



## Note

## Novel germylenes and stannylenes based on pyridine-containing dialcohol ligands

Mengmeng Huang<sup>a</sup>, El'mira Kh. Lermontova<sup>b</sup>, Kirill V. Zaitsev<sup>a</sup>, Andrei V. Churakov<sup>b</sup>, Yuri F. Oprunenko<sup>a</sup>, Judith A.K. Howard<sup>c</sup>, Sergej S. Karlov<sup>a,\*</sup>, Galina S. Zaitseva<sup>a</sup><sup>a</sup> Chemistry Department, Moscow State University, B-234 Leninskie Gory, 119899 Moscow, Russia<sup>b</sup> Institute of General and Inorganic Chemistry, RAS, Leninskii Pr. 31, Moscow 119991, Russia<sup>c</sup> Department of Chemistry, University of Durham, South Road, DH1 3LE Durham, UK

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## ABSTRACT

The reactions between  $M[N(\text{SiMe}_3)_2]_2$  ( $M = \text{Ge}, \text{Sn}$ ) and three pyridine-based dialcohols yielded germylenes and stannylenes **1–6**. The composition and structures of the novel compounds were established by elemental analyses,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The structures of insoluble species were confirmed by conversion to the corresponding dibromides **7–9**. The single crystal structures of stannylene **4** and germylene **5** were determined by X-ray diffraction analyses. The germanium compound was found to be monomeric whilst the tin compound is a dimer. Both compounds possess strong transannular MN interaction in the solid phase.

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## 1. Introduction

The carbene analogues of heavier group 14 elements are compounds of the general formula  $\text{R–M–R}'$  ( $\text{R}$  and  $\text{R}' =$  any monovalent substituent;  $\text{M} = \text{Si}, \text{Ge}, \text{Sn},$  or  $\text{Pb}$ ). Although these compounds were known before (see for example, the synthesis of  $\text{Cp}_2\text{Sn}$  in 1956 [1] and the review concerning the reactivity of unstable silylenes [2]), they have been a focus of theoretical and experimental interest since the early 1970s when stable dialkyl and diamido derivatives of  $\text{Ge}, \text{Sn},$  and  $\text{Pb}$  were prepared by Lappert and co-workers [3]. Since then, several reviews dealing with preparation, chemical properties and structures of these compounds were published [4]. It was demonstrated that many of these compounds are relatively stable and may be studied as “usual” molecular substances by appropriate techniques. Several factors stabilizing the low-valent metal centre were found, one of them was the electron stabilization resulting from intramolecular interaction of metal centre with  $\pi$ -donors covalently bonded to the metal atom ( $-\text{OR}, -\text{NR}_2$  group) or additional transannular interaction of metal centre with a donor group [5]. The preparation of these compounds allowed to study in details the structure and reactivity of heavier group 14 element carbene analogues [6]. These compounds may represent the promising ligands for transition metal catalysts [7].

Germylenes and stannylenes of the formulas  $\text{M}(\text{OR})_2$  and  $\text{M}(\text{NR}_2)_2$  are able to exist in dimeric state where the metal atoms of one monomeric unit form additional bond with O or N atoms of the other unit [8]. One can suggest that these dimers have less reactivity than monomeric “heavier” carbenes. Obviously, small ligands bonded to metal atoms promote dimerization of target germylenes and stannylenes, whereas bulky ligands stabilize the monomeric form. However, at the moment there are just few systematic investigations on the balance between steric volume of ligands and the structure of germylenes (stannylenes) [8e]. In addition, very bulky ligands decrease the reactivity of such compounds, as it was recently found for bulky carbenes. The transition metal complexes with such carbene ligands possess poor catalytic activity [9].

To our opinion, dialkanolamines are very promising ligands for stabilization of monomeric structures of germylenes and stannylenes due to the following factors: a) possible additional transannular interaction with nitrogen atom of the ligands; b) the possibility to design easily the structure of such ligands, for instance, replacing the H atoms of methylene groups with different substituents. In spite of this, dialkanolamines were not previously studied as ligands for germylenes and stannylenes except the preparation of  $\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Ge}$  [10] and  $\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Sn}$  [11]. When this report was under review the report of Jurkschat et al. on X-ray study of dimeric  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Sn}]_2$  was published [11c]. It should be noted that recently monoalkanolamine ligand  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{O}-$  was used to stabilize stannylene and germylene compounds [12].

\* Corresponding author. Tel.: +7 4959393887; fax: +7 4959328846.  
E-mail address: [sergej@org.chem.msu.ru](mailto:sergej@org.chem.msu.ru) (S.S. Karlov).

