

## Article

# Molecular Structures of the Pyridine-2-olates PhE(pyO)<sub>3</sub> (E = Si, Ge, Sn)—[4+3]-Coordination at Si, Ge vs. Heptacoordination at Sn

Sarah Kuß <sup>1</sup>, Erica Brendler <sup>2</sup>  and Jörg Wagler <sup>1,\*</sup> 

<sup>1</sup> Institut für Anorganische Chemie, TU Bergakademie Freiberg, D-09596 Freiberg, Germany

<sup>2</sup> Institut für Analytische Chemie, TU Bergakademie Freiberg, D-09596 Freiberg, Germany

\* Correspondence: joerg.wagler@chemie.tu-freiberg.de; Tel.: +49-3731-39-4343

**Abstract:** The phenyltetrel pyridine-2-olates PhE(pyO)<sub>3</sub> (E = Si, Ge, Sn; pyO = pyridine-2-olate) were synthesized from the respective chlorides PhECl<sub>3</sub> and 2-hydroxypyridine (2-pyridone) with the aid of a sacrificial base (triethylamine). Their solid-state structures were determined by single-crystal X-ray diffraction. PhSi(pyO)<sub>3</sub> exhibits a three-fold capped tetrahedral Si coordination sphere ([4+3]-coordination, Si···N separations ca. 3.0 Å), in accordance with structures of previously reported silicon pyridine-2-olates. PhGe(pyO)<sub>3</sub> adopts a related [4+3]-coordination mode, which differs in terms of the tetrahedral faces capped by the pyridine N atoms. Additionally, shorter Ge···N separations (2.8–2.9 Å) indicate a trend toward tetrel hypercoordination. PhSn(pyO)<sub>3</sub> features heptacoordinate tin within a pentagonal bipyramidal Sn coordination sphere (Sn···N separations 2.2–2.4 Å). For the Si and Sn compounds, <sup>29</sup>Si and <sup>119</sup>Sn NMR spectroscopy indicates retention of their tetrel coordination number in chloroform solution.



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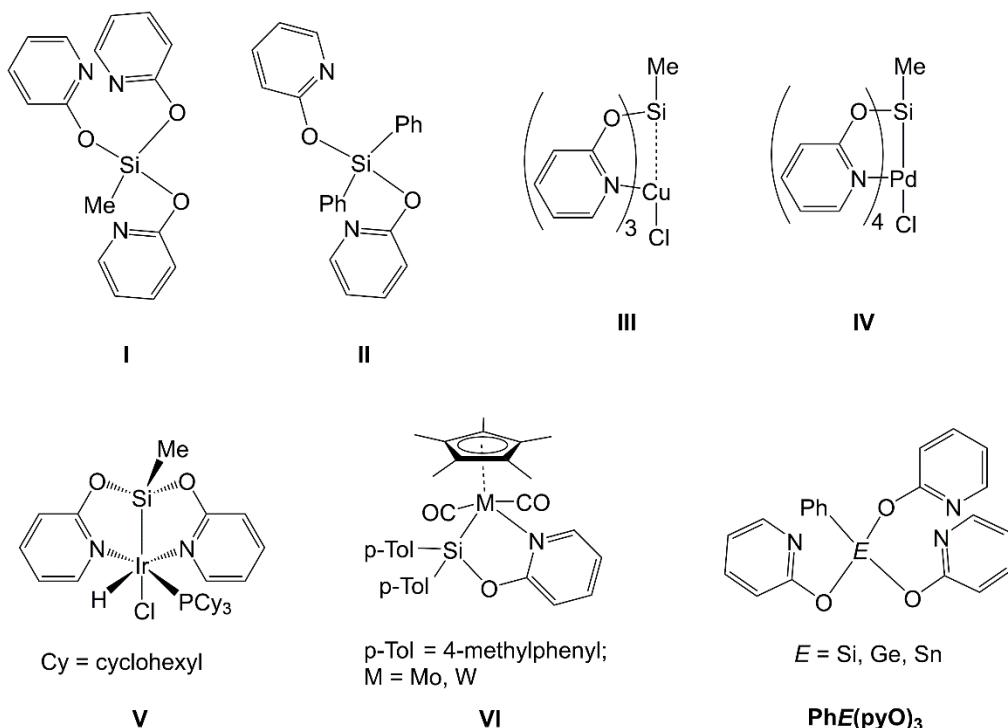


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## 1. Introduction

In previous studies [1–3] it was shown that in silicon pyridine-2-olates the potentially bidentate pyO group (pyO = pyridine-2-olate) is essentially monodentate, bound to Si through an Si–O bond and capping tetrahedral faces of the Si coordination sphere by rather remote N···Si coordination (e.g., in compounds I [2] and II [3], Figure 1). In addition, it has been shown that pyridine-2-olates may serve as bridging ligands with their N atom coordinating to a transition metal (TM) atom, thus fostering the formation of heteronuclear Si···TM complexes with higher-coordinate Si atom, for example in compounds III and IV [2] and some others [2,4]. Whereas in pyO-TM-silyl-complexes with tetracoordinate Si atom and thus formally covalent TM–Si bond (such as V [5] and VI [6]) pyO ligand(s) may buttress this diatomic core and thus simply add some stability, in cases with formally dative bonding or weak TM···Si attraction the availability of dangling N-donor sites in silicon pyridine-2-olates may be a key toward their binding to transition metals. With the perspective of extending studies of pyO-bridged TM-tetrel-complexes to heavier congeners of Si, the mode(s) of pyO-coordination at the heavier congeners (Ge, Sn) may hint at their suitability as starting materials for pyO-bridged tetrel-TM complexes. So far, molecular structures (in terms of crystallographically proven configurations) of germanium pyridine-2-olates are unknown [7]. For Sn-pyO-compounds, two crystal structures have been reported for compounds with penta- [8] or penta- and hexacoordinate Sn [9] in which the pyridine-2-olate is bridging two Sn atoms (with Sn–O and Sn–N bonds). These examples, however, involve a distannamethane motif [8] or a combination of different Sn sites (SnBu<sub>2</sub> and SnBu<sub>3</sub> groups) [9]. Crystallographic studies of pyO coordination in rather simple organotin compounds are yet to be performed. In the current study, we present a systematic comparison of the solid-state structures of the series of related phenyltetrel

compounds  $\text{PhE}(\text{pyO})_3$  ( $E = \text{Si, Ge, Sn}$ ). Whereas our interest in these compounds mainly arises from aspects of coordination chemistry (coordination of bidentate ligands at the tetrel and as bridging ligands between tetrel and transition metal), the exploration of coordination compounds of heavier tetrels with pyridine bases may also be of interest for other research fields. Both pyridine bases as ligands [10,11] and tin as a central atom [12] are the focus of the development of anti-cancer drugs.



**Figure 1.** Selected pyridine-2-olate compounds of silicon with remote  $\text{N}\cdots\text{Si}$  coordination (I,II), with hypercoordinate Si atom featuring a metal atom in the coordination sphere (III,IV) and with tetracoordinate Si bound to a transition metal atom (V,VI) as well as a generic representation of the compounds ( $\text{PhE}(\text{pyO})_3$ ) under investigation in this paper.

