

#### Main-Group Chemistry

## Less Is More: Three-Coordinate C,N-Chelated Distannynes and Digermynes

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Abstract: We report here the synthesis of new C,N-chelated chlorostannylenes and germylenes  $L^{3}MCI$  (M = Sn(1), Ge (2)) and L<sup>4</sup>MCI (M=Sn(3), Ge (4)) containing sterically demand-L<sup>3,4</sup> C,N-chelating ligands  $(L^3 = [2, 4-di-tBu-6$ ing  $L^4 = [2, 4-di-tBu-6-{(C_6H_3-2', 6'-iPr_2)N} =$  $(Et_2NCH_2)C_6H_2]^{-1}$ CH}C<sub>6</sub>H<sub>2</sub>]<sup>-</sup>). Reductions of 1-4 yielded three-coordinate C,Nchelated distannynes and digermynes [L<sup>3,4</sup>M]<sub>2</sub> for the first time (5:  $L^3$ , M = Sn, 6:  $L^3$ , M = Ge, 7:  $L^4$ , M = Sn, 8:  $L^4$ , M = Ge). For comparison, the four-coordinate distannyne [L<sup>5</sup>Sn]<sub>2</sub> (10) stabilized by N,C,N-chelate L<sup>5</sup> (L<sup>5</sup>=[2,6-{(C<sub>6</sub>H<sub>3</sub>-2',6'-Me<sub>2</sub>)N= CH<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>-</sup>) was prepared by the reduction of chlorostanny-

# lene L<sup>5</sup>SnCl (9). Hence, we highlight the role of donor-driven stabilization of tetrynes. Compounds 1–10 were characterized by means of elemental analysis, NMR spectroscopy, and in the case of 1, 2, 5–7, and 10, also by single-crystal X-ray diffraction analysis. The bonding situation in either three- or four-coordinate distannynes 5, 7, and 10 was evaluated by DFT calculations. DFT calculations were also used to compare the nature of the metal–metal bond in three-coordinate C,N-chelating distannyne $[L^3Sn]_2$ (5) and related digermyme $[L^3Ge]_2$ (6).

#### Introduction

Heavier Group 14 analogues of alkynes have been known since the pioneering work of Power et al.<sup>[1]</sup> These compounds, like the corresponding silicon,<sup>[2]</sup> germanium,<sup>[3]</sup> and tin<sup>[4]</sup> congeners are of importance with the regard to their bonding situation. It was demonstrated that depending on the organic substituents, single-, double-, and triple-bonded structures have been proposed.<sup>[5]</sup>

The design of a variety of rather bulky organic substituents R was essential for the success in making distannynes  $[RSn]_2$  ( $R = C_6H_3$ -2,6-*i*Pr<sub>2</sub>,  $C_6H_2$ -2,4,6-*i*Pr<sub>3</sub>,  $C_6H_3$ -2,6- $[C_6H_2$ -2,4,6-Me<sub>3</sub>]<sub>2</sub>, Si(*i*Pr)[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>).<sup>[6]</sup> It was also demonstrated that employment of intramolecularly coordinating ligands is an alternative for the stabilization of organotin(I) species  $[RSn]_2$ .<sup>[7]</sup> The thermodynamically stabilized ditin compounds are characterized by the presence of a tin-tin single bond, whereas kinetically

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- Supporting information for this article (including crystallographic parameters of compounds 1, 2, 5–7, and 10 (see Table S3) and the dependence of M–M (Ge, Sn) bond distances and C–M–M bond angles in structurally characterized tetrynes (see Tables S1 and S2 and Figures S1 and S2)) is available on the WWW under http://dx.doi.org/10.1002/chem.201500695.

stabilized ditin compounds bearing bulky organic substituents are characterized by the presence of a tin-tin multiple bond.<sup>[4–7]</sup> In context with these studies and as part of a systematic study concerning the influence of different electronic and steric properties of organic substituents on the character of the tin-tin bond in discussed ditin complexes [RSn]2, we started to focus on sterically demanding C,N-chelating ligands that could combine both kinetic and thermodynamic stabilizations of the ditin compounds. All the above discussed compounds are prepared by the reductive protocol of the starting heteroleptic stannylenes of the type RSnX (X = halide) and that is why the stabilization of latter compounds is crucial for the synthesis of the ditin compounds. In this context, we have shown that the sterically demanding C,N-chelating ligand L<sup>1</sup> is suitable for the stabilization of homoleptic stannylenes, and despite the steric bulk of ligand L<sup>1</sup>, the corresponding chlorostannylene L<sup>1</sup>SnCl could not be isolated. In contrast, the use of C,Nchelating ligand L<sup>2</sup> (see below) provided the C,N-chelated chlorostannylene L<sup>2</sup>SnCl. Despite the strong donor capacity of an imine C=N moiety in the ligand L<sup>2</sup>, the latter ligand was insufficient to stabilize the ditin compound [L<sup>2</sup>Sn]<sub>2</sub> and we have shown the latter compound underwent a disproportionation reaction.<sup>[8]</sup> This could be also a reason of an insufficient protecting effect of the organic substituent in the ortho position and that is why synthesis of ditin compounds containing related C,N-chelating ligand bearing sterically demanding organic groups in the ortho position towards tin atom was of current interest. For this reason we have prepared the C,N-chelating ligands L<sup>3,4</sup> containing a tBu group in the ortho position towards a metal atom in the desired C,N-chelated chlorotetrylenes (Scheme 1).

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Scheme 1. C,N-chelating ligands used for the stabilization of distannynes and digermynes.

We report here the synthesis of new C,N-chelated chlorostannylenes and germylenes  $L^{3}MCI$  (M = Sn(1), Ge (2)) and  $L^{4}MCI$ (M = Sn(3), Ge (4)) containing sterically demanding C,N-chelating ligands  $L^{3,4}$  ( $L^3 = [2,4-di-tBu-6-(Et_2NCH_2)C_6H_2]^-$ .  $L^4 = [2,4-di-tBu-6-(Et_2NCH_2)C_6H_2]^-$ .  $tBu-6-{(C_6H_3-2',6'-iPr_2)N=CH}C_6H_2]^-$ ). Attempts to convert 1-4 into the corresponding distannynes and digermynes provided the first three-coordinate C,N-chelated distannynes and digermynes  $[L^{3,4}M]_2$  (5: L<sup>3</sup>, M = Sn, 6: L<sup>3</sup>, M = Ge, 7: L<sup>4</sup>, M = Sn, 8: L<sup>4</sup>, M=Ge). For comparison, the four-coordinate distannyne  $[L^{5}Sn]_{2}$  (10) stabilized by the N,C,N-chelate ligand  $L^{5}$  ( $L^{5} = [2,6 \{(C_6H_3-2', 6'-Me_2)N=CH\}_2C_6H_3]^-$  was prepared by the reduction of chlorostannylene L $^{5}$ SnCl (9). Compounds 1–10 were characterized by means of elemental analysis, NMR spectroscopy, and in the case of 1, 2, 5-7, and 10, also by single-crystal X-ray diffraction analysis. The bonding situation in either three-coordinate or four-coordinate distannynes 5, 7, and 10 was evaluated by DFT calculations. DFT calculations were also used to compare the nature of the metal-metal bond in three-coordinate C,N-chelated distannyne [L<sup>3</sup>Sn]<sub>2</sub> (5) and related digermyme  $[L^{3}Ge]_{2}$  (**6**).

#### **Results and Discussion**

### Synthesis and characterization of C,N-chelated distannynes and digermynes 5–8

Treatment of the corresponding organolithium compounds  $L^{3,4}Li$  with  $MCl_2$  (M = Sn, Ge) provided stable C,N-chelated chlorostannylenes and germylenes  $L^{3}MCI$  (M = Sn(1), Ge (2)) and  $L^{4}MCI$  (M = Sn(3), Ge (4)) (Scheme 2).