Here we present the synthesis and structural investigations of a series of novel germlyenes and stannylenes **1–6** based on pyridine-containing dialcohol ligands (dialkanolamine analogues) of different size. It should be noted that this kind of ligands have already been used for preparation of group 14 element ( $M^{+4}$ ) derivatives [13]. Compounds **4** and **5** are the first structurally characterised germlyenes and stannylenes based on dialcohol ligands with N-containing functional group except dimeric  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Sn}]_2$  (see above and [11c]). The reactions of the “heavier” carbenes (**1–3**) with bromine led to  $\text{Ge}^{+4}$  and  $\text{Sn}^{+4}$  derivatives **7–9**. Further design of these ligands will allow the discriminative preparation of closely related germlyenes and stannylenes as monomeric or dimeric species with different chemical behaviour.

## 2. Results and discussion

The reaction between  $M[\text{N}(\text{SiMe}_3)_2]_2$  and alcohols is a standard approach to di(alkoxy)germylenes and stannylenes [14]. We used this method for the synthesis of **1–6** (Scheme 1). The target derivatives were obtained in a moderate or good yields (31–74%). The structures of the prepared compounds were confirmed by elemental analysis data and  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy (for compounds soluble in ordinary deuterated solvents).  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra are in consistency with the suggested structures. According to  $^{119}\text{Sn}$  NMR spectroscopy data (see Experimental part) stannylenes **4** and **6** are dimeric in solution. The latter was confirmed by upfield drift of  $^{119}\text{Sn}$  resonance resulted from additional base coordination on tin centre in dimeric structure [15]. According to data of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy hydrogen atoms of  $\text{CH}_2$  groups in “heavier carbenes” **3** and **4** as well as phenyl groups in the same compounds are magnetically non-equivalent. At the same time, phenyl groups in **1** are magnetically equivalent. We can suppose that there is not dynamic processes in this compound at room temperature due to the presence of pyridine ring and the strong intramolecular interaction metal–nitrogen in these compounds. To our opinion the main reason of this difference is different conformations of six-membered (**3** and **4**,  $=\text{C}-\text{C}-\text{O}-\text{Ge}-\text{N}=\text{C}$ ) and five-membered (**1**,  $=\text{C}-\text{C}-\text{O}-\text{Ge}-\text{N}=\text{C}$ , all atoms lie in the same plane) rings.

In order to get an additional evidence supporting the structure of insoluble stannylene **2**, we carried out the reaction of **2** with molecular bromine. This reaction as well as analogous reactions of **1** and **3** with  $\text{Br}_2$  led to the expected derivatives of virtually pentacoordinated germanium and tin **7–9** (Scheme 1).

Thus, we can conclude that compounds **1–6** are “heavier” carbenes and they exist as monomers or coordination oligomers (obvi-

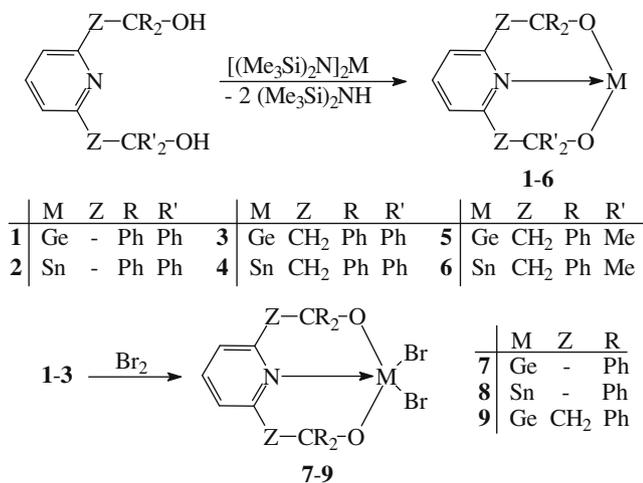
ously, dimers). On the contrary, the reaction of  $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$  with 2,6-(pyridine)dimethanol led to insoluble compound “Py  $(\text{CH}_2\text{O})_2\text{Ge}$ ”, which does not lead to expected  $\text{Py}(\text{CH}_2\text{O})_2\text{GeBr}_2$  in the reaction with bromine. This dibromide was previously obtained in another way [13e]. We can suppose that “Py  $(\text{CH}_2\text{O})_2\text{Ge}$ ” has a polymer structure. Consequently, the presence of substituents at carbon atoms is necessary for the existence of germlyenes and stannylenes in monomeric or dimeric form.

To the best of our knowledge compounds **4** and **5** are the first derivatives of tin(II) (except dimeric  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Sn}]_2$  [11c]) and germanium(II) based on dialkanolamine or analogous cage ligand that have been structurally characterised. The molecular structures of **4** and **5** are shown in Figs. 1 and 2. Table 1 summarises significant geometrical parameters for these compounds.