## 2. Materials and Methods

### 2.1. General Considerations

Starting materials 2-hydroxypyridine (ABCR, Karlsruhe, Germany, 98%), phenyltrichlorosilane (Wacker, Burghausen, Germany), phenyltrichlorogermaine (Gelest, Tullytown, PA, USA, 95%) and phenyltrichlorostannane (Sigma-Aldrich, Steinheim, Germany, 98%) were used as received without further purification. THF, diethyl ether, and triethylamine were distilled from sodium/benzophenone and kept under argon atmosphere. Chloroform, stabilized with amylenes (Honeywell, Seelze, Germany,  $\geq 99.5\%$ ) and  $\text{CDCl}_3$  (Deutero, Kastellaun, Germany, 99.8%) were stored over activated molecular sieves (3 Å) for at least 7 days and used without further purification. All reactions were carried out under an atmosphere of dry argon utilizing standard Schlenk techniques. Solution NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{119}\text{Sn}$ ) (cf. Figures S1–S9 in the supporting information) were recorded on Bruker Avance III 500 MHz and Bruker Nanobay 400 MHz spectrometers.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  chemical shifts are reported relative to  $\text{Me}_4\text{Si}$  (0 ppm) as internal reference.  $^{119}\text{Sn}$  chemical shifts are reported relative to  $\text{Me}_4\text{Sn}$  (0 ppm) with external referencing.  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals were assigned in accord with mutual coupling patterns (in case of  $^1\text{H}$ ) and according to the shifts of corresponding  $^1\text{H}$  or  $^{13}\text{C}$  NMR signals in related compounds  $\text{MeSi}(\text{pyO})_3$  [2],  $\text{Ph}_2\text{Si}(\text{pyO})_2$  [3] and  $\text{PhP}(\text{pyO})_2$  [13]. Furthermore,  $^1\text{H}$ – $^{13}\text{C}$  HSQC techniques were employed for  $^{13}\text{C}$  NMR signal assignment of compound  $\text{PhSn}(\text{pyO})_3$ . The  $^{119}\text{Sn}$  MAS NMR spectrum of  $\text{PhSn}(\text{pyO})_3$  was recorded on a Bruker Avance 400 WB spectrometer using a 4 mm zirconia ( $\text{ZrO}_2$ ) rotor and an MAS frequency of  $v_{\text{spin}} = 13$  kHz. The

chemical shift is reported relative to  $\text{Me}_4\text{Sn}$  (0 ppm) and was referenced with the aid of a sample of  $\text{SnO}_2$  ( $\delta_{\text{iso}} = -603$  ppm). Determination of the chemical shift anisotropy (CSA) tensor principal components from the spinning sideband spectrum was carried out with the SOLA module contained in the Bruker software package TOPSPIN. Principal components  $\delta_{11}$ ,  $\delta_{22}$ ,  $\delta_{33}$  as well as span  $\Omega$  and skew  $\kappa$  are reported according to the Herzfeld–Berger notation [14,15]. Elemental analyses were performed on an Elementar Vario MICRO cube. For single-crystal X-ray diffraction analyses, crystals were selected under an inert oil and mounted on a glass capillary (which was coated with silicone grease). Diffraction data were collected on a Stoe IPDS-2/2T diffractometer (STOE, Darmstadt, Germany) using Mo  $\text{K}\alpha$ -radiation. Data integration and absorption correction were performed with the STOE software XArea and XShape, respectively. The structures were solved by direct methods using SHELXS-97 or SHELXT and refined with the full-matrix least-squares methods of  $F^2$  against all reflections with SHELXL-2014/7 [16–19]. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were isotropically refined in idealized position (riding model). For details of data collection and refinement (incl. the use of SQUEEZE in the refinement of the structure of  $\text{PhSi}(\text{pyO})_3 \cdot \text{THF}$ ) see Appendix A, Table A1. Graphics of molecular structures were generated with ORTEP-3 [20,21] and POV-Ray 3.7 [22]. CCDC 2217508 ( $\text{PhSi}(\text{pyO})_3 \cdot \text{THF}$ ), 2217510 ( $\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$ ), 2217509 ( $\text{PhGe}(\text{pyO})_3$ ), and 2217511 ( $\text{PhSn}(\text{pyO})_3$ ) contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/> (accessed on 4 November 2022).

## 2.2. Syntheses and Characterization

Compound  $\text{PhSi}(\text{pyO})_3 \cdot \text{THF}$  ( $\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_4\text{Si}$ ). A Schlenk flask was charged with magnetic stirring bar and 2-hydroxypyridine (2.00 g, 20.8 mmol), then evacuated and set under Ar atmosphere prior to adding THF (70 mL) and triethylamine (2.50 g, 24.7 mmol). The resultant mixture was stirred at room temperature, and phenyltrichlorosilane (1.60 g, 7.56 mmol) was added dropwise via syringe through a septum. Upon completed addition of silane, stirring was continued for 30 min, whereupon the flask was stored at 5 °C overnight. Thereafter, the triethylamine hydrochloride precipitate was removed by filtration and washed with THF (2 × 5 mL). From the combined filtrate and washings, the solvent was removed under reduced pressure (condensation into a cold trap) to afford a colorless solid. This crude product was dissolved into hot THF (4 mL) and allowed to crystallize upon cooling to room temperature. From this coarse crystalline product (thick colorless needles) of  $\text{PhSi}(\text{pyO})_3 \cdots \text{THF}$  the supernatant was removed by decantation; the crystals were washed with THF (2 × 5 mL) and briefly dried in vacuum. Yield: 2.29 g (4.98 mmol, 66%). The yield is reported with respect to the composition  $\text{PhSi}(\text{pyO})_3 \cdots \text{THF}$ , which is in accord with the composition of a single crystal taken from the freshly crystallized product for single-crystal X-ray diffraction analysis.  $^1\text{H}$  NMR spectroscopy (cf. Figure S1 in the supporting information) already indicates some loss of THF upon drying. This effect was also found with elemental analysis: elemental analysis for  $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_3\text{Si} \cdots 0.5 \text{ THF}$  (423.52 g·mol<sup>-1</sup>): C, 65.23%; H, 5.00%; N, 9.92%; found C, 65.21%; H, 5.10%; N, 9.96%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.11–8.07 (m, 2H, Ph-o), 8.01 (m, br, 3H,  $\text{H}^6$ ), 7.52 (m, br, 3H,  $\text{H}^4$ ), 7.44–7.32 (m, 3H, Ph-m/p), 6.92 (d, br, 3H, 8.2 Hz,  $\text{H}^3$ ), 6.82 (m, br, 3H,  $\text{H}^5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 160.3 ( $\text{C}^2$ ), 147.3 ( $\text{C}^6$ ), 139.1 ( $\text{C}^4$ ), 135.6 (Ph-o), 130.9 (Ph-p), 129.0 (Ph-i), 127.6 (Ph-m), 118.2 ( $\text{C}^5$ ), 113.0 ( $\text{C}^3$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) –64.7.

Some crystals of the chloroform solvate  $\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$  ( $\text{C}_{22}\text{H}_{18}\text{Cl}_3\text{N}_3\text{O}_3\text{Si}$ ) were obtained by recrystallization of the THF solvate in chloroform.

Compound  $\text{PhGe}(\text{pyO})_3$  ( $\text{C}_{21}\text{H}_{17}\text{GeN}_3\text{O}_3$ ). A Schlenk flask was charged with magnetic stirring bar and 2-hydroxypyridine (0.25 g, 2.63 mmol), then evacuated and set under Ar atmosphere prior to adding THF (5 mL) and triethylamine (0.40 g, 3.96 mmol). The resultant mixture was stirred at room temperature, and phenyltrichlorogermane (0.25 g, 0.97 mmol) was added dropwise via syringe through a septum. Upon completion, addition of the germane, a thick suspension was obtained. Therefore, further THF (2 mL) was added with