Compounds 1 and 2 are white crystalline materials that are well soluble in organic solvents such as toluene, benzene, THF, Et<sub>2</sub>O or in *n*-hexane, whereas compounds 3 and 4 are yellow crystalline material that are well soluble in organic solvents such as toluene, benzene, THF, or Et<sub>2</sub>O. Compounds 1–4 were characterized by using NMR spectroscopy. The <sup>1</sup>H and <sup>119</sup>Sn NMR spectroscopy (for 1 and 3) proves the existence of the intramolecular N $\rightarrow$ M coordination in the solution of C<sub>6</sub>D<sub>6</sub> of 1–4. Thus, the <sup>1</sup>H NMR spectra of 1 and 2 revealed AX spin system for the methylene *CH<sub>2</sub>N* protons and four signals for the *CH<sub>2</sub>* together with two signals for the *CH<sub>3</sub>* protons of Et groups. The <sup>1</sup>H NMR spectra of **3** and **4** revealed two signals for the *CH* and four signals for the *CH*<sub>3</sub> protons of the *i*Pr groups. In addition, the <sup>119</sup>Sn NMR spectra of **1** and **3** display a sharp signal at  $\delta = 269.4$  ppm ( $\delta =$ 154.7 ppm for **3**), which is similar to that of the related N $\rightarrow$ Sn coordinated organostannylenes [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]SnCl ( $\delta =$ 156 ppm),<sup>[9a]</sup> [C<sub>6</sub>H<sub>3</sub>(NMe<sub>2</sub>)<sub>2</sub>-



Scheme 2. Synthesis of compounds 1-4.

2,6]SnCl ( $\delta$  = 380 ppm),<sup>[9b]</sup> and {C<sub>9</sub>H<sub>6</sub>N[CH(SiMe<sub>3</sub>)]-8}SnCl ( $\delta$  = 327 ppm),<sup>[9c]</sup> respectively.

Single crystals suitable for X-ray diffraction analysis of 1 and 2 were obtained from hexane solutions at -20 °C. The molecular structure of 1 and 2 together with selected geometric parameters are depicted in Figure 1.



**Figure 1.** Molecular structures of compounds **1** (A) and **2** (B). There are two independent molecules of **2** in the crystal structure. One molecule of **2** and the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: For **1**: Sn1–C1 2.1453(18), Sn1–N1 2.345(3), Sn1–Cl1 2.665(2); C1-Sn1-Cl1 119.67(6), C1-Sn1-N1 86.56(7). For **2**: Ge1–C1 2.008(7), Ge1–N1 2.125(6), Ge1–Cl1 2.324(3); C1-Ge1-Cl1 96.7(2), C1-Ge1-N1 83.1(3).



The tin and germanium atoms, respectively, are three-coordinated in **1** and **2** by C1 and N1 atoms of L<sup>3</sup> ligand and one chlorine atom Cl1. The nitrogen, carbon, and chlorine atoms form a basal plane and define distorted trigonal pyramidal geometry of Sn and Ge atoms due the presence of stereochemically active electron lone pair. The N1-Sn1 and N1-Ge1 distances (2.345(3) Å in **1** and 2.125(6) Å in **2**) are the result of strong  $N \rightarrow Sn^{\text{H}}$  and  $N \rightarrow Ge^{\text{H}}$  interactions.

Treatment of **1** with K[BHEt<sub>3</sub>] and treatment of **2** with KC<sub>8</sub> in THF resulted in red solutions that provided, after the work up, dark-red C,N-chelated distannyne  $[L^3Sn]_2$  (**5**) and orange C,N-chelated digermyne  $[L^3Ge]_2$  (**6**), respectively (Scheme 3). In a similar manner, the treatment of **3** with KC<sub>8</sub> in THF yielded a blue-green solution that provided, after the work up, the



Scheme 3. Synthesis of compounds 5–8.

dark-blue/green C,N-chelated distannyne  $[L^4Sn]_2$  (7). In contrast, when compound 4 was reduced by KC<sub>8</sub> in THF, the decomposition was observed only. The digermyne  $[L^4Ge]_2$  (8) was, however, prepared by the treatment of 4 with potassium in toluene at -78 °C as an air- and moisture-sensitive deepblue crystals (Scheme 3).

Compounds **5–8** were characterized by using NMR spectroscopy. The <sup>1</sup>H and <sup>119</sup>Sn NMR spectroscopy (for **5** and **7**) proves the existence of the intramolecular  $N \rightarrow M$  coordination in the  $C_6D_6$  solution of **5–8**.

Thus, the <sup>1</sup>H NMR spectra of **5** and **6** revealed an AX spin system for the methylene  $CH_2N$  protons and four signals for the  $CH_2$  protons together with two signals for the  $CH_3$  protons of the Et groups. The <sup>1</sup>H NMR spectra of **7** and **8** revealed two signals for the *CH* and four signals for the  $CH_3$  protons of *i*Pr groups. In addition, the <sup>119</sup>Sn NMR spectrum (C<sub>6</sub>D<sub>6</sub>) of **5** re-

**Full Paper** vealed a broad resonance at  $\delta = 688.1$  ppm for which, however, no <sup>119</sup>Sn–<sup>117</sup>Sn coupling could be detected. This value is very close to the value found for [Sn{(2,6-Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub> ( $\delta =$ 612 ppm),<sup>[7b]</sup> in which the tin atom is stabilized by two N $\rightarrow$ Sn coordination. The <sup>119</sup>Sn NMR spectrum of **7** revealed a broad

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close to the value found for  $[Sn{(2,6-Me_2NCH_2)_2C_6H_3]}_2$  ( $\delta = 612 \text{ ppm}$ ),<sup>[7b]</sup> in which the tin atom is stabilized by two N $\rightarrow$ Sn coordination. The <sup>119</sup>Sn NMR spectrum of **7** revealed a broad resonance at  $\delta = 264.1 \text{ ppm}$ , which is upfield-shifted when compared with that of **5** and  $[Sn{(2,6-Me_2NCH_2)_2C_6H_3]}_2$ .<sup>[7b,h]</sup> On the other hand, the value of  $\delta$  <sup>119</sup>Sn in **7** is shifted downfield when compared with the related N $\rightarrow$ Sn coordinated distannynes containing N,C,N-pincer ligands with C=N imine functionality ( $\delta = 79$  for  $[Sn{(tBuN=CH)_2C_6H_3]}_2$  and 115 and 134 ppm in  $[Sn{(2,6-iPr_2C_6H_3)=C(CH_3)]_2C_6H_3]_2$ , respectively).<sup>[7g,a]</sup> The value of  $\delta$  <sup>119</sup>Sn in **7** is thus similar to the value found in tBuNC adduct of single-bonded amido-distannyne L<sup>†</sup>SnSnL<sup>†</sup>

 $\begin{aligned} &(\delta\!=\!241 \text{ ppm, } L^{\dagger}\!=\!-N(Ar^{\dagger})(SiiPr_3),\\ &Ar^{\dagger}\!=\!C_6H_2\{C(H)Ph_2\}_2iPr\!-\!2,\!4,\!6),^{[10]}\\ &\text{ in which the tin centrum is three-coordinate, similar to $\mathbf{7}$.} \end{aligned}$ 

Single crystals suitable for Xray diffraction analysis of 5-7were obtained from hexane solutions at -20 °C. The molecular structures of 5-7 are shown in Figures 2–4 and selected geometrical parameters are given in Table 1.

The Sn1–Sn2 distances of 2.9692(17) Å in **5** and 2.9393(6) Å in **7** lie between 2.668(1) and 3.066(1) Å of the parent compounds Ar'SnSnAr' and Ar\*SnS-nAr\*, respectively, in which  $Ar' = C_6H_3$ -2,6- $(C_6H_3$ -2,6- $iPr_2)_2$  and  $Ar^* = C_6H_2$ -2,6- $(C_6H_3$ -2,6- $iPr_2)_2$ -4-

SiMe<sub>3</sub>.<sup>[1,6c]</sup> The Sn–Sn bond lengths are close to those found in related intramolecularly coordinated distannynes (range of 2.8981(1)–486(6) Å) stabilized by Y,C,Y-chelating ligands (Y=N, O),<sup>[7a, b, e, g]</sup> but they are shorter



Figure 2. Molecular structure of 5. Hydrogen atoms are omitted for clarity.