According to X-ray data, germylene **5** is monomeric in the solid state. The primary coordination environment of the Ge atom is formed by two covalent bonded oxygen atoms and one dative bonded nitrogen atom and may be treated as a trigonal pyramid with a lone pair in one vertex. To our knowledge, this is the second example of X-ray studied monomeric germylene with O,N,O coordination environment. The  $\text{N} \rightarrow \text{Ge}$ -bond in **5** is comparable with that in  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OGe}-\text{OC}(\text{O})\text{CH}_3$  (2.108(1) Å) with tricoordinated germanium atom [12c]. The  $\text{Ge}-\text{OCH}_2$  bond length (1.832(1) Å) in  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OGe}-\text{OC}(\text{O})\text{CH}_3$  is also close to  $\text{Ge}(1)-\text{O}(1)$  bond distance in **5**. It should be noted that the length of  $\text{Ge}(1)-\text{O}(1)$  bond in **5** is close to the  $\text{Ge}-\text{O}$  bond lengths in  $\text{Ge}[\text{OC}(t\text{-Bu})_3]_2$  (1.896(6) and 1.83(1) Å), which is the only structurally characterised monomeric dialkoxy germylene [16]. Thus, additional intramolecular interaction in **5** does not considerably elongate the  $\text{Ge}-\text{O}$  bonds. Of interest, the germanium atom in **5** lies almost in the plane of pyridine ring. The  $\text{Ge}-\text{N}$  bond is nearly perpendicular to the O-Ge-O plane, allowing ideal interaction of nitrogen lone electron pair with the vacant Ge orbital.

In contrast to **5**, closely related stannylene **4** is dimeric in the solid state (as well as in benzene solution, see above). The dimerization results from the formation of an additional bond between the tin atom of one monomeric unit and the oxygen atom of the other. The central  $(\text{Sn}-\text{O})_2$  units are non-planar and form a puckered rectangle with a pseudo-twofold axis passing through the centre. Non-coordinated oxygen atoms occupy *cis*-positions relative to  $(\text{Sn}-\text{O})_2$  core. The same *cis*-configuration was found in  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Sn}]_2$  [11c]. The coordination polyhedron of the Sn atom in compound **4** represents a distorted tetragonal pyramid with three oxygen atoms and nitrogen atom in the base of the pyramid and a lone pair in its vertex. The  $\text{Sn}-\text{N}$  bond length in **4** is close to that previously found in  $\text{N}_3\text{Sn}(\text{OCH}_2\text{CH}_2)\text{NMe}_2$  (2.505(5) Å) [12b],  $(\text{Me}_3\text{Si})_2\text{N}-\text{Sn}(\text{OCH}_2\text{CH}_2)\text{NMe}_2$  (2.617(3), 2.615(3) Å) and  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Sn}]_2$  (2.41(1), 2.45(1) Å) [11c] which are dimeric due to  $\text{Sn}-\text{O}$  bond formation [12d]. The central  $(\text{Sn}-\text{O})_2$  unit possesses two different pairs of  $\text{Sn}-\text{O}$  bond:  $\text{Sn}(1)-\text{O}(4)$  (2.183(3) Å) and  $\text{Sn}(2)-\text{O}(2)$  (2.182(3) Å) may be considered as covalent and  $\text{Sn}(1)-\text{O}(2)$  bond (2.355(3) Å) and  $\text{Sn}(2)-\text{O}(4)$  (2.301(3) Å) are dative. Two other non-coordinative  $\text{Sn}-\text{O}$  bonds are considerably shorter: 2.058(3) and 2.064(3) Å. Analogous correlation of  $\text{Sn}-\text{O}$  bond lengths were found in  $[\text{MeN}(\text{CH}_2\text{CH}_2\text{O})_2\text{Sn}]_2$  [11c].

In conclusion, metathetical exchange reactions between  $M[\text{N}(\text{SiMe}_3)_2]_2$  ( $M = \text{Ge}, \text{Sn}$ ) and the pyridine-containing dialcohol ligands afford compounds **1–6** in moderate to good yields. The structures of closely related dimeric stannylene **4** and monomeric germylene **5** were studied by X-ray diffraction analysis. Stannylenes **4** and **6** were found to be dimeric in solution according to  $^{119}\text{Sn}$  NMR spectroscopy data. The mentioned above ligands and related compounds are promising for discriminative synthesis of monomeric and dimeric stannylenes/germylenes. Further studies on chemical behaviour of these novel class of “heavier” carbenes are in progress.



Scheme 1. Preparation of complexes **1–9**.