stirring, before the flask was stored at 5 °C for five days. Thereafter, the triethylamine hydrochloride precipitate was removed by filtration and washed with THF (3 mL). From the combined filtrate and washings, the solvent was removed under reduced pressure (condensation into a cold trap) to afford a viscous oily residue. This crude product was dissolved into THF (0.5 mL), then diethyl ether (1 mL) was added at room temperature, and the solution was stored undisturbed at room temperature for crystallization to commence. In the course of some days, crystals of  $\text{PhGe}(\text{pyO})_3$  formed. For enhanced yield, the flask was stored at –24 °C overnight prior to isolation of the product, which was achieved by decantation of the supernatant, washing with diethyl ether (1 mL), and drying in vacuum. Yield: 0.26 g (0.60 mmol, 68%). A single crystal was taken from this product for single-crystal X-ray diffraction analysis. Elemental analysis for  $\text{C}_{21}\text{H}_{17}\text{GeN}_3\text{O}_3$  (431.99 g·mol<sup>–1</sup>): C, 58.39%; H, 3.97%; N, 9.73%; found C, 58.23%; H, 4.38%; N, 9.79%. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.13–8.09 (m, 2H, Ph-o), 7.86 (m, 3H, H<sup>6</sup>), 7.49 (m, 3H, H<sup>4</sup>), 7.44–7.34 (m, 3H, Ph-m/p), 6.80 (d, 3H, 8.3 Hz, H<sup>3</sup>), 6.70 (m, 3H, H<sup>5</sup>); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 163.3 (C<sup>2</sup>), 145.9 (C<sup>6</sup>), 139.5 (C<sup>4</sup>), 134.3 (Ph-o), 133.8 (Ph-i), 130.8 (Ph-p), 128.2 (Ph-m), 116.2 (C<sup>5</sup>), 111.7 (C<sup>3</sup>).

Compound  $\text{PhSn}(\text{pyO})_3$  ( $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_3\text{Sn}$ ). A Schlenk flask was charged with magnetic stirring bar and 2-hydroxypyridine (2.03 g, 21.4 mmol), then evacuated and set under Ar atmosphere prior to adding THF (40 mL) and triethylamine (2.66 g, 26.3 mmol). The resultant mixture was stirred in an ice/ethanol bath (ca. –10 °C), and phenyltrichlorostannane (2.18 g, 7.21 mmol) was added dropwise via syringe through a septum. Upon completed addition of the stannane, the mixture was stored at 5 °C for five days, whereupon the triethylamine hydrochloride precipitate was removed by filtration and washed with THF (10 mL). From the combined filtrate and washings, the solvent was removed under reduced pressure (condensation into a cold trap) to afford a white solid residue. This crude product was recrystallized from hot THF. The colorless solid product thus obtained was filtered off, washed with THF (2 mL) and dried in vacuum. Yield: 2.13 g (4.46 mmol, 63%). A single crystal was taken from this product for single-crystal X-ray diffraction analysis. Elemental analysis for  $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_3\text{Sn}$  (478.09 g·mol<sup>–1</sup>): C, 52.76%; H, 3.58%; N, 8.79%; found C, 52.64%; H, 3.67%; N, 8.73%. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.71–7.62 (m, 5H, Ph-o, H<sup>6</sup>), 7.57 (m, 3H, H<sup>4</sup>), 7.33–7.29 (m, 3H, Ph-m/p), 6.68 (d, 3H, 8.4 Hz, H<sup>3</sup>), 6.58 (m, 3H, H<sup>5</sup>); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 167.0 (22 Hz, C<sup>2</sup>), 145.6 (1451 Hz, 1386 Hz, Ph-i), 142.3 (C<sup>6</sup>), 141.8 (18 Hz, C<sup>4</sup>), 133.7 (77 Hz, Ph-o), 129.5 (25 Hz, Ph-p), 128.6 (128 Hz, 122 Hz, Ph-m), 112.5 (C<sup>5</sup>), 111.3 (36 Hz, C<sup>3</sup>); <sup>119</sup>Sn{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) –609; <sup>119</sup>Sn CP/MAS NMR:  $\delta_{\text{iso}}$  (ppm) –617.

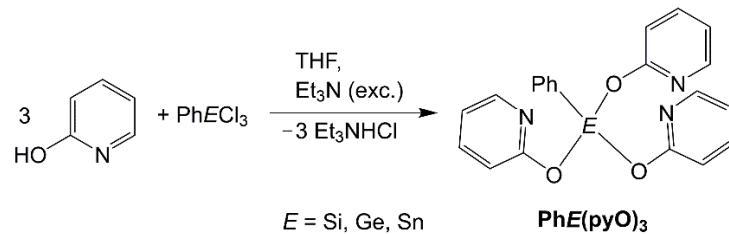
Note: For some <sup>13</sup>C signals we observed <sup>117</sup>/<sup>119</sup>Sn satellites, the <sup>117</sup>Sn and <sup>119</sup>Sn contributions of which are not resolved. Therefore, the average  $J(^{117}/^{119}\text{Sn}-^{13}\text{C})$  coupling constants are given in parentheses for those signals where applicable. For the pair of Ph-o and Ph-m <sup>13</sup>C NMR signals (at 133.7 and 128.6 ppm) the larger  $J(^{117}/^{119}\text{Sn}-^{13}\text{C})$  coupling is observed for the signal at 128.6 ppm. The assignment to o- and m-position is in accord with <sup>13</sup>C NMR data of other phenyltin compounds, e.g.,  $\text{PhSn}(\text{ESiMe}_2)_3\text{SiMe}$  (E = S, Se, Te), which give rise to signals of Ph-o and Ph-m carbon atoms around 134–135 ppm and 128–129 ppm, respectively [23], and for  $\text{Me}_3\text{SnPh}$  the same phenomenon of  $^3J(\text{SnC}) > ^2J(\text{SnC})$  has been reported [24].

### 3. Results and Discussion

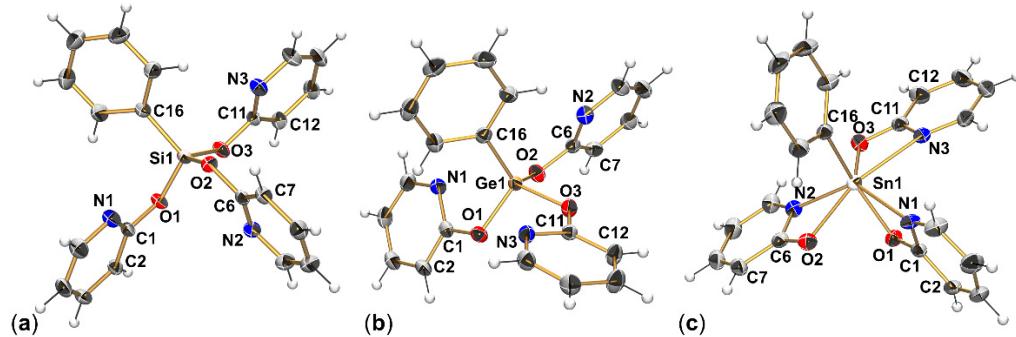
#### 3.1. Crystallographic Analysis of the Molecular Structures of $\text{PhE}(\text{pyO})_3$ (E = Si, Ge, Sn)

Compounds  $\text{PhE}(\text{pyO})_3$  (E = Si, Ge, Sn) were synthesized from the respective chlorides  $\text{PhECl}_3$  and 2-hydroxypyridine in THF with the aid of triethylamine as a sacrificial base (Scheme 1). In all cases, the crystalline products obtained were of sufficient quality for single-crystal X-ray diffraction analysis (Table A1). The crystallographically determined molecular structures of  $\text{PhE}(\text{pyO})_3$  (E = Si, Ge, Sn) are shown in Figure 2 and selected interatomic separations and bond angles are given in Table 1. Whereas the Ge- and Sn-compound crystallized from THF without including solvent of crystallization, compound  $\text{PhSi}(\text{pyO})_3$  crystallized as a THF solvate  $\text{PhSi}(\text{pyO})_3 \cdots \text{THF}$  with severely disordered sol-

vent. Recrystallization from chloroform afforded an isomorphous solvate  $\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$ , the disordered solvent of which could be refined in a satisfactory manner. As the structure models of  $\text{PhSi}(\text{pyO})_3$  in the two solvates are of similar quality, and the molecular conformation of the silane in those structures is the same, the data from the solvate  $\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$  will be used in the further discussion as a representative example.