Figure 3. Molecular structure of 7. Hydrogen atoms are omitted for clarity.

bonded amido-digermyne L\*GeGeL\* (2.7093(7) Å, L\*=  $-N(Ar^*)(SiMe_3)$ ,  $Ar^* = C_6H_2\{C(H)Ph_2\}_2Me-2,4,6)$ .<sup>[12]</sup> The intramolecular Ge–N distances are 2.190(3) Å for Ge1–N1 and 2.184(3) Å for Ge2–N2 being somewhat longer than those found in related N→Ge coordinated digermynes (range of 1.986(3)–36(3) Å).<sup>[11]</sup> The C1-Ge1-Ge2 and C20-Ge2-Ge1 angles with values of 97.76(10) and 96.87(10)°, respectively, lie between 89.10(9) and 116.11(10)° of the parent N→Ge coordinated digermynes.<sup>[11]</sup>

Prepared C,N-chelated distannynes 5 and 7 contain three-coordinate tin atoms. As a result, the  $N \rightarrow Sn$  interaction in 5 and 7 is stronger than the values found in single-bonded distannynes containing N,C,N-ligands. In the C,N-chelated digermyne 6, the Ge—Ge bond length is longer than in the related singlebonded digermynes stabilized by N,C,N-pincer-type ligand (Figure 4). This elongation of the Ge—Ge bond cannot be result

of the stronger  $N \rightarrow Ge$  interaction in **6**, since the  $N \rightarrow Ge$  coordination in **6** is weaker than in related digermynes containing N,C,N-pincer ligands.

#### Synthesis and characterization of N,C,N-chelated distannyne [L<sup>5</sup>Sn]<sub>2</sub> (10)

An intramolecularly coordinated distannyne  $[L^5Sn]_2$  (**10**) stabilized by sterically demanding pincer type ligand  $L^5$  was also synthesized, with the aim of possible comparison of the bonding situation in three-coordinate C,N-chelated distannynes  $[L^3Sn]_2$  (**5**) and  $[L^4Sn]_2$  (**7**). Treatment of the



when compared with single-bonded amido-distannyne L<sup>†</sup>SnSnL<sup>†</sup> (3.1429(7) Å, L<sup>†</sup>=-N(Ar<sup>†</sup>)(Si*i*Pr<sub>3</sub>), Ar<sup>†</sup>=C<sub>6</sub>H<sub>2</sub>{C(H)Ph<sub>2</sub>}<sub>2</sub>*i*Pr-2,4,6).<sup>[10]</sup> The intramolecular Sn–N distances are 2.373(5) Å for Sn1–N1 and 2.371(5) Å for Sn2–N2 in **5** (2.228(4) Å for Sn1–N1 and 2.223(4) Å for Sn2–N2 in **7**). These are shorter than the Sn–N distances found in related N→Sn coordinated distannynes stabilized by N,C,N-pincer type ligands (the range of 2.4129(16)–2.6879(17) Å).<sup>[7a,b,g]</sup> The Sn–N interactions found in **5** and **7** represent one of the strongest coordination found in N→Sn coordinated distannynes. The C1-Sn1-Sn2 and C20-Sn2-Sn1 angles have values of 93.45(15) and 93.82(18)° in **5**, whereas wider angles C1-Sn1-Sn2 (105.30(14)°) and C28-Sn2-Sn1 (103.37(14)°) were found in **7**. However, these bonding angles lie between 96.63(5) and 121.26(4)° of the parent Y,C,Y-chelated distannynes (Y=N, O).<sup>[7a,b,e,g]</sup>

The Ge1–Ge2 distance of 2.6180(6) Å is longer than 2.5059(5) and 2.5685(5) Å of the parent  $N \rightarrow Ge$  intramolecularly coordinated digermynes  $[Ge\{(2,6-iPr_2C_6H_3N=CH)_2C_6H_3\}]_2$  and  $[Ge\{2-(2,6-iPr_2C_6H_3N=C(CH_3))C_6H_2(OCH_2O)\}]_2$ .<sup>[11]</sup> The Ge–Ge bond length is, however, shorter when compared with single-



Figure 4. Molecular structure of 6. Hydrogen atoms are omitted for clarity.

corresponding organolithium compound L<sup>5</sup>Li with SnCl<sub>2</sub> provided the stable N,C,N-chelated chlorostannylene L<sup>5</sup>SnCl (9). Treatment of 9 with KC<sub>8</sub> in THF provided dark-blue N,C,N-chelated distannyne  $[L^5Sn]_2$  (10) as air- and moisture-sensitive crystals (Scheme 4).



Scheme 4. Synthesis of N,C,N-chelated distannyne 10.

Compound **10** was characterized by using NMR spectroscopy. The <sup>1</sup>H and <sup>119</sup>Sn NMR spectroscopy proves the existence of the intramolecular N $\rightarrow$ Sn coordination in the solution of C<sub>6</sub>D<sub>6</sub> of the N,C,N-chelated distannyne [L<sup>5</sup>Sn]<sub>2</sub> (**10**). The <sup>1</sup>H spectrum of **10** revealed one signal for the CH–N group and one signal for the Me groups. In addition, the <sup>119</sup>Sn NMR spectrum of **10** revealed a broad resonance at  $\delta = 118$  ppm, which is upfield-shifted when compared with that of **5** ( $\delta = 688.1$  ppm), **7** ( $\delta = 264.1$  ppm), and [Sn{(2,6-Me\_2NCH\_2)\_2C\_6H\_3}]<sub>2</sub> ( $\delta = 612$  ppm).<sup>[7b]</sup> The value of  $\delta$  <sup>119</sup>Sn in **10** is close to the values found in structurally related N $\rightarrow$ Sn coordinated distannyne [SnC<sub>6</sub>H<sub>3</sub>{2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C(CH<sub>3</sub>)}<sub>2</sub>]<sub>2</sub> ( $\delta = 115$  and 134, respectively)<sup>[7a]</sup> and [{tBuN=CH}<sub>2</sub>]<sub>2</sub> ( $\delta = 79$  ppm)<sup>[7g]</sup> containing N,C,N-pincer ligands with a C=N imine functionality.

Single crystals suitable for X-ray diffraction analysis of **10** were obtained from hexane solutions at -20 °C. The molecular structure of **10** consists of two independent molecules and is shown in Figure 5. Selected geometrical parameters are given in the Table 1.



Figure 5. Molecular structure of 10. Hydrogen atoms are omitted for clarity.

The Sn1–Sn2 distance of 2.9250(5) Å (Sn3–Sn4=2.9086(5) Å) lie between 2.8981(1) and 3.0486(6) Å of the parent distannynes stabilized by Y,C,Y-pincer ligands (Y=N, O),<sup>[7a,b,e,g]</sup> but they are shorter when compared with that of single-bonded amido-distannyne L<sup>†</sup>SnSnL<sup>†</sup> (3.1429(7) Å, L<sup>†</sup>=–N(Ar<sup>†</sup>)(Si*i*Pr<sub>3</sub>), Ar<sup>†</sup>=C<sub>6</sub>H<sub>2</sub>{C(H)Ph<sub>2</sub>}<sub>2</sub>*i*Pr-2,4,6).<sup>[10]</sup> The intramolecular Sn–N distances vary between 2.449(3) Å for Sn4–N7 and 2.664(6) Å for Sn3–N6 and they are within the range of 2.4129(16)–2.6879(17) Å found in related N→Sn coordinated distannynes,<sup>[7a,b,g]</sup> but longer than those found in **5** and **7**. As the result

of the presence of  $N \rightarrow Sn$  coordination, both tin atoms of 10 are four-coordinated. Interestingly, structurally related  $N \rightarrow Sn$  coordinated distannyne [Sn{(2,6 $iPr_2C_6H_3N=C(CH_3))_2C_6H_3]_2$ , reported by Roesky and co-workers, contains one nitrogen donor of the pincer ligand uncoordinated,<sup>[7a]</sup> whereas tin atoms in distannynes [Sn{(2,6- $Me_2NCH_2)_2C_6H_3]_2^{[7b]}$ and [Sn{(tBuN=CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}]<sub>2</sub>,<sup>[7g]</sup> for ex-

ample, compounds containing sterically less-demanding pincer substituents, are coordinated by both nitrogen atoms of pincer ligands, in a similar manner as **10**. It is evident that the steric bulk of chelating ligands can affect the tin coordination environment in intramolecularly coordinated distannynes.