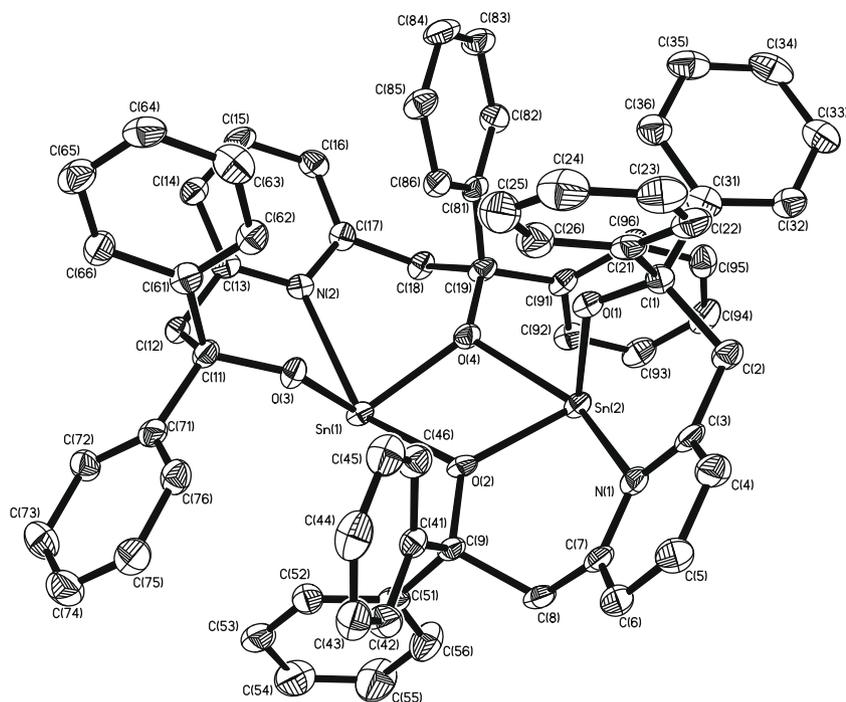


Fig. 1. Molecular structure of **4**. Hydrogen atoms are omitted for clarity.

### 3. Experimental

All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques.  $\text{Ge}[\text{N}(\text{SiMe}_3)_2]$  [16],  $\text{Sn}[\text{N}(\text{SiMe}_3)_2]$  [16],  $\text{Py}(\text{CPh}_2\text{OH})_2$  [17],  $\text{Py}(\text{CH}_2\text{CMe}_2\text{OH})(\text{CH}_2\text{CPh}_2\text{OH})$  [18] and  $\text{Py}(\text{CH}_2\text{CPh}_2\text{OH})_2$  [19] were synthesised according to the literature procedures.  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz) and  $^{119}\text{Sn}$  NMR (149 MHz) spectra were recorded with a Bruker 400 spectrometer (in  $\text{CDCl}_3$ ,  $\text{C}_6\text{D}_6$  and

$\text{THF-d}_8$  at 295 K). Chemical shifts in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are given in ppm relative to internal  $\text{Me}_4\text{Si}$ . Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University.

#### 3.1. Synthesis of $\text{Py}(\text{CPh}_2\text{O})_2\text{Ge}$ (**1**)

A solution of  $\text{Py}(\text{CPh}_2\text{OH})_2$  (0.71 g, 1.6 mmol) in toluene (10 ml) was added to a stirred solution of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$  (0.61 g, 1.6 mmol) in toluene (10 ml), and the mixture was stirred at room temperature. After 4 days the solid was filtered off to give **1** as a yellow solid. Yield 0.45 g (55%).  $^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ , ppm):  $\delta = 7.19\text{--}7.31$  (m, 8H),  $7.36\text{--}7.42$  (m, 12H) (aromatic hydrogens),  $7.91$  (d,  $J = 7.67$  Hz, 2H,  $\text{H}_\beta\text{-C}_5\text{H}_3\text{N}$ ),  $8.28$  (t,  $J = 7.67$  Hz, 1H,  $\text{H}_\gamma\text{-C}_5\text{H}_3\text{N}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF-d}_8$ , ppm):  $\delta = 84.74$  ( $\text{CPh}_2$ ), 124.71, 128.50, 128.53, 128.82, 144.35, 145.54, 156.27 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups). *Anal. Calc.* for  $\text{C}_{31}\text{H}_{23}\text{NO}_2\text{Ge}$  (514.1299): C, 72.42; H, 4.51; N, 2.72. *Found:* C, 72.54; H, 4.52; N, 2.71%.

Table 1

Selected bond lengths (Å) and angles (degrees) in **4** and **5**.