**Scheme 1.** Generic scheme of the syntheses of compounds  $\text{PhSi}(\text{pyO})_3$ ,  $\text{PhGe}(\text{pyO})_3$ , and  $\text{PhSn}(\text{pyO})_3$ . The reactions were performed at room temperature for  $\text{PhSi}(\text{pyO})_3$  and  $\text{PhGe}(\text{pyO})_3$  and at  $-10\text{ }^\circ\text{C}$  for  $\text{PhSn}(\text{pyO})_3$ .



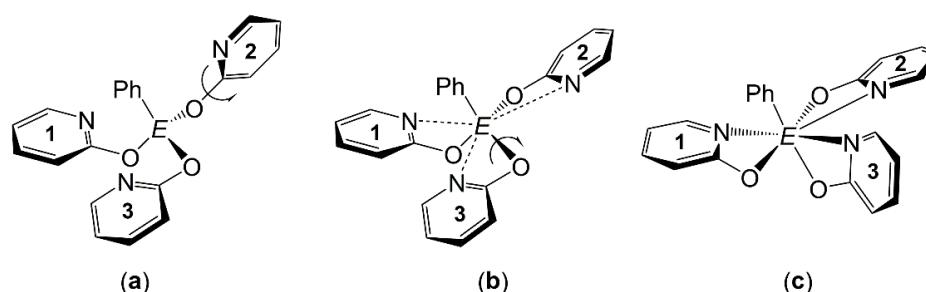
**Figure 2.** Molecular structures of (a)  $\text{PhSi}(\text{pyO})_3$  (in the crystal structure of the solvate  $\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$ ), (b)  $\text{PhGe}(\text{pyO})_3$ , and (c)  $\text{PhSn}(\text{pyO})_3$  with thermal displacement ellipsoids at the 50% probability level and labels of selected non-hydrogen atoms. Selected interatomic distances ( $\text{\AA}$ ) and angles are listed in Table 1.

**Table 1.** Selected interatomic separations [ $\text{\AA}$ ] and bond angles [deg] in the tetrel ( $E = \text{Si, Ge, Sn}$ ) coordination spheres of  $\text{PhSi}(\text{pyO})_3$ ,  $\text{PhGe}(\text{pyO})_3$  and  $\text{PhSn}(\text{pyO})_3$  and their pyO ligands.

Bond	$\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$	$\text{PhGe}(\text{pyO})_3$	$\text{PhSn}(\text{pyO})_3$
$E1-\text{O}1$	1.640(1)	1.790(2)	2.120(2)
$E1-\text{O}2$	1.636(1)	1.777(2)	2.257(2)
$E1-\text{O}3$	1.642(1)	1.785(2)	2.133(2)
$E1 - \text{N}1$	2.968(2)	2.789(2)	2.281(3)
$E1 - \text{N}2$	3.002(2)	2.923(2)	2.212(3)
$E1 - \text{N}3$	3.000(2)	2.908(2)	2.406(3)
$E1-\text{C}16$	1.842(2)	1.919(2)	2.138(2)
$\text{O}1-E1-\text{O}2$	115.85(6)	101.36(6)	84.64(9)
$\text{O}1-E1-\text{O}3$	96.91(6)	103.17(6)	93.00(9)
$\text{O}2-E1-\text{O}3$	112.54(6)	98.20(6)	138.85(9)
$\text{O}1-\text{C}1-\text{N}1$	117.50(13)	116.77(17)	113.0(3)
$\text{O}2-\text{C}6-\text{N}2$	117.30(13)	117.65(17)	113.9(3)
$\text{O}3-\text{C}11-\text{N}3$	117.45(13)	117.89(17)	113.5(3)
$\text{O}1-\text{C}1-\text{C}2$	117.55(13)	119.37(18)	126.2(3)
$\text{O}2-\text{C}6-\text{C}7$	117.96(13)	118.23(18)	126.7(3)
$\text{O}3-\text{C}11-\text{C}12$	117.47(13)	118.03(17)	124.3(3)

In compounds  $\text{Ph}E(\text{pyO})_3$   $E = \text{Si}, \text{Ge}$  the tetrel atom is essentially tetracoordinate, whereas in  $\text{PhSn}(\text{pyO})_3$  the tin atom is clearly heptacoordinate within a pentagonal bipyramidal coordination sphere. In the latter, O1 and C16 occupy the axial positions ( $\text{O1-Sn1-C16}$   $161.61(14)^\circ$ ), and the equatorial angles of pairs of neighboring bonds are  $58.1(1)^\circ$  ( $\text{O3-Sn1-N3}$ ) and  $59.2(1)^\circ$  ( $\text{O2-Sn1-N2}$ ) for the two chelate motifs and ca.  $80^\circ$  in the case of the remaining three angles spanned by O2,N1 ( $80.4(1)^\circ$ ); O3,N2 ( $79.7(1)^\circ$ ); N1,N3 ( $80.4(1)^\circ$ ). Nonetheless, the molecular metrics of  $\text{PhGe}(\text{pyO})_3$  already hint at a transition toward hypercoordination of the heavy tetrel atom. Whereas the  $E\cdots\text{O}$  bond lengths increase in an expected manner with an increasing atomic radius of  $E$ , the  $E\cdots\text{N}$  separations already undergo some significant shortening (by more than  $0.1 \text{ \AA}$  on average) upon going from  $E = \text{Si}$  to  $\text{Ge}$ . Thus, with respect to the N atom's van der Waals radius of  $1.55 \text{ \AA}$  and the tetrels' van der Waals radii of  $2.10$  ( $\text{Si}$ ),  $2.11$  ( $\text{Ge}$ ), and  $2.17 \text{ \AA}$  ( $\text{Sn}$ ) [25], the average  $E\cdots\text{N}$  separations are  $81.9\%$ ,  $78.5\%$ , and  $61.8\%$  of the sum of van der Waals radii for the Si, Ge, and Sn compound, respectively. Further evidence for pronounced  $E\cdots\text{N}$  attraction upon going from  $E = \text{Si}$  to  $\text{Ge}$  can be found in the O-C-N angle deformation of all pyridine-2-olate groups. Whereas in the silicon compound the O-C-N angles and their corresponding O-C-C angles are very similar (both ca.  $117.5^\circ$ ), the O-C-N angles in the Ge compound are slightly smaller than the corresponding O-C-C angles, thus indicating the pronounced attractive  $\text{Ge}\cdots\text{N}$  interaction. At the Ge atom in compound  $\text{PhGe}(\text{pyO})_3$ , the trend of bond angles adheres to VSEPR, i.e., within the  $\text{GeC}_1\text{O}_3$  coordination sphere, all O-Ge-O angles are smaller than the tetrahedral angle. In sharp contrast,  $\text{PhSi}(\text{pyO})_3$  features one very small O-Si-O angle ( $\text{O1-Si1-O3}$   $96.91(6)^\circ$ ), whereas the other two O-Si-O angles ( $112.54(6)$  and  $115.85(6)^\circ$ ) are noticeably wider than the tetrahedral angle. (Similar features are found in compound  $\text{MeSi}(\text{pyO})_3$  [2].) This phenomenon can be attributed to the molecular conformation of  $\text{PhSi}(\text{pyO})_3$  with respect to its enhanced coordination sphere (i.e., [4+3]-coordination). In the case of  $\text{PhGe}(\text{pyO})_3$ , each of the pyridine N atoms is capping a tetrahedral face *trans* to a Ge-O bond and thus widens the O-Ge-C angles. The tetrahedral face *trans* to the Ge-C bond lacks this effect and thus allows for mutual shrinkage of the O-Ge-O angles (sum of O-Ge-O angles  $302.7^\circ$ ). In the case of  $\text{PhSi}(\text{pyO})_3$ , N2 is capping the tetrahedral face *trans* to the Si-C bond and thus widens the O-Si-O angles (sum of O-Si-O angles  $325.3^\circ$ ). As the tetrahedral face *trans* to Si1-O2 is devoid of a remote donor atom (thus not exerting any additional widening to angle O1-Si1-O3), and the capping of tetrahedral faces by N1 and N3 enforces further widening of angles O1-Si1-O2 and O3-Si1-O2, respectively, bond angle O1-Si1-O3 becomes particularly narrow. Noteworthy, with respect to the overall deformation of the tetrahedral coordination sphere about the tetrel atom, the geometry parameter  $\tau_{4'}$  [26] (Si: 0.91, Ge: 0.83) indicates particular deformation in the case of the Ge compound. It originates from a noticeably wide angle O2-Ge1-C16 ( $124.3(1)^\circ$ ). This feature arises from a C-H $\cdots$ N2 contact, in which a phenyl ortho-H atom interferes with pyridine atom N2 and thus competes with the capping of the tetrahedral face *trans* to Ge1-O1 by atom N2.