The literature search thus indicates a wide range of Sn-Sn and Ge-Ge bond lengths for structurally related distanynnes and digermynes that mutually differ by the substituents. Therefore, crystal structures of distannynes and digermynes of the type aryl-M-M-aryl have been analyzed to find a correlation between the M-M bond length and the combination of C-M-M angle. It can be generalized that the distanynnes with a Sn-Sn multiple bond have the Sn-Sn bond lengths in the range of 2.646-2.716 Å and the C-Sn-Sn moiety is in plane with the aromatic system of the Sn-bound ligand with bond angles of 121.85–125.21° (see the Supporting Information, Figure S1 and Table S1). In contrast, in the related compound with Sn-Sn single bond, that range of Sn-Sn bond lengths is 2.898-3.066 Å and the C-Sn-Sn moiety is basically perpendicular to the aromatic system of the Sn-bound aromatic ring with the bond angles 93.45-101.98° (see the Supporting Information, Figure S1 and Table S1). From this point of view, complex 7 represents rare example of the single-bonded distannyne with a wide C-Sn-Sn angle as the result of crystal packing effect of ligand L<sup>4</sup>. This can be further demonstrated by the value of C-Sn-Sn-C torsion angle that is 73.15°. Similar trends have been found in digermynes. The digermynes with Ge-Ge multiple bond have the Ge-Ge bond lengths in the range of 2.212-2.306 Å and the C-Ge-Ge moiety is in plane with the aromatic system of the Ge-bound ligand with bond angles of 136.1-121.9°. In contrast, there are two compounds with Ge-Ge single bond having the Ge-Ge bond lengths in the range of 2.506-2.569 Å and the narrow values of the C-Ge-Ge bond angles at 89.1-98.2°. Careful interpretation also suggests that the Ge-Ge bond length regularly decrease with the narrower C-Ge-Ge angle. Nearly linear correlation of both mentioned values (Ge-Ge bond and C-Ge-Ge angle) has been found (see the Supporting Information, Figure S2 and Table S2). The C,Nchelated complex 6 is, however, out of this range and represents the single-bonded digermyne with an extra-long Ge-Ge bond.

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#### **DFT calculations**

As the intramolecularly coordinated distannyne [L<sup>5</sup>Sn]<sub>2</sub> (10) stabilized by sterically demanding pincer type ligand L<sup>5</sup> contains four-coordinate tin atoms, whereas C,N-chelated distannynes  $[L^{3}Sn]_{2}$  (5) and  $[L^{4}Sn]_{2}$  (7) contain three-coordinate tin atoms, the bonding situation was evaluated by DFT calculations. DFT calculations also enable the comparison of the nature of the metal-metal bond in C,N-chelated distannyne [L<sup>3</sup>Sn]<sub>2</sub> (5) and related digermyme [L<sup>3</sup>Ge]<sub>2</sub> (6). For these main group complexes, M06-2X has proven to be a highly useful functional with good predictive ability for molecular properties. Table 1 summarizes the key geometric data in comparison to the experimental data for 5, 6, 7, and 10 and shows a good accordance between both data sets. In the next step, natural bond orbitals and charges as well as Wiberg bond indices (WBI) have been calculated (Tables 2 and 3 and Figure 6) for these four complexes.

The Wiberg indices give an impression of the bond strength of the regarded bonds. Compound **5** is stabilized by an amine donor of ligand  $L^3$ , whereas compound **7** possesses an imine

Table 2.         NBO charges (in e-units) in 5–7 and 10 (M06-2X/def2-TZVP).					
	5 (M=Sn)	6 (M=Ge)	7 (M=Sn)	10 (M=Sn)	
М	0.49	0.36	0.65	0.72	
Ν	-0.48	-0.46	-0.59	-0.50	
С	-0.45	-0.41	-0.43	-0.43	

Table 3. Wiberg bond indices in 5–7 and 10 (M06-2X/def2-TZVP).							
	5 (M=Sn)	<b>6</b> (M = Ge)	7 (M=Sn)	10 (M=Sn)			
M-M	0.91	0.93	0.79	0.77			
M-N	0.23	0.29	0.29	0.18			
M–C	0.64	0.75	0.64	0.64			

 

 5: lone pair s: 78%; p: 22%
 5: Sn-Sn bond
 6: lone pair s: 72%; p: 28%
 6: Ge-Ge bond

 6: lone pair s: 72%; p: 28%
 6: Ge-Ge bond
 6: Ge-Ge bond

 7: lone pair s: 81%; p: 19%
 7: Sn-Sn bond
 10: lone pair s: 81%; p: 19%
 10: Sn-Sn bond

Figure 6. Natural bond orbitals of the lone pairs (only one per compound shown) and the metal–metal bonds of 5–7 and 10.

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donor of ligand  $L^4$  and the latter coordinates the metal center through a stronger  $N \rightarrow Sn$  interaction. This is reflected in a Wiberg index of 0.23 for the  $N{\rightarrow}Sn$  interaction for  ${\bf 5}$  and of 0.29 for 7. As result, the NBO charges increase for tin atom going from 5 (0.49) to 7 (0.65). Simultaneously, the WBI decreases for the Sn-Sn bond going from 5 (0.91) to 7 (0.79) since the tin atoms obtain more stabilization from the imine donors. Similarly to 7, the WBI for the Sn-Sn bond is 0.77 in compound 10, which indicates a similar character of the Sn-Sn bond in  ${\bf 7}$  and  ${\bf 10}.$  In contrast, a weaker  $N{\rightarrow}Sn$  interaction in  ${\bf 5}$ resulted in a large value of the WBI indicating a large Sn-Sn bond strength, that is, however, still a single bond, as the length of the Sn-Sn bond is in the range of a standard Sn-Sn single bond.<sup>[13]</sup> In comparison between the three-coordinate distannyne 7 and the four-coordinate distannyne 10, it appears that the imine-donors in 10 donate less each, since the tin atom is four-coordinate here.

With regard to the molecular orbitals, natural bond orbitals are helpful to visualize the lone pairs and the metal-metal bonds because they are more localized than the canonical orbitals (Figure 6). In all four compounds, the lone pair possesses a large p-contribution, which gives the lone pair a predominant direction.

The different strength of  $N \rightarrow Sn$  interaction again influences the nature of the lone pair. The p-contribution of the lone pair decreases slightly going from **5** (22%) to **7** and **10** (19%) since the tin atoms obtain more stabilization from the imine donors. Since the p-contribution is significant and giving a strong directionality, we interpret these data as a stereochemically active lone pair.

DFT calculations were also used to compare the nature of the metal-metal bond in three-coordinate distannyne **5** and digermyme **6**, stabilized by ligand L<sup>3</sup>. The NBO charges decreases for the central atom going from tin in **5** (0.49) to germanium in **6** (0.36), whereas the WBI remains constant for the metal-metal bond going from **5** (0.91) to **6** (0.93). The p-contribution of the lone pair increases going from **5** (22%) to **6** 

(28%). This clearly demonstrates that ligand L<sup>3</sup> is able to stabilize strong metal-metal bonds in the discussed compounds. It is also evident that the strength of N $\rightarrow$ Sn interaction may influence the nature of the lone pair and the strength of metal-metal bond.