<b>4</b>			
Sn(1)–O(3)	2.058(3)	O(4)–Sn(1)–O(2)	69.6(1)
Sn(1)–O(4)	2.183(3)	O(3)–Sn(1)–N(2)	78.0(1)
Sn(1)–O(2)	2.355(3)	O(4)–Sn(1)–N(2)	79.8(1)
Sn(1)–N(2)	2.503(4)	O(2)–Sn(1)–N(2)	142.1(1)
Sn(2)–O(1)	2.064(3)	O(1)–Sn(2)–O(2)	101.8(1)
Sn(2)–O(2)	2.182(3)	O(1)–Sn(2)–O(4)	85.6(1)
Sn(2)–O(4)	2.301(3)	O(2)–Sn(2)–O(4)	70.6(1)
Sn(2)–N(1)	2.494(4)	O(1)–Sn(2)–N(1)	78.4(1)
O(3)–Sn(1)–O(4)	103.5(1)	O(2)–Sn(2)–N(1)	80.3(1)
O(3)–Sn(1)–O(2)	87.6(1)	O(4)–Sn(2)–N(1)	143.1(1)
<b>5</b>			
Ge(1)–O(1)	1.827(1)	O(1)–Ge(1)–O(2)	97.24(5)
Ge(1)–O(2)	1.881(1)	O(1)–Ge(1)–N(1)	92.67(5)
Ge(1)–N(1)	2.110(1)	O(2)–Ge(1)–N(1)	83.63(5)

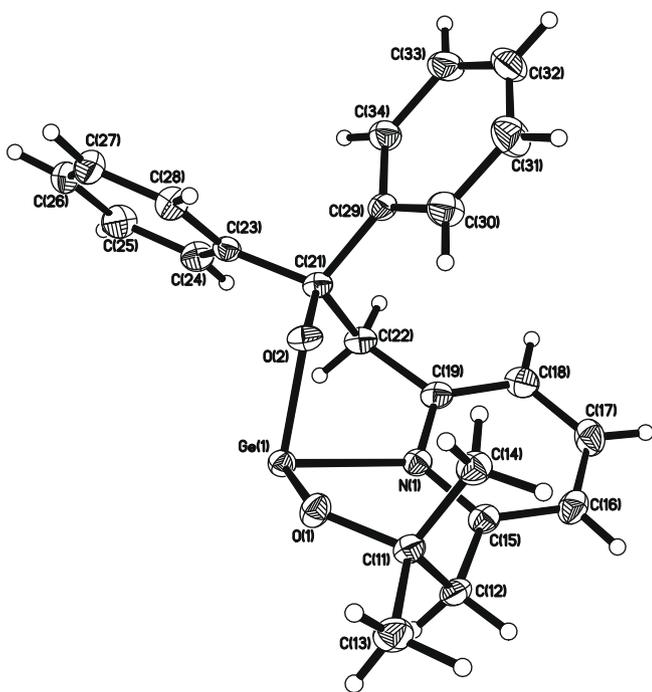


Fig. 2. Molecular structure of **5**.

### 3.2. Synthesis of $\text{Py}(\text{CPh}_2\text{O})_2\text{Sn}$ (**2**)

Analogously to **1**, complex **2** was prepared from  $\text{Py}(\text{CPh}_2\text{OH})_2$  (0.44 g, 1.0 mmol) and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$  (0.45 g, 1.0 mmol) in toluene (20 mL). The product was isolated by filtration to give **2** as a white solid. Yield 0.38 g (67%). NMR spectra were not recorded due to insolubility of **2**. *Anal. Calc.* for  $\text{C}_{31}\text{H}_{23}\text{NO}_2\text{Sn}$  (560.2299): C, 66.46; H, 4.14; N, 2.50. Found: C, 66.52; H, 4.15; N, 2.49%.

### 3.3. Synthesis of $\text{Py}(\text{CH}_2\text{CPh}_2\text{O})_2\text{Ge}$ (**3**)

Analogously to **1**, complex **3** was prepared from  $\text{Py}(\text{CH}_2\text{CPh}_2\text{OH})_2$  (0.79 g, 1.7 mmol) and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$  (0.66 g, 1.7 mmol) in toluene (20 mL). The product was isolated by filtration to give **3** as a white solid. Yield 0.67 g (74%).  $^1\text{H}$  NMR (400 MHz, THF-*d*8, ppm):  $\delta$  = 3.63, 4.13 (2d,  $J$  = 13.8 Hz, 4H, 2  $\text{CH}_2$ ), 6.67–6.97, 7.05–7.10, 7.27–7.37, 7.39–7.44, 7.72–7.78 (5m, 20H, aromatic hydrogens), 7.01 (d,  $J$  = 7.89 Hz, 2H,  $\text{H}_{\beta\text{-C}_5\text{H}_3\text{N}}$ ), 7.52 (t,  $J$  = 7.89 Hz, 1H,  $\text{H}_{\gamma\text{-C}_5\text{H}_3\text{N}}$ ).  $^{13}\text{C}$  NMR (100 MHz THF-*d*8, ppm):  $\delta$  = 47.17 ( $\text{CH}_2$ ), 77.72 ( $\text{CPh}_2$ ), 126.15, 126.87, 127.12, 127.20, 127.41, 127.88, 128.30, 128.41, 140.45, 149.85, 155.88 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups). *Anal. Calc.* for  $\text{C}_{33}\text{H}_{27}\text{GeNO}_2$  (542.183): C, 73.10; H, 5.02; N, 2.58. Found: C, 73.35; H, 5.03; N, 2.59%.