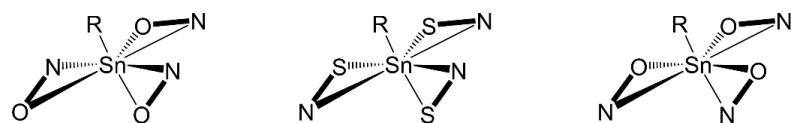
In addition to visualizing the conformational differences between the two [4+3]-coordinate tetrel compounds  $\text{PhSi}(\text{pyO})_3$  and  $\text{PhGe}(\text{pyO})_3$ , the view in Figure 2 demonstrates the relationship of the conformation of  $\text{PhGe}(\text{pyO})_3$  and the conformation of the pentagonal bipyramidal Sn-coordination compound  $\text{PhSn}(\text{pyO})_3$ . Scheme 2 illustrates this hypothetical transition, starting from the molecular conformation of  $\text{PhGe}(\text{pyO})_3$  (Scheme 2a). In addition to the N atoms approaching the tetrel  $E$ , partial rotation of the pyO ligands indexed with "2" and "3" about the bonds shown with rotation arrows in Scheme 2a,b affords the molecular configuration of  $\text{PhSn}(\text{pyO})_3$  (Scheme 2c).



**Scheme 2.** Schematic representation of the ligand motion (of corresponding pyO moieties “1”, “2” and “3”) which relates the molecular conformations of PhGe(pyO)<sub>3</sub> (starting point (**a**)) and PhSn(pyO)<sub>3</sub> (represented by (**c**)) to one another via (**b**).

The increasing intensity of N···E coordination in the series  $E = \text{Si} < \text{Ge} < \text{Sn}$  is also reflected by the systematic changes in corresponding bond lengths within the pyO moieties (Table A2). Whereas most bond length differences merely allow for a vague hint at a trend (the changes, albeit seemingly systematic, are not significant within the boundaries of the standard deviations), significant shortening of the C–O bonds and, to a lesser extent, lengthening of the adjacent C–N bond is observed. Thus, the response of the pyO ligand's C–C-bond backbone to mono- vs. bidentate coordination is less pronounced than the response of the related N-oxide (1-oxy-2-pyridinone, OPO) in compound (*t*Bu)<sub>2</sub>Si(OPO)<sub>2</sub>, which features both a monodentate and a chelating OPO moiety within the same molecule [27].

The molecular conformation of PhSn(pyO)<sub>3</sub> requires some further discussion in context with the literature data. Even though this is the first crystallographically characterized “simple” stannane with more than one pyO substituent, some related compounds of the type RSn(pyS)<sub>3</sub> (pyS = pyridine-2-thiolate) have been reported and characterized crystallographically (with R = p-tolyl [28], Me and Ph [29]). In these compounds, the Sn atom is also heptacoordinate within an almost pentagonal bipyramidal coordination sphere, and the hydrocarbyl group as well as one chelate ligand’s chalcogen atom occupy axial positions. Their equatorial chelate ligands, however, are arranged in a *cis* fashion (thus giving rise to an equatorial N,N,N,S,S atom sequence), whereas in PhSn(pyO)<sub>3</sub> *trans*-arrangement of the two equatorial chelates is found (and an equatorial N,N,O,N,O atom sequence arises therefrom). With a different (O,N)-bidentate ligand system (ox = oxinate, 8-quinolinolate), compound RSn(ox)<sub>3</sub> (R = 4-chlorophenyl) with pentagonal bipyramidal Sn coordination sphere has been reported [30]. The conformation of this compound is less related to PhSn(pyO)<sub>3</sub> as it exhibits two differences: mutual *cis*-arrangement of the equatorial chelates and N-axial-O-equatorial arrangement of the third chelate ligand. Figure 3 illustrates this conformational difference.



R = Ph,  
(ON) = pyridine-2-olate

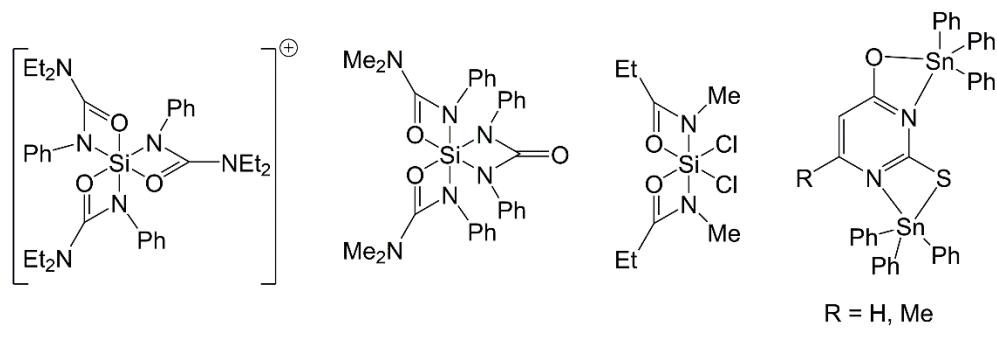
R = p-Tol, Ph, Me,  
 (SN) = pyridine-2-thiolate

R = p-Cl-C<sub>6</sub>H<sub>4</sub>,  
 (ON) = 8-quinolinolate

**Figure 3.** Generic illustration of the conformational difference between PhSn(pyO)<sub>3</sub>, related pyridine-2-thiolates RSn(pyS)<sub>3</sub> [28,29] and 8-quinolinolate (4-Cl-C<sub>6</sub>H<sub>4</sub>)Sn(ox)<sub>3</sub> [30]. The motifs “N–O” and “N–S” serve as abbreviations of the different bidentate (N,O)- and (N,S)-donor ligands.

Apart from the comparison of PhSn(pyO)<sub>3</sub> with more or less related organotin-tris(chelates) with pentagonal bipyramidal Sn coordination sphere, the context of (Si,Ge,Sn)-hypercoordination within related four-membered (E,O,C,N)-chelate rings formed by mono-anionic chelators and tetravalent tetrels must be addressed. A search in the Cambridge

Crystal Structure Database [7] yielded a very limited number of (Si,Ge,Sn)-compounds with hypercoordinate (i.e., coordination number greater than four) tetrel atoms and such monoanionic (O,N)-chelating ligands. In the case of silicon, the portfolio is limited to three different compounds with hexacoordinate Si atoms, VII [31], VIII [32], and IX [33] (Figure 4). Enhanced Lewis acidity of the Si atom (caused by one or combinations of the parameter(s) such as small rings, electron-withdrawing substituents, and the cationic nature of the complex) may be an essential prerequisite. No representatives of hypercoordinate Ge compounds were found. Even the portfolio of structurally characterized hypercoordinate tetravalent tin compounds with this structural motif is very limited. For tin coordination numbers 6, 7, and 8, no appropriate hits were encountered. For Sn coordination number 7 only one multinuclear tin complex was found which features an (Sn,O,C,N)-chelate within a greater system of charge-delocalized multidentate ligands [34]. Even with tin coordination number 5, only two representatives (compounds X) were encountered. Interestingly, their four-membered (Sn,O,C,N)-chelates are derived from the pyridine-2-olate system [35].



