^{77}Se NMR spectra, which display ^{77}Se – ^{119}Sn and $^{117/119}\text{Sn}$ – ^{77}Se satellites, respectively. Single-crystal X-ray diffraction studies upon the microcrystalline compound **4** revealed a distorted tetrahedral coordination geometry around the tin atom in each molecule. CH \cdots Cg secondary interactions lead to a 3D supramolecular network containing dimeric units based on N \cdots H intermolecular interactions.

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Supplementary material

CCDC 2420318 contains the supplementary crystallographic data for compound **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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