### 3.4. Synthesis of $\text{Py}(\text{CH}_2\text{CPh}_2\text{O})_2\text{Sn}$ (**4**)

A solution of  $\text{Py}(\text{CH}_2\text{CPh}_2\text{OH})_2$  (0.53 g, 1.1 mmol) in toluene (10 mL) was added to a stirred solution of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$  (0.50 g, 1.1 mmol) in toluene (10 mL), and the mixture was stirred at room temperature. After 4 days all volatiles were removed under reduced pressure. Then ether (20 mL) was added to the residue, the precipitate was filtered to give **4** as a white powder. Yield 0.52 g (51%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  = 3.14, 3.68 (2d,  $J$  = 12.50 Hz, 4H, 2  $\text{CH}_2$ ), 5.83 (d,  $J$  = 7.83 Hz, 2H,  $\text{H}_{\beta\text{-C}_5\text{H}_3\text{N}}$ ), 6.29 (t,  $J$  = 7.83 Hz, 1H,  $\text{H}_{\gamma\text{-C}_5\text{H}_3\text{N}}$ ), 6.87–6.97, 6.98–7.10, 7.25–7.40, 7.62–7.75 (4m, 20H, aromatic hydrogens).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  = 48.82 ( $\text{CH}_2$ ), 80.47 ( $\text{CPh}_2$ ), 122.67, 125.61, 125.64, 126.49, 126.71, 126.76, 127.33, 128.51, 129.27, 136.75, 156.22 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups).  $^{119}\text{Sn}$  NMR (149 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  = –485.89 (br s). *Anal. Calc.* for  $\text{C}_{33}\text{H}_{27}\text{NO}_2\text{Sn}$  (588.283): C, 67.37; H, 4.63; N, 2.38. Found: C, 67.45; H, 4.62; N, 2.38%.

### 3.5. Synthesis of $\text{Py}(\text{CH}_2\text{CPh}_2\text{O})(\text{CH}_2\text{CMe}_2\text{O})\text{Ge}$ (**5**)

Analogously to **4**, complex **5** was prepared from  $\text{Py}(\text{CH}_2\text{CPh}_2\text{OH})(\text{CH}_2\text{CMe}_2\text{OH})$  (0.38 g, 1.1 mmol) and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$  (0.43 g, 1.1 mmol) in toluene (20 mL). The product was isolated by filtration to give **5** as a white solid. Yield 0.17 g (34%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  = 0.90, 1.59 (2s, 6H, 2  $\text{CH}_3$ ), 2.32, 2.83 (2d,  $J$  = 14.15 Hz, 2H, 2  $\text{CH}_2$ ), 3.54 (s, 2H,  $\text{CH}_2\text{CPh}_2$ ); 6.19 (t,  $J$  = 7.32 Hz, 2H,  $\text{H}_{\beta\text{-C}_5\text{H}_3\text{N}}$ ), 6.63 (t,  $J$  = 7.32 Hz, 1H,  $\text{H}_{\gamma\text{-C}_5\text{H}_3\text{N}}$ ), 6.81–6.86, 6.95–7.03, 7.10–7.13, 7.20–7.25, 7.54–7.58, 7.77–7.82 (6m, 10H, aromatic hydrogens).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  = 30.10, 34.06 (2 $\text{CH}_3$ ), 47.17 ( $\text{CH}_2\text{CMe}_2$ ), 47.83 ( $\text{CH}_2\text{CPh}_2$ ), 69.08 ( $\text{CMe}_2$ ), 77.34 ( $\text{CPh}_2$ ), 123.18, 124.06, 126.70, 127.11, 127.44, 127.88, 128.51, 1289.28, 138.78, 149.16, 151.09, 155.81, 156.43 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups). *Anal. Calc.* for  $\text{C}_{23}\text{H}_{23}\text{GeNO}_2$  (418.0443): C, 66.08; H, 5.55; N, 3.35. Found: C, 65.98; H, 5.53; N, 3.36.