**Figure 4.** Literature known examples of structurally confirmed hypercoordinate tetravalent tetrel (*E*) compounds (compounds VII–X) with (E,O,C,N)-four-membered rings formed by mono-anionic (O,N)-chelating ligands.

In summary, structural characterization of hypercoordinate tetrels with four-membered (E,O,C,N)-chelates by mono-anionic chelators is still a rather unexplored field. With respect to pyridine-2-olate as a simple representative of such ligands, we may conclude that in the case of silicon compounds the lower tendency of the light tetrel toward hypercoordination can be seen as the major reason, as shown with  $\text{PhSi}(\text{pyO})_3$  and other examples [1–3]. In the case of Sn compounds, however, the lack of crystallographic evidence for solely Sn–O bound pyridine-2-olates with non-coordinating pyridine N atom [7] and the previously mentioned lack of structurally characterized Sn-pyO-chelates is highlighting a field of tetrel coordination chemistry yet to be explored.

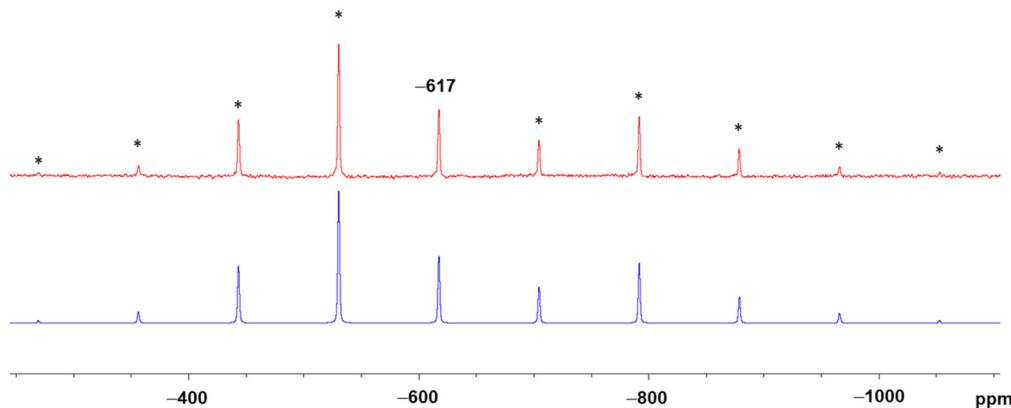
### 3.2. NMR Spectroscopic Analyses of $\text{PhE}(\text{pyO})_3$ ( $E = Si, Ge, Sn$ )

Compounds  $\text{PhE}(\text{pyO})_3$  ( $E = Si, Ge, Sn$ ) were characterized by NMR spectroscopy in  $\text{CDCl}_3$  solution and, in the case of  $\text{PhSn}(\text{pyO})_3$ , with  $^{119}\text{Sn}$  solid-state NMR spectroscopy.

In the  $\text{CDCl}_3$  solution, the Si atom of compound  $\text{PhSi}(\text{pyO})_3$  is tetracoordinate, indicated by  $\delta^{29}\text{Si} = -64.7$  ppm. This signal is upfield shifted with respect to that of the corresponding methyl compound  $\text{MeSi}(\text{pyO})_3$  ( $\delta^{29}\text{Si} = -46.5$  ppm [2]), which is a common observation with pairs of corresponding  $\text{PhSi}$  and  $\text{MeSi}$  compounds (e.g.,  $\text{PhSi}(\text{OEt})_3$   $\delta^{29}\text{Si} = -57.8$  ppm [36],  $\text{MeSi}(\text{OEt})_3$   $\delta^{29}\text{Si} = -44.5$  ppm [37]). In principle, compound  $\text{PhSi}(\text{pyO})_3$  has a similar  $^{29}\text{Si}$  NMR shift as the tetracoordinate phenyl silicon compound  $\text{PhSi}(\text{OEt})_3$ .

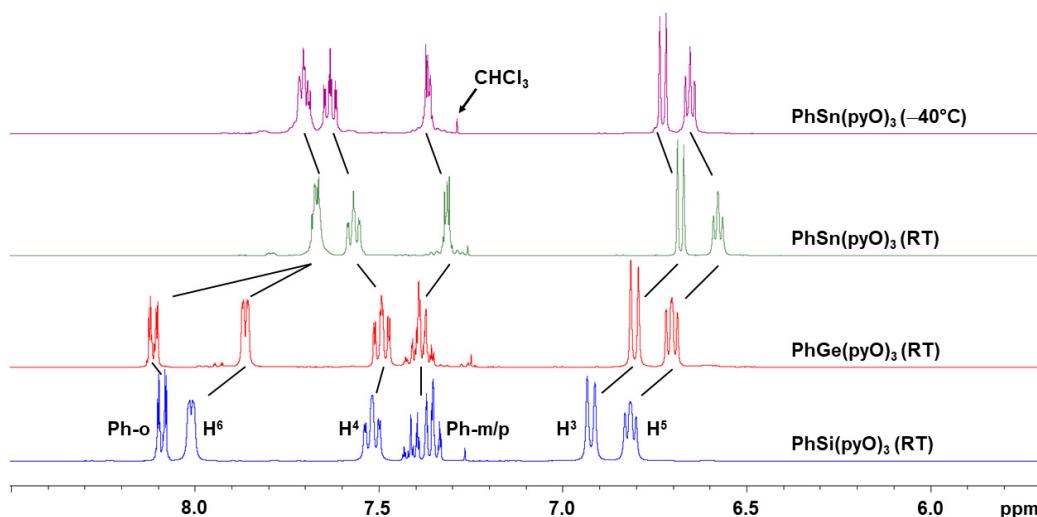
For compound  $\text{PhSn}(\text{pyO})_3$  the  $^{119}\text{Sn}$  NMR shifts were recorded in the solid state ( $-617$  ppm, Figure 5) as well as in  $\text{CDCl}_3$  at different temperatures ( $20\ ^\circ\text{C}$ :  $-609$  ppm,  $-40\ ^\circ\text{C}$ :  $-614$  ppm). These chemical shifts are basically speaking for retention of the tin coordination number 7 in the  $\text{CDCl}_3$  solution. Furthermore, these shifts are similar to those

of other stannanes with heptacoordinate Sn atom and ArylSn(O,N)<sub>3</sub> coordination, e.g., p-TolSn(quinoline-8-olate)<sub>3</sub> ( $-611$  ppm), p-TolSn(pyridine-2-carboxylate)<sub>3</sub> ( $-620$  ppm) [30].



**Figure 5.**  $^{29}\text{Si}$  MAS NMR spectrum of  $\text{PhSn}(\text{pyO})_3$  recorded at a spinning frequency of  $13\text{ kHz}$  (top, red trace) and simulated spectrum using the CSA tensor data derived from the experimental spectrum (bottom, blue trace). The asterisked (\*) peaks are spinning sidebands. CSA tensor data:  $\delta_{\text{iso}} = -617.4\text{ ppm}$ ,  $\delta_{11} = -393.5\text{ ppm}$ ,  $\delta_{22} = -502.2\text{ ppm}$ ,  $\delta_{33} = -956.5\text{ ppm}$ ,  $\Omega = 563\text{ ppm}$ ,  $\kappa = 0.61$ .