#### Conclusion

We have demonstrated that the application of C,Nchelating ligands  $L^{3,4}$  containing a *t*Bu group in the *ortho* position towards metal atoms provided stable C,N-chelated chlorostannylenes and germylenes **1–4**. Both ligands  $L^{3,4}$  have been also shown to be sufficient for the stabilization of C,N-chelated distannynes and digermynes **5–8** containing three-coordinate metal centers. The tetrynes were so far stabilized by either sterical bulky terphenyl ligands (two-coordinate metal center), or by Y,C,Y-pincer ligands (four-coordinate metal center). The design of new C,N-chelat-



ing ligands L<sup>3,4</sup> thus provided a new type of tetrynes having three-coordinate metal atoms. The values of Sn–Sn bond lengths found in distannynes **5** and **7** suggest that, despite the three-coordinate tin center, these compounds are still single-bonded species, similar to those stabilized by Y,C,Y-pincer-type ligands. However, a wide C-Sn-Sn angle has been found in the complex **7** as the result of crystal-packing effect of ligand L<sup>4</sup>. In contrast, C,N-chelated digermyne **6** represents the example with the longest Ge–Ge bond length found in diaryldigermynes.

DFT studies further showed that the strength of metal-metal bond as well as the character of lone electron pair can be tuned by the  $N \rightarrow M$  (M=Sn, Ge) interaction. Compounds 5 and **6**, which are stabilized by an amine donor of ligand L<sup>3</sup>, have large values of the WBI for the metal-metal bonds, whereas compounds 7 and 10, in which tin atoms obtain more stabilization from the imine donors, showed weaker metal-metal bonds with a lower WBI. All the data thus demonstrated that both ligands L<sup>3,4</sup> differ mutually. It has been further demonstrated that p-contribution of the lone pair can be tuned by the appropriate ligand system ( $L^3$  vs.  $L^4$ ) and the higher p-character of lone pair can increase the bonding character of the M-M bond. The DFT studies thus demonstrated that in contrast to strictly single-bonded tetrynes that are stabilized by Y,C,Y-chelating ligands, the use of C,N-chelating ligands may tune the nature of the metal-metal bond.

#### **Experimental Section**

#### **General procedures**

All reactions were carried out under argon, using standard Schlenk techniques. Solvents were dried by standard methods, and distilled prior to use. Starting compounds L<sup>5</sup>Br was prepared according to the literature<sup>[14]</sup> and SnCl<sub>2</sub> and GeCl<sub>2</sub>\*dioxane were purchased from Sigma Aldrich. The <sup>1</sup>H, <sup>13</sup>C, and <sup>119</sup>Sn NMR spectra were recorded on a Bruker Avance500 spectrometer at 300 K in C<sub>6</sub>D<sub>6</sub>. The <sup>1</sup>H, <sup>13</sup>C, and <sup>119</sup>Sn NMR chemical shifts ( $\delta$ ) are given in ppm and referenced to external Me<sub>4</sub>Si. Elemental analyses were performed on an LECO-CHNS-932 analyzer.

#### Syntheses

L<sup>3</sup>Br: Diethylamine (15.8 g, 216 mmol) was added to a solution of 2-bromo-1-bromomethyl-3,5-di-tert-butylbenzene<sup>[15]</sup> (26.1 g, 72 mmol) in Et<sub>2</sub>O (150 mL) at room temperature and the reaction mixture was stirred overnight. After that, the insoluble material was filtered off and the filtrate was evaporated to give crude product as yellow oil. The crude product was dissolved in Et<sub>2</sub>O (150 mL) and HCl (aq) (1:2, 150 mL) was added. The organic phase was discarded, to the aqueous phase KOH was added and the mixture was extracted with  $Et_2O$  (2×200 mL). The organic phase was dried over MgSO<sub>4</sub> and evaporated under reduced pressure to give L<sup>3</sup>Br as white solid. Yield: 23.5 g (92%). M.p. 38–40  $^\circ\text{C};~^1\text{H}$  NMR (C\_6D\_6, 400.13 MHz):  $\delta = 0.95$  (t, 6 H, CH<sub>3</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 7.2 Hz), 1.32 (s, 9 H,  $C(CH_3)$ ), 1.61 (s, 9H,  $C(CH_3)$ ), 2.44 (q, 4H,  $CH_2(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2 Hz$ ), 3.77 (s, 2H, CH<sub>2</sub>N), 7.52 (d, 1H, ArH,  ${}^{4}J({}^{1}H, {}^{1}H) = 2.4$  Hz), 7.86 ppm (d, 1H, ArH,  ${}^{4}J({}^{1}H, {}^{1}H) = 2.4 \text{ Hz}$ );  ${}^{13}C$  NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta =$ 12.4 (CH<sub>3</sub>(Et)), 30.2 (C(CH<sub>3</sub>)), 31.2 (C(CH<sub>3</sub>)), 34.7 (C(CH<sub>3</sub>)), 37.3 (C(CH<sub>3</sub>)), 47.6 (CH<sub>2</sub>(Et)), 59.6 (CH<sub>2</sub>N), 121.9, 123.4, 125.6, 141.1, 147.1, 149.1 ppm (Ar-C); elemental analysis calcd (%) for  $C_{19}H_{32}BrN$  (354.38): C 64.4, H 9.1; found: C 64.6, H 9.0.

L<sup>4</sup>Br: 2,6-Diisopropylaniline (14.9 g, 84 mmol) was added to a solution of 2-bromo-3,5-di-tert-butylbenzaldehyde (25 g, 84 mmol) in methanol (75 mL) at room temperature. After the addition of a few drops of formic acid, the precipitation of yellow solid was observed. The reaction mixture was stirred overnight. The yellow solid was filtered off, washed with cold methanol, and dried under vacuum to give L4Br. Yield: 28 g (73%). M.p. 129–131  $^\circ\text{C};~^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta = 1.21$  (d, 12 H, CH<sub>3</sub>,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz), 1.25 (s, 9H, C(CH<sub>3</sub>)), 1.51 (s, 9H, C(CH<sub>3</sub>)), 3.21 (sept, 2H, CH, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 7.15–7.17 (m, 3 H, ArH), 7.67 (d, 1 H, ArH, <sup>4</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 2.4 Hz), 8.53 (d, 1H, ArH,  ${}^{4}J({}^{1}H, {}^{1}H) = 2.4$  Hz), 8.99 ppm (s, 1H, CH=N); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta = 24.0$  ((CH<sub>3</sub>)<sub>2</sub>CH), 28.8 ((CH<sub>3</sub>)<sub>2</sub>CH),  $30.6 \ (C(CH_3)_3), \ 31.5 \ (C(CH_3)_3), \ 35.3 \ (C(CH_3)_3), \ 37.9 \ (C(CH_3)_3), \ 123.8,$ 124.1, 125.1, 125.2, 128.8, 137.5, 138.1, 148.7, 150.3, 150.8 (Ar-C), 164.1 ppm (CH=N); elemental analysis calcd (%) for C<sub>27</sub>H<sub>38</sub>BrN (456.51): C 71.0, H 8.4; found: C 70.8, H 8.3.