### 3.6. Synthesis of $\text{Py}(\text{CH}_2\text{CPh}_2\text{O})(\text{CH}_2\text{CMe}_2\text{O})\text{Sn}$ (**6**)

Analogously to **4**, complex **6** was prepared from  $\text{Py}(\text{CH}_2\text{CPh}_2\text{OH})(\text{CH}_2\text{CMe}_2\text{OH})$  (0.45 g, 1.3 mmol) and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$  (0.57 g, 1.3 mmol) in toluene (20 mL). The product was isolated

by filtration to give **6** as a white solid. Yield 0.19 g (31%).  $^1\text{H}$  NMR (400 MHz  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  = 0.98, 1.70 (2s, 6H, 2 $\text{CH}_3$ ), 2.21, 3.19, (2d,  $J$  = 13.90 Hz, 2H,  $\text{CH}_2\text{CMe}_2$ ), 3.42, 3.96 (2d,  $J$  = 12.64 Hz, 2H,  $\text{CH}_2\text{CPh}_2$ ), 6.14, 6.23 (2d,  $J$  = 7.32 Hz, 2H,  $\text{H}_{\beta\text{-C}_5\text{H}_3\text{N}}$ ), 6.67 (t,  $J$  = 7.32 Hz, 1H,  $\text{H}_{\gamma\text{-C}_5\text{H}_3\text{N}}$ ), 7.10–7.12, 7.17–7.19, 7.26–7.30, 7.57–7.60 (4m, 10H, aromatic hydrogens).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , ppm):  $\delta$  = 29.86, 33.94 (2 $\text{CH}_3$ ), 47.72 ( $\text{CH}_2\text{CMe}_2$ ), 51.34 ( $\text{CH}_2\text{CPh}_2$ ), 74.63 ( $\text{CMe}_2$ ), 80.24 ( $\text{CPh}_2$ ), 121.91, 123.17, 126.09, 126.85, 127.10, 127.91, 136.89, 148.45, 148.20, 151.45, 153.02, 157.05, 157.67 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups).  $^{119}\text{Sn}$  NMR (149 MHz, THF-*d*8, ppm):  $\delta$  = –443.62 (br s). *Anal. Calc.* for  $\text{C}_{23}\text{H}_{23}\text{SnNO}_2$  (464.1443): C, 59.52; H, 4.99; N, 3.02. Found: C, 59.44; H, 4.98; N, 3.01%.

### 3.7. Reaction of $\text{Py}(\text{CH}_2\text{OH})_2$ with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$

A solution of  $\text{Py}(\text{CH}_2\text{OH})_2$  (0.18 g, 1.3 mmol) in toluene (10 mL) was added to a stirred solution of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$  (0.52 g, 1.3 mmol) in toluene (10 mL), and the mixture was stirred at room temperature. After 4 days a yellow solid was filtered to give 0.21 g (77%) of “ $\text{Py}(\text{CH}_2\text{O})_2\text{Ge}$ ”. NMR spectra were not recorded due to insolubility of “ $\text{Py}(\text{CH}_2\text{O})_2\text{Ge}$ ”. *Anal. Calc.* for  $\text{C}_7\text{H}_7\text{GeNO}_2$  (209.746): C, 40.08; H, 3.36; N, 6.68. Found: C, 40.11; H, 3.37; N, 6.66%.

### 3.8. Synthesis of $\text{Py}(\text{CPh}_2\text{O})_2\text{GeBr}_2$ (**7**)

To a stirred solution of **1** (0.23 g, 0.4 mmol) in THF (10 mL) a solution of  $\text{Br}_2$  (0.07 g, 0.4 mmol) was added dropwise at room temperature. After 7 days all volatiles were removed under reduced pressure. Then ether (20 mL) was added to the residue, the precipitate was filtered to give **7** as a white powder. Yield 0.12 g (41%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.20–7.30, 7.31–7.36 (2m, 20H, aromatic hydrogens), 7.61 (d,  $J$  = 7.58 Hz, 2H,  $\text{H}_{\beta\text{-C}_5\text{H}_3\text{N}}$ ), 8.07 (t,  $J$  = 7.58 Hz, 1H,  $\text{H}_{\gamma\text{-C}_5\text{H}_3\text{N}}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 83.94 ( $\text{CPh}_2$ ), 123.34, 127.62, 128.05, 128.27, 142.58, 143.83, 155.84 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups). *Anal. Calc.* for  $\text{C}_{31}\text{H}_{23}\text{Br}_2\text{GeNO}_2$  (673.9379): C, 55.25; H, 3.44; N, 2.08. Found: C, 55.24; H, 3.43; N, 2.08%.

### 3.9. Synthesis $\text{Py}(\text{CPh}_2\text{O})_2\text{SnBr}_2$ (**8**)

Analogously to **7**, complex **8** was prepared from **2** (0.12 g, 0.2 mmol) and a solution of  $\text{Br}_2$  (0.04 g, 0.2 mmol) in THF (10 mL). The product was isolated by filtration to give **8** as a white solid. Yield 0.13 g (87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.26–7.38 (m, 20H, aromatic hydrogens), 7.59 (d,  $J$  = 7.83 Hz, 2H,  $\text{H}_{\beta\text{-C}_5\text{H}_3\text{N}}$ ), 8.04 (t,  $J$  = 7.83 Hz, 1H,  $\text{H}_{\gamma\text{-C}_5\text{H}_3\text{N}}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 82.32 ( $\text{CPh}_2$ ); 123.84, 127.85, 127.88, 128.22, 141.62, 145.34, 158.37 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups). *Anal. Calc.* for  $\text{C}_{31}\text{H}_{23}\text{Br}_2\text{NO}_2\text{Sn}$  (720.0379): C, 51.71; H, 3.22; N, 1.95. Found: C, 51.60; H, 3.23; N, 1.95%.