In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of each of the compounds  $\text{PhE}(\text{pyO})_3$  ( $E = \text{Si, Ge, Sn}$ ), the three pyO moieties give rise to one set of four ( $^1\text{H}$ ) or five ( $^{13}\text{C}$ ) signals, which was expected at least for the Si compound in accord with previously reported pyO-functionalized silanes [23]. In the case of compound  $\text{PhSn}(\text{pyO})_3$ , it confirms that the  $\text{SnCN}_3\text{O}_3$  coordination sphere itself is highly flexible and undergoes rapid exchange processes. Even cooling to  $-40\text{ }^\circ\text{C}$  did not cause any signal broadening or decoalescence effects (Figure 6).



**Figure 6.** Section of the  $^1\text{H}$  NMR spectra of  $\text{CDCl}_3$  solutions of (from bottom to top)  $\text{PhSi}(\text{pyO})_3$ ,  $\text{PhGe}(\text{pyO})_3$ , and  $\text{PhSn}(\text{pyO})_3$  at room temperature as well as of  $\text{PhSn}(\text{pyO})_3$  at  $-40\text{ }^\circ\text{C}$ . The spectra are internally referenced to  $\text{SiMe}_4$  (cf. spectra shown in Figures S1, S4, and S6 in the supplementary material).

To evaluate the pyO@Ge coordination chemistry of  $\text{PhGe}(\text{pyO})_3$  in  $\text{CDCl}_3$  solution, a comparison of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of this compound with those of the lighter and heavier congener was engaged. In  $^{13}\text{C}$  NMR spectra, it was found that the C<sup>2</sup> and C<sup>6</sup> positions of the pyO groups are highly responsive to coordinative changes at the N atom. In the spectrum of a  $\text{CDCl}_3$  solution of compound  $\text{PhP}(\text{pyO})_2$  [13] the signals of interest emerge at  $161.8\text{ ppm}$  (C<sup>2</sup>) and  $147.4\text{ ppm}$  (C<sup>6</sup>). The spectrum of the related compound  $\text{PhSb}(\text{pyO})_2$  [38], which exhibits pronounced Sb···N attraction, exhibits the

corresponding signals at 167.0 ppm ( $C^2$ ) and 140.6 ppm ( $C^6$ ). The corresponding signals of the related arsenic compound  $\text{PhAs}(\text{pyO})_2$  [39] emerge at intermediate positions. Even though this trend may also be influenced by electronic effects through the  $E\text{-O-C}_5\text{N}$   $\sigma$ - and  $\pi$ -bond system (originating from different  $E\text{-O}$  bonds caused by the different elements  $E$ ), the relevance of the electronic effects caused by  $\text{N}\rightarrow\text{tetrel}$  coordination is underlined by corresponding data of a set of literature known pyridine-2-thiolate (pyS) compounds [3,40,41], which show that the same trends are observed for  $C^2$  and  $C^6$ , but these trends are more responsive to hypercoordination ( $E(\text{S},\text{N})$ -chelation vs. absence of  $E\cdots\text{N}$  coordination) rather than to the element  $E$  itself (cf. Table A3).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound  $\text{PhGe}(\text{pyO})_3$  in  $\text{CDCl}_3$  solution resemble both the signal patterns ( $^1\text{H}$  coupling patterns) and the chemical shifts of corresponding signals (both  $^1\text{H}$  and  $^{13}\text{C}$ ) of the related silicon compound. For a comparison of their  $^1\text{H}$  NMR signals, see Figure 6. For the series of spectra of  $\text{PhE}(\text{pyO})_3$  ( $E = \text{Si, Ge, Sn}$ ) recorded at room temperature, systematic shift trends are observed for corresponding  $^1\text{H}$  signals of the pyO moieties. The upfield shift of the  $^1\text{H}$  NMR signal of the pyO protons in position 6 from  $E = \text{Si}$  via  $\text{Ge}$  to  $\text{Sn}$  is the most prominent trend among their pyO  $^1\text{H}$  signals and thus underlines the changes in  $\text{N}\cdots E$  coordination, which can be derived from  $^{13}\text{C}$  NMR data (Table 2). A trend toward hypercoordination of the Ge atom is indicated by the  $^{13}\text{C}$  NMR shifts of the pyO carbon atoms in positions 2 and 6. Their signals are further downfield shifted ( $C^2$ , by 3 ppm) and upfield shifted ( $C^6$ , by 1.4 ppm) in the Ge compound.

**Table 2.**  $^{13}\text{C}$  NMR shifts of  $C^2$  and  $C^6$  of the pyridine-2-olate (pyO) ligands of compounds  $\text{PhE}(\text{pyO})_3$  in  $\text{CDCl}_3$ .

Compound	$E\cdots\text{N}(\text{pyS})$ Coordination? <sup>1</sup>	$\delta^{13}\text{C}(C^2)$	$\delta^{13}\text{C}(C^6)$
$\text{PhSi}(\text{pyO})_3$	0	160.3	147.3
$\text{PhGe}(\text{pyO})_3$	intermediate	163.3	145.9
$\text{PhSn}(\text{pyO})_3$	1	167.0	141.8

<sup>1</sup> According to the number of pyO groups in the molecule and the coordination number of  $E$ , all pyO groups (1) or no pyO groups (0) establish  $E\cdots\text{N}$  coordination. The  $^{13}\text{C}$  NMR shift trends indicate intermediate  $E\cdots\text{N}$  coordination for the Ge compound.

#### 4. Conclusions

In general, compounds such as the herein presented set  $\text{PhE}(\text{pyO})_3$  represent potential starting materials for the syntheses of heteronuclear complexes. For compounds such as  $\text{MeSi}(\text{pyO})_3$  [2],  $\text{Si}(7\text{-azaindolyl})_4$  [42],  $\text{ClSi}(\text{mt})_3$  [43],  $\text{Si}(\text{mt})_4$  [44],  $\text{FPhE}(\text{o-C}_6\text{H}_4\text{-P}^{\text{i}}\text{Pr}_2)_2$  ( $E = \text{Si, Sn}$ ) [45],  $\text{FE}(\text{o-C}_6\text{H}_4\text{-PPh}_2)_3$  ( $E = \text{Si, Ge, Sn}$ ) [46],  $\text{FSi}(\text{CH}_2\text{CH}_2\text{PMe}_2)_2$  [47],  $\text{MeSi}(\text{OCH}_2\text{PMe}_2)_2(\text{CH}_2\text{CH}_2\text{PMe}_2)$  [48] it has been shown that their dangling donor atoms (N, S, P) may bind to transition metals and, in some cases, foster establishing of formally dative bonding of the transition metal to the tetrel. As dangling donor arms of their potentially bidentate substituents may be essential for binding to another metal atom (because of the absence of other reactive groups within the molecule), compounds  $\text{PhSi}(\text{pyO})_3$  and  $\text{PhGe}(\text{pyO})_3$  with their absent or poor  $E\cdots\text{N}$  coordination appear more suitable for that purpose than the related tin compound, in which the N atoms are engaged in a competing situation, i.e.,  $\text{Sn}\cdots\text{N}$  coordination also in solution. The flexibility/mobility of the Sn coordination sphere, however, may still render compounds such as  $\text{PhSn}(\text{pyO})_3$  suitable for the same purpose. Detailed studies of the ligand qualities of Ge- and Sn-pyO-compounds are yet to be performed. For compounds of the type  $\text{RSi}(\text{pyO})_3$  we had already confirmed the suitability as a ligand for  $\text{Cu(I)}$  in the case of  $R = \text{Me}$  [2], and a study of related silanes ( $R = \text{Ph, Benzyl, Allyl}$ ) is currently underway.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12121802/s1>: NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ ) and, where applicable,  $^{29}\text{Si}$ { $^1\text{H}$ } or  $^{119}\text{Sn}$ { $^1\text{H}$ }) of  $\text{CDCl}_3$  solutions of compounds  $\text{PhSi}(\text{pyO})_3$  (Figures S1–S3),  $\text{PhGe}(\text{pyO})_3$  (Figures S4, S5), and  $\text{PhSn}(\text{pyO})_3$  (Figures S6–S9).