L<sup>3</sup>SnCl (1): A hexane solution of *n*BuLi (3.8 mL of 1.6 M) was added to a stirred solution of L<sup>3</sup>Br (2.05 g, 5.78 mmol) in Et<sub>2</sub>O (30 mL) at  $0\,^\circ\text{C}$ . The mixture was allowed to warm up to room temperature and stirred for 1 h. After that, the resulting yellow solution of L<sup>3</sup>Li was cooled to -78 °C and added dropwise to the solution of SnCl<sub>2</sub> (1.09 g, 5.78 mmol) in THF (15 mL) pre-cooled to  $-78\,^\circ\text{C}$  to give pale-yellow solution. The reaction mixture was left to warm up to room temperature and stirred for 4 h. Then, all volatiles were removed under reduced pressure, the residue was suspended in hexane (40 mL) and the insoluble material was filtered off. The filtrate was evaporated and the residue was extracted with hexane (30 mL) once again. The hexane filtrate was concentrated and cooled to -30 °C to afford colorless crystals of 1. Yield: 1.51 g (61%); M.p. 114–117 °C<sup>1</sup>H NMR ( $C_6 D_{6'}$  400.13 MHz):  $\delta = 0.41$  (t, 3 H,  $CH_3(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2 Hz$ , 0.75 (t, 3 H,  $CH_3(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8 Hz$ ), 1.35 (s, 9H, C(CH<sub>3</sub>)), 1.54 (s, 9H, C(CH<sub>3</sub>)), 2.12 (m, 1H, CH<sub>2</sub>(Et), <sup>3</sup>J(<sup>1</sup>H,  $^{1}$ H) = 7.2 Hz), 2.20 (m, 1 H, CH<sub>2</sub>(Et),  $^{3}$ J( $^{1}$ H,  $^{1}$ H) = 7.2 Hz), 2.65 (m, 1 H,  $CH_2(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8 Hz)$ , 3.13 (m, 1 H,  $CH_2(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8 Hz)$ , 3.46 and 4.42 (AX system, 2 H, CH<sub>2</sub>N), 7.09 (s, 1 H, ArH), 7.55 ppm (s, 1 H, ArH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta = 7.9$ , 11.3 (CH<sub>3</sub>(Et)), 32.0 (C(CH<sub>3</sub>)), 34.5 (C(CH<sub>3</sub>)), 35.3 (C(CH<sub>3</sub>)), 38.3 (C(CH<sub>3</sub>)), 42.3, 46.3 (CH2(Et)), 63.3 (CH2N), 120.2, 121.9, 146.7, 150.9, 158.9, 167.4 (Ar-C) ppm;  $^{\rm 119}{\rm Sn}$  NMR (C\_6D\_6, 149.23 MHz):  $\delta\!=\!$  269.4 ppm; elemental analysis calcd (%) for  $C_{19}H_{32}CINSn$  (428.62): C 53.2, H 7.5; found: C 53.4, H 7.4.

L<sup>3</sup>GeCl (2): A hexane solution of *n*BuLi (1.92 mL of 1.6 м) was added to a stirred solution of L<sup>3</sup>Br (1.04 g, 2.94 mmol) in Et<sub>2</sub>O (20 mL) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 1 h. After that the resulting yellow solution of  $L^{3}Li$  was cooled to -78 °C and added dropwise to the solution of GeCl<sub>2</sub>.dioxane (0.68 g, 2.94 mmol) in THF (15 mL) pre-cooled to -78°C to give pale-yellow solution. The reaction mixture was left to warm up to room temperature and stirred overnight. Then, all volatiles were removed under reduced pressure, the residue was suspended in hexane (40 mL), and the insoluble material was filtered off. The filtrate was evaporated and the residue was extracted with hexane (30 mL) once again. The hexane filtrate was concentrated and cooled to  $-30^{\circ}$ C to afford colorless crystals of 2. Yield: 0.44 g (39%). For **2**: M.p. 99–103 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta = 0.55$  (t, 3 H, CH<sub>3</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 7.2 Hz), 0.95 (t, 3 H,  $CH_3(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8 Hz$ , 1.40 (s, 9H, C(CH<sub>3</sub>)), 1.68 (s, 9H, C(CH<sub>3</sub>)), 2.15 (m, 1 H, CH<sub>2</sub>(Et),  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2$  Hz), 2.32 (m, 1 H, CH<sub>2</sub>(Et),  ${}^{3}J({}^{1}H,$  $^{1}$ H) = 7.2 Hz), 2.63 (m, 1 H, CH<sub>2</sub>(Et),  $^{3}$ J( $^{1}$ H,  $^{1}$ H) = 7.2 Hz), 3.23 (m, 1 H,  $CH_2(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2 Hz)$ , 3.35 and 4.35 (AX system, 2H,  $CH_2N$ ), 7.03 (s, 1 H, ArH), 7.50 ppm (s, 1 H, ArH);  $^{13}{\rm C}~{\rm NMR}~({\rm C_6D_6},$ 

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100.61 MHz):  $\delta$  = 7.2, 10.3 (CH<sub>3</sub>(Et)), 31.6 (C(CH<sub>3</sub>)), 33.7 (C(CH<sub>3</sub>)), 34.8 (C(CH<sub>3</sub>)), 37.7 (C(CH<sub>3</sub>)), 42.0, 46.2 (CH<sub>2</sub>(Et)), 61.9 (CH<sub>2</sub>N), 118.4, 121.1, 144.3, 150.9, 154.3, 156.6 ppm (Ar-C); elemental analysis calcd (%) for C<sub>19</sub>H<sub>32</sub>ClNGe (382.56): C 59.7, H, 8.4; found: C 59.9, H 8.5.

L<sup>4</sup>SnCl (3): A hexane solution of *n*BuLi (1.66 mL of 1.6 м) was added to a stirred solution of L<sup>4</sup>Br (1.01 g, 2.21 mmol) in THF (20 mL) at  $-78\,^\circ\text{C}$ . The mixture was allowed to warm up to  $-40\,^\circ\text{C}$ and stirred for 1 h at this temperature. After that the resulting redorange solution of L<sup>4</sup>Li was cooled to  $-78\,^\circ\text{C}$  and added dropwise to the solution of  $SnCl_2$  (0.42 g, 2.21 mmol) in THF (15 mL) precooled to -78°C to give orange solution. The reaction mixture was left to warm up to room temperature and stirred 1 h. Then, all volatiles were removed under reduced pressure, the residue was suspended in toluene (40 mL), and the insoluble material was filtered off. The toluene filtrate was evaporated and the solid was washed with hexane to afford yellow powder material characterized as **3**. Yield: 1.05 g (89%). M.p. 182–185°C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta = 1.08$  (d, 3 H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 8.0 Hz), 1.15 (d, 3 H,  $CH_{3}$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.0 Hz$ ), 1.30 (d, 3 H,  $CH_{3}$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.0 Hz$ ), 1.38 (s, 9H, C(CH<sub>3</sub>)), 1.54 (d, 3H, CH<sub>3</sub>,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.0$  Hz), 1.64 (s, 9H, C(CH<sub>3</sub>)), 3.15 (sept, 1 H, CH, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 8.0 Hz), 3.76 (sept, 1 H, CH,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.0 \text{ Hz}$ ), 7.18 (t, 1 H, ArH,  ${}^{3}J({}^{1}H, {}^{1}H) = 4.0 \text{ Hz}$ ), 7.30 (d, 1 H, ArH,  ${}^{3}J({}^{1}H, {}^{1}H) = 4.0$  Hz), 7.57 (s, 1 H, ArH), 7.93 (s, 1 H, ArH), 8.27 ppm (s, 1 H, CH=N);  $^{13}$ C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta$  = 23.9, 24.5, 24.6, 25.9 ((CH<sub>3</sub>)<sub>2</sub>CH), 28.3, 29.6 ((CH<sub>3</sub>)<sub>2</sub>CH), 31.1 (C(CH<sub>3</sub>)<sub>3</sub>), 33.4 (C(CH<sub>3</sub>)<sub>3</sub>), 34.6 (C(CH<sub>3</sub>)<sub>3</sub>), 38.4 (C(CH<sub>3</sub>)<sub>3</sub>), 123.6, 125.0, 128.5, 129.5, 140.8, 142.4, 142.8, 143.2, 151.0, 159.8 (Ar-C), 177.5 ppm (CH=N);  $^{\rm 119} {\rm Sn}$  NMR (C\_6D\_6, 149.23 MHz):  $\delta\,{=}\,154.7$  ppm; elemental analysis calcd (%) for  $C_{\rm 27}H_{\rm 38}CISnN$  (530.76): C 61.1, H 7.2; found: C 61.3, H 7.4.