### 3.10. Synthesis $\text{Py}(\text{CH}_2\text{CPh}_2\text{O})_2\text{GeBr}_2$ (**9**)

Analogously to **7**, complex **9** was prepared from **3** (0.21 g, 0.4 mmol) and a solution of  $\text{Br}_2$  (0.07 g, 0.4 mmol) in THF (10 mL). The product was isolated by filtration to give **9** as a white solid. Yield 0.16 g (59%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 4.29 (s, 4H,  $\text{CH}_2$ ), 6.48 (d,  $J$  = 7.58 Hz, 2H,  $\text{H}_{\beta\text{-C}_5\text{H}_3\text{N}}$ ), 7.19–7.24, 7.26–7.31, 7.37–7.44 (3m, 21H, aromatic hydrogens and  $\text{H}_{\gamma\text{-C}_5\text{H}_3\text{N}}$  groups).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 43.52 ( $\text{CH}_2$ ); 84.43 ( $\text{CPh}_2$ ); 125.94, 126.10, 128.10, 128.22, 140.02, 144.92, 155.12 (aromatic carbons and  $\text{C}_5\text{H}_3\text{N}$  groups). *Anal. Calc.* for  $\text{C}_{33}\text{H}_{27}\text{Br}_2\text{GeNO}_2$  (701.991): C, 56.46; H, 3.88; N, 2.00. Found: C, 56.38; H, 3.89; N, 2.00%.

**Table 2**  
Details of crystallographic experiments for **4** and **5**.

	<b>4</b>	<b>5</b>
Formula	C <sub>80</sub> H <sub>70</sub> N <sub>2</sub> O <sub>4</sub> Sn <sub>2</sub>	C <sub>23</sub> H <sub>23</sub> N <sub>1</sub> O <sub>2</sub> Ge <sub>1</sub>
Fw	1360.76	418.01
Crystal system	monoclinic	monoclinic
Space group, Z	P2 <sub>1</sub> /c 4	P2 <sub>1</sub> /n 4
a (Å)	16.974(2)	10.4147(3)
b (Å)	16.2324(19)	13.1728(4)
c (Å)	22.966(3)	14.1632(5)
β (°)	95.498(2)	100.757(1)
V (Å <sup>3</sup> )	6288.8(13)	1908.92(10)
d <sub>calc</sub> (g cm <sup>-3</sup> )	1.437	1.454
Abs coeff. (mm <sup>-1</sup> )	0.849	1.623
F(0 0 0)	2784	864
θ Range (°)	1.74–27.00	2.13–28.00
Reflections collected	56 811	19 321
Unique reflections (R <sub>int</sub> )	13 660 (0.0902)	4607 (0.0247)
Data/parameters	13 660/795	4607/336
R <sub>1</sub> [I > 2σ(I)]/wR <sub>2</sub> (all data)	0.0595/0.1580	0.0252/0.0694
Largest difference in peak/hole (e Å <sup>-3</sup> )	2.192/−1.624	0.441/−0.216

### 3.11. Reaction of "Py(CH<sub>2</sub>O)<sub>2</sub>Ge" with Br<sub>2</sub>

To a stirred solution of "Py(CH<sub>2</sub>O)<sub>2</sub>Ge" (0.09 g, 0.4 mmol) in THF (10 ml) a solution of Br<sub>2</sub> (0.07 g, 0.4 mmol) was added dropwise at room temperature. After 7 days all volatiles were removed under reduced pressure. Then ether (20 ml) was added to the residue, the precipitate was filtered to give a white powder. According to NMR data, a mixture of unidentified compounds was obtained.

### 3.12. X-ray crystallographic study

Experimental details are given in Table 2. The data were collected on a Bruker SMART APEX II diffractometer using Mo Kα radiation (0.71073 Å) at 150 K. The structures were solved by direct methods and refined by full-matrix least-squares based on F<sup>2</sup> with anisotropic thermal parameters for all non-hydrogen atoms (SHELXTL-Plus). In **5**, all hydrogen atoms were found from difference Fourier syntheses and refined isotropically. As for **4**, all hydrogen atoms were placed in calculated positions and refined using a riding model [20].

### Supplementary material

CCDC 717017 and 717018 contain the supplementary crystallographic data for complexes **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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