**Author Contributions:** Conceptualization, J.W.; investigation, S.K., E.B., and J.W.; writing—original draft preparation, J.W.; writing—review and editing, E.B. and J.W.; visualization, J.W.; supervision, J.W. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## Appendix A

**Table A1.** Crystallographic data from data collection and refinement for PhSi(pyO)<sub>3</sub> (its THF solvate, and chloroform solvate), PhGe(pyO)<sub>3</sub>, and PhSn(pyO)<sub>3</sub>.

Parameter	PhSi(pyO) <sub>3</sub> · THF <sup>1</sup>	PhSi(pyO) <sub>3</sub> · CHCl <sub>3</sub> <sup>2</sup>	PhGe(pyO) <sub>3</sub>	PhSn(pyO) <sub>3</sub> <sup>3</sup>
Formula	C <sub>25</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub> Si	C <sub>22</sub> H <sub>18</sub> Cl <sub>3</sub> N <sub>3</sub> S <sub>3</sub> Si	C <sub>21</sub> H <sub>17</sub> GeN <sub>3</sub> O <sub>3</sub>	C <sub>21</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> Sn
M <sub>r</sub>	459.57	506.83	431.96	478.07
T (K)	200(2)	180(2)	180(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P̄1	P2 <sub>1</sub>
a (Å)	12.1634(6)	12.2304(4)	9.7609(3)	8.4129(3)
b (Å)	17.0246(10)	16.8989(4)	9.7775(3)	10.9605(2)
c (Å)	11.4268(7)	11.3681(3)	9.8668(3)	10.8580(3)
α (°)	90	90	82.957(2)	90
β (°)	101.450(4)	101.160(2)	83.434(2)	98.385(2)
γ (°)	90	90	86.564(2)	90
V (Å <sup>3</sup> )	2319.1(2)	2395.13(11)	927.42(5)	990.51(5)
Z	4	4	2	2
ρ <sub>calc</sub> (g · cm <sup>-3</sup> )	1.32	1.46	1.55	1.60
μ <sub>MoKα</sub> (mm <sup>-1</sup> )	0.1	0.5	1.7	1.3
F(000)	968	1040	440	476
θ <sub>max</sub> (°), R <sub>int</sub>	28.0, 0.0243	28.0, 0.0454	28.0, 0.0428	29.0, 0.0270
Completeness	99.8%	99.9%	100%	99.9%
Reflns collected	15,889	26,422	24,367	56,321
Reflns unique	5587	5563	4480	5258
Restraints	0	73	0	1
Parameters	253	353	254	254
GoF	1.072	1.053	1.077	1.256
R1, wR2 [I > 2σ(I)]	0.0425, 0.1078	0.0420, 0.0983	0.0310, 0.0687	0.0184, 0.0416
R1, wR2 (all data)	0.0639, 0.1203	0.0570, 0.1059	0.0368, 0.0708	0.0203, 0.0433
Largest peak/hole (e · Å <sup>-3</sup> )	0.23, -0.39	0.30, -0.34	0.30, -0.50	0.93, -0.96

<sup>1</sup> The solvent molecule (THF) was severely disordered over many sites and could not be refined in a satisfactory manner. Therefore, the solvent was treated with SQUEEZE as implemented in PLATON [49–51]. This procedure detected per unit cell, solvent accessible volume of 562 Å<sup>3</sup>, and contributions of 160 electrons therein (well in accord with 160 electrons for the four THF molecules per unit cell, which have been omitted from refinement).

<sup>2</sup> The solvent molecule (chloroform) was refined disordered over three sites with site occupancy factors 0.269(6), 0.316(4) and 0.415(6). <sup>3</sup> The absolute structure parameter  $\chi_{\text{Flack}}$  of this non-centrosymmetric structure refined to -0.035(6).

**Table A2.** Bond lengths [Å] of the pyridine-2-olate moieties in  $\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$ ,  $\text{PhGe}(\text{pyO})_3$  and  $\text{PhSn}(\text{pyO})_3$ .

Bond <sup>1</sup>	$\text{PhSi}(\text{pyO})_3 \cdot \text{CHCl}_3$	$\text{PhGe}(\text{pyO})_3$	$\text{PhSn}(\text{pyO})_3$
O1–C1	1.362(2)	1.350(2)	1.314(4)
O2–C6	1.364(2)	1.350(2)	1.288(4)
O3–C11	1.360(2)	1.350(2)	1.315(4)
N1–C1	1.322(2)	1.327(3)	1.347(4)
N2–C6	1.321(2)	1.324(3)	1.348(4)
N3–C11	1.319(2)	1.324(3)	1.337(4)
C1–C2	1.386(2)	1.391(3)	1.408(4)
C5–C6	1.387(2)	1.389(3)	1.421(4)
C11–C12	1.392(2)	1.391(3)	1.403(4)
C2–C3	1.379(2)	1.379(3)	1.375(5)
C7–C8	1.379(2)	1.376(3)	1.368(5)
C12–C13	1.379(2)	1.374(3)	1.380(6)
C3–C4	1.385(3)	1.387(3)	1.399(5)
C8–C9	1.386(2)	1.388(3)	1.394(6)
C13–C14	1.384(3)	1.389(3)	1.391(6)
C4–C5	1.372(3)	1.376(3)	1.370(5)
C9–C10	1.371(3)	1.375(3)	1.379(5)
C14–C15	1.374(3)	1.372(3)	1.378(6)
N1–C5	1.345(2)	1.343(3)	1.341(4)
N2–C10	1.349(2)	1.349(3)	1.347(4)
N3–C15	1.347(2)	1.347(3)	1.353(4)

<sup>1</sup> For clarity of presentation, groups of corresponding bonds within the set of individual ligands of each molecule were summarized within a block of the same shading.

**Table A3.**  $^{13}\text{C}$  NMR shifts of C<sup>2</sup> and C<sup>6</sup> of the pyridine-2-thiolate (pyS) ligands of a series of related silicon and tin compounds in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  solution.

Compound	E	Solvent	$E \cdots \text{N(pyS)}$ Coordination? <sup>1</sup>	$\delta^{13}\text{C}(\text{C}2)$	$\delta^{13}\text{C}(\text{C}6)$
$\text{PhClSi}(\text{pyS})_2$ [40]	Si	$\text{CD}_2\text{Cl}_2$	1	167.5	140.8
$\text{MeClSi}(\text{pyS})_2$ [40]	Si	$\text{CD}_2\text{Cl}_2$	1	168.1	140.4
$\text{Si}(\text{pyS})_4$ [41]	Si	$\text{CDCl}_3$	0.5	163.4	144.7
$\text{Sn}(\text{pyS})_4$ [41]	Sn	$\text{CDCl}_3$	0.5	162.9	145.7
$\text{Ph}_2\text{Si}(\text{pyS})_2$ [3]	Si	$\text{CDCl}_3$	0	158.1	147.5
$\text{Me}_2\text{Si}(\text{pyS})_2$ [3]	Si	$\text{CDCl}_3$	0	158.7	148.8

<sup>1</sup> According to the number of pyS groups in the molecule and the coordination number of E, all pyS groups (1) or no pyS groups (0) establish E···N coordination. In the case of compounds E(pyS)<sub>4</sub>, the coordination number of E is 6. In these compounds, two E···N coordinating and two non-E···N-coordinating pyS groups exchange in a dynamic equilibrium (thus, a formal contribution of 0.5 of each pyS group to the overall E···N coordination arises therefrom).

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