L<sup>4</sup>GeCl (4): A hexane solution of *n*BuLi (1.59 mL of 1.6 м) was added to a stirred solution of L4Br (0.97 g, 2.12 mmol) in THF (20 mL) at -78 °C. The mixture was allowed to warm up to -40 °C and stirred for 1 h at this temperature. After that the resulting redorange solution of L<sup>4</sup>Li was cooled to -78 °C and added dropwise to the solution of  $\text{GeCl}_2$ -dioxane (0.49 g, 2.12 mmol) in THF (15 mL) pre-cooled to -78°C to give orange solution. The reaction mixture was left to warm up to room temperature and stirred 1 h. Then, all volatiles were removed under reduced pressure, the residue was suspended in hexane (30 mL) and the insoluble material was filtered off. The hexane filtrate was concentrated and cooled to -30°C to afford orange crystals of 4. Yield: 0.65 g (63%). M.p. 169–173 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta = 0.94$  (d, 3 H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H,  $^{1}$ H) = 7.0 Hz), 0.98 (d, 3 H, CH<sub>3</sub>,  $^{3}$ J( $^{1}$ H,  $^{1}$ H) = 8.0 Hz), 1.21 (d, 3 H, CH<sub>3</sub>,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.0 \text{ Hz}$ , 1.23 (s, 9H, C(CH<sub>3</sub>)), 1.33 (d, 3H, CH<sub>3</sub>,  ${}^{3}J({}^{1}H, {}^{1}H) =$ 8.0 Hz), 1.57 (s, 9 H, C(CH<sub>3</sub>)), 3.15 (sept, 1 H, CH, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 7.0 Hz), 3.44 (sept, 1 H, CH,  ${}^{3}J({}^{1}H, {}^{1}H) = 8.0$  Hz), 7.03 (t, 1 H, ArH,  ${}^{3}J({}^{1}H, {}^{1}H) =$ 5.0 Hz), 7.14 (d, 1 H, ArH, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 5.0 Hz), 7.44 (s, 1 H, ArH), 7.74 (s, 1H, ArH), 7.95 ppm (s, 1H, CH=N); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta = 24.6, 24.7, 25.2, 26.5$  ((CH<sub>3</sub>)<sub>2</sub>CH), 28.8, 30.0 ((CH<sub>3</sub>)<sub>2</sub>CH), 31.6 (C(CH<sub>3</sub>)<sub>3</sub>), 33.5 (C(CH<sub>3</sub>)<sub>3</sub>), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 38.9 (C(CH<sub>3</sub>)<sub>3</sub>), 124.2, 125.3, 127.1, 129.5, 141.1, 142.2, 143.9, 152.0, 158.3, 166.6 (Ar-C), 173.7 ppm (CH=N); elemental analysis calcd (%) for C<sub>27</sub>H<sub>38</sub>ClGeN (484.69): C 66.9, H, 7.9; found: C 66.6, H 7.8.

L<sup>3</sup>SnSnL<sup>3</sup> (5): A THF solution of K[(Et)<sub>3</sub>BH] (2.26 mL, 1 M) was added dropwise to a stirred solution of 1 (0.97 g, 2.26 mmol) in THF (20 mL) at room temperature and the color of the solution changed from pale yellow to dark red. The reaction mixture was stirred for 2 h and then all volatiles were removed under reduced pressure. The residue was suspended in toluene (20 mL) and the insoluble material was filtered off. The toluene filtrate was evaporated and washed with small amount of cold hexane to afford red powder material characterized as **5**. Yield: 0.55 g (62%). M.p. 182–

185 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta$ =0.55 (t, 6 H, CH<sub>3</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H)=7.2 Hz), 1.00 (t, 6 H, CH<sub>3</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H)=7.2 Hz), 1.15 (s, 18 H, C(CH<sub>3</sub>)), 1.41 (s, 18 H, C(CH<sub>3</sub>)), 2.66 (m, 2 H, CH<sub>2</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H)=7.2 Hz), 3.19 (m, 2 H, CH<sub>2</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H)=7.2 Hz), 3.19 (m, 2 H, CH<sub>2</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H)=7.2 Hz), 3.76 (m, 2 H, CH<sub>2</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H)=7.2 Hz), 3.83 and 4.15 (AX system, 4 H, CH<sub>2</sub>N), 7.09 (s, 2 H, ArH), 7.42 ppm (s, 2 H, ArH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta$ =9.2, 12.5 (CH<sub>3</sub>(Et)), 32.2 (C(CH<sub>3</sub>)), 32.3 (C(CH<sub>3</sub>)), 35.0 (C(CH<sub>3</sub>)), 37.7 (C(CH<sub>3</sub>)), 46.6, 48.2 (CH<sub>2</sub>(Et)), 67.5 (CH<sub>2</sub>N), 119.4, 121.3, 143.3, 147.6, 158.0, 166.7 ppm (Ar-*C*); <sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 149.23 MHz):  $\delta$ =688.4 ppm; elemental analysis calcd (%) for C<sub>38</sub>H<sub>64</sub>N<sub>2</sub>Sn<sub>2</sub> (786.33): C 58.1, H 8.2; found: C 58.4, H 8.5.

L<sup>3</sup>GeGeL<sup>3</sup> (6): A solution of 2 (0.44 g, 1.14 mmol) in THF (15 mL) was added to freshly prepared  $\mathrm{KC}_{\mathrm{8}}$  (0.17 g, 1.25 mmol) at room temperature and the color of the solution immediately changed from pale yellow to dark-red/orange. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure and the residue was extracted with hexane (30 mL). The hexane filtrate was concentrated and cooled to  $-30\,^\circ\text{C}$  to afford orange crystals of 6. Yield: 0.19 g (48%). M.p. 128–131  $^\circ\text{C}.$   $^1\text{H}$  NMR  $(C_6D_6, 400.13 \text{ MHz}): \delta = 0.79 \text{ (t, 6H, CH}_3(\text{Et}), {}^3J({}^1\text{H}, {}^1\text{H}) = 7.2 \text{ Hz}), 0.91$ (t, 6H, CH<sub>3</sub>(Et),  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2$  Hz), 1.18 (s, 18H, C(CH<sub>3</sub>)), 1.40 (s, 18 H, C(CH<sub>3</sub>)), 2.44 (m, 2 H, CH<sub>2</sub>(Et),  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2$  Hz), 2.81 (m, 2 H,  $CH_2(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2 Hz)$ , 3.54 (m, 2 H,  $CH_2(Et)$ ,  ${}^{3}J({}^{1}H, {}^{1}H) = 7.2 Hz)$ , 3.69 (m, 2 H, CH<sub>2</sub>(Et), <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 7.2 Hz), 3.46 and 4.46 (AX system, 4H, CH<sub>2</sub>N), 7.00 (s, 2H, ArH), 7.35 ppm (s, 2H, ArH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta = 9.9$ , 10.1 (CH<sub>3</sub>(Et)), 32.1 (C(CH<sub>3</sub>)), 32.8 (C(CH<sub>3</sub>)), 34.9 (C(CH<sub>3</sub>)), 37.8 (C(CH<sub>3</sub>)), 46.7, 46.9 (CH<sub>2</sub>(Et)), 65.9 (CH<sub>2</sub>N), 118.3, 121.6, 141.2, 146.9, 154.8, 160.4 ppm (Ar-C); elemental analysis calcd (%) for C38H64N2Ge2 (694.16): C 65.8, H 9.3; found: C 66.0, H 9.4

