# **ORGANOMETALLICS**

# Synthesis and Characterization of Rigid Ditopic N-Heterocyclic Benzobisgermylenes and -stannylenes

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**Supporting Information** 

**ABSTRACT:** A rigid ditopic benzobisgermylene, **4a**, was prepared by the reaction of the 1,2,4,5-tetra(alkylamine)benzene **3a** and Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. The analogous reaction of two 1,2,4,5-tetra-(alkylamine)benzenes, **3b**,c, with Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> led to the oxidation of the tetramine ligand and formation of *N*-alkyl-2-(alkylamine)-*N'*-alkyl-5-(alkylamine)-1,4-benzoquinonediimines (**5b**,c) and tin(0). The *p*-benzoquinonediimines **5b**,c subsequently react with remaining Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to yield distantylene complexes of type [*N*-alkyl-2-(alkylamino)-*N'*-alkyl-5-(alkylamino)-1,4-benzoquinonediimine]di[bis-(trimethylsilyl)aminotin(II)] (**6b**,c). The 2,5-di(alkylamine)-1,4-benzoquinonediimines **5b**,c can also be obtained directly by aerial oxidation of the 1,2,4,5-tetrakis(alkylamine)benzenes **3b**,c. They react with two equivalents of Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> also under transmetalation



and formation of [N-alkyl-2-(alkylamino)-N'-alkyl-5-(alkylamino)-1,4-benzoquinonediimine]di[bis(trimethylsilyl)aminotin(II)] (**6b,c**). The molecular structures of **3b**, **4a**, **6b**, and **6c** have been established by X-ray diffraction.

# 1. INTRODUCTION

Germylenes  $(R_2Ge:)^{1a,b}$  and stannylenes  $(R_2Sn:)^{1a,c}$  are divalent species of germanium and tin, which in spite of some differences in their electronic properties and reactivity can be considered as the heavier analogues of carbenes.<sup>1</sup> Particularly N-heterocyclic carbenes have been studied in detail since the first stable derivative of this type was isolated by Arduengo in 1991.<sup>2</sup> Various applications for these compounds as spectator ligands in organometallic chemistry and catalysis,<sup>3</sup> material science,<sup>4</sup> biologically relevant complexes,<sup>5</sup> and most recently even metallosupramolecular chemistry<sup>6</sup> have been reported. Stable N-heterocyclic germylenes and stannylenes<sup>1f,g,7</sup> received less attention, although the first derivatives of this type were known some years before the first N-heterocyclic carbenes had been isolated.

The first representative of an N-heterocyclic germylene  $(A1)^8$  was prepared in 1982 by Veith et al. (Figure 1). Its heavier analogue, the stannylene A2 was also prepared by Veith et al. in 1975.<sup>9</sup> Both compounds have been known more than 10 years before the first stable N-heterocyclic carbene (B1) was described. Shortly after the preparation of the Arduengo-carbene B1,<sup>2</sup> the analogous germanium(II) compound (B2) was synthesized and characterized by Herrmann et al.<sup>10</sup> The synthesis of the corresponding stannylene (B3) has also been reported.<sup>11</sup>

The isolation and complete characterization of the