L<sup>4</sup>SnSnL<sup>4</sup> (7): A solution of 3 (0.62 g, 1.17 mmol) in THF (15 mL) was added to freshly prepared  $KC_8$  (0.18 g, 1.29 mmol) at room temperature and the color of the solution immediately changed from yellow to dark-blue/green. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure and the residue was extracted with hexane (30 mL). The hexane filtrate was concentrated and cooled to 4°C to afford dark-brown crystals of **7**. Yield: 0.34 g (58%). M.p. 139–143°C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta = 0.87$  (d, 6H, CH<sub>3</sub>,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz), 0.95 (s, 18H, C(CH<sub>3</sub>)), 1.15 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 1.19 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H,  $^{1}$ H)=6.8 Hz), 1.32 (s, 18 H, C(CH<sub>3</sub>)), 1.53 (d, 6 H, CH<sub>3</sub>,  $^{3}$ J( $^{1}$ H,  $^{1}$ H)= 6.8 Hz), 3.25 (sept, 2 H, CH, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 3.47 (sept, 2 H, CH,  ${}^{3}J({}^{1}H, {}^{1}H) = 6.8$  Hz), 7.06 (d, 4H, ArH,  ${}^{3}J({}^{1}H, {}^{1}H) = 5.0$  Hz), 7.16 (t, 2H, ArH,  ${}^{3}J({}^{1}H, {}^{1}H) = 5.0$  Hz), 7.34 (s, 2 H, ArH), 7.69 (s, 2 H, ArH), 8.29 ppm (s, 2 H, CH=N); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta$  = 24.0, 24.7, 25.0, 26.4 ((CH<sub>3</sub>)<sub>2</sub>CH), 28.4, 28.5 ((CH<sub>3</sub>)<sub>2</sub>CH), 31.1 (C(CH<sub>3</sub>)<sub>3</sub>), 31.2  $(C(CH_3)_3)$ , 34.1  $(C(CH_3)_3)$ , 36.8  $(C(CH_3)_3)$ , 123.7, 123.9, 124.6, 128.3, 141.4, 142.5, 145.0, 147.1, 158.7, 168.2 (Ar-C), 184.6 ppm (CH=N);  $^{\rm 119}{\rm Sn}$  NMR (C<sub>6</sub>D<sub>6</sub>, 149.23 MHz):  $\delta\!=\!264.1;$  elemental analysis calcd (%) for C<sub>54</sub>H<sub>76</sub>Sn<sub>2</sub>N<sub>2</sub> (990.60): C 65.5, H 7.7; found: C 65.6, H 7.8.

**L<sup>4</sup>GeGeL<sup>4</sup>** (8): A solution of **4** (0.21 g, 0.43 mmol) in toluene (30 mL) was added to freshly deposited potassium mirror (18 mg, 0.47 mmol) at -78 °C. The reaction mixture was allowed to warm up to room temperature and stirred 5 days. During this time the color of the mixture changed from orange to dark blue and potassium was consumed. The resulting suspension was filtered and toluene filtrate was concentrated and cooled to 4 °C to afford darkblue crystals of **8**. Yield: 60 mg (31%). M.p. 127–130 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.13 MHz):  $\delta$  = 0.90 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 0.97 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 1.10 (s, 18H, C(CH<sub>3</sub>)), 1.22 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 1.34 (s, 18H, C(CH<sub>3</sub>)), 1.52 (d, 6H, CH<sub>3</sub>, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 3.23 (sept, 2H, CH, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 3.37 (sept, 2H, CH, <sup>3</sup>J(<sup>1</sup>H, <sup>1</sup>H) = 6.8 Hz), 7.10–7.15 (m, 6H, ArH), 7.41 (s, 2H, ArH),

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7.72 (s, 2H, ArH), 8.24 ppm (s, 2H, CH=N); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.61 MHz):  $\delta$  = 23.5, 25.0, 25.1, 26.8 ((CH<sub>3</sub>)<sub>2</sub>CH), 28.1, 28.6 ((CH<sub>3</sub>)<sub>2</sub>CH), 31.1 (C(CH<sub>3</sub>)<sub>3</sub>), 31.8 (C(CH<sub>3</sub>)<sub>3</sub>), 34.3 (C(CH<sub>3</sub>)<sub>3</sub>), 36.8 (C(CH<sub>3</sub>)<sub>3</sub>), 123.2, 123.6, 125.3, 127.1, 139.0, 142.4, 143.3, 146.9, 155.5, 159.6 (Ar-C), 174.8 ppm (CH=N); elemental analysis calcd (%) for C<sub>54</sub>H<sub>76</sub>Ge<sub>2</sub>N<sub>2</sub> (898.48): C 72.2, H 8.5; found: C 72.0, H 8.4.

L<sup>5</sup>SnCl (9): A hexane solution of *n*BuLi (0.84 mL of 1.6 м) was added to a stirred solution of L<sup>5</sup>Br (0.56 g, 1.34 mmol) in Et<sub>2</sub>O (30 mL) at -70 °C and stirred for 3 h. The Et<sub>2</sub>O was filtrated and remaining solid was dissolved in toluene and the resulting solution of L<sup>5</sup>Li was added dropwise to the toluene suspension of SnCl<sub>2</sub> (0.26 g, 1.34 mmol) at  $-70\,^\circ\text{C}.$  The reaction mixture was left to warm up to room temperature and stirred for 24 h. Then all volatiles were removed under reduced pressure, the residue was suspended in toluene/hexane (40 mL) and insoluble material was filtered off. The filtrate was concentrated and cooled to  $-30\,^\circ\text{C}$  to afford orange powder of 9. Yield: 0.51 g (77%). M.p. 168.1-171.3 °C. <sup>1</sup>H NMR (500.18 MHz,  $C_6D_6$ , 25 °C):  $\delta = 2.43$  (s, 12 H, NCH<sub>3</sub>), 7.20-7.48 (m, 9H, ArH), 7.93 ppm (s, 2H, N=CH); <sup>13</sup>C NMR (125.77 MHz,  $C_6D_6$ , 25 °C):  $\delta$  = 18.8 (CH<sub>3</sub>), 125.3, 128.2, 128.8, 128.9, 133.0, 142.2, 148.4, 169.1, 179.7 ppm; <sup>119</sup>Sn NMR (186,49 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 25.5$  ppm; elemental analysis calcd (%) for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>ClSn (493.6): C 58.4, H 4.7; found: C 58.6, H 4.9.

L<sup>5</sup>SnSnL<sup>5</sup> (10): A solution of **9** (0.51 g, 1.03 mmol) in THF (15 mL) was added to freshly prepared KC<sub>8</sub> (0.15 g, 1.11 mmol) at room temperature and the color of the solution immediately changed from orange to dark green. The reaction mixture was stirred for 4 h. The solvent was removed under reduced pressure and the residue was extracted with hexane (30 mL). The hexane filtrate was concentrated let to crystallize to afford black crystals of **10**. Yield: 0.27 g (57%). M.p. 118 °C with decomp.; <sup>1</sup>H NMR (500.18 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 2.44 (s, 24 H, NCH<sub>3</sub>), 7.22–7.44 (m, 18 H, ArH), 7.92 ppm (s, 4H, N=CH); <sup>119</sup>Sn NMR (186.49 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 118.0 ppm.

#### **Computational details**

The calculations were performed with Gaussian  $09^{[16]}$  by using the hybrid functional M06–2X<sup>[17]</sup> with the Ahlrichs def2-TZVP basis set,<sup>[18]</sup> which includes an effective core potential on tin. Tight conversion criteria were applied. Both stationary points were characterized by frequency analysis and show the correct number of negative eigenvalues (zero for a local minimum). Based on the geometry obtained by the M06–2X/def2-TZVP method, a NBO analysis was performed by using this method with NBO 6.0.<sup>[19]</sup> The Wiberg indices were used as implemented in Gaussian 09.

#### Crystallography

The X-ray data (Table S1, see the Supporting Information) for colorless (1 and 2), orange (5 and 6), dark brown (7), and black crystals (10) were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius Kappa CCD diffractometer with Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å), a graphite monochromator, and the  $\phi$  and  $\chi$  scan mode. All attempts to get crystal structure of deep-blue crystals of 8 provided structures with strongly disordered central germanium atoms only and were not useful for further discussion. Data reductions were performed with DENZO-SMN.<sup>[20]</sup> The absorption was corrected by integration methods.<sup>[21]</sup> Structures were solved by direct methods (Sir92)<sup>[22]</sup> and refined by full matrix leastsquare based on  $F^2$  (SHELXL97).<sup>[23]</sup> Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors  $H_{iso}(H) = 1.2 U_{eq}$  (pivot atom) or of 1.5  $U_{eq}$  for the methyl moiety with C-H = 0.98, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings, respectively. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC-1037996 (1), CCDC-1037997 (5), CCDC-1037998 (6), CCDC-1037999 (2), CCDC-1038000 (10), and 1038001 (7) contain the supplementary crystallographic data for this paper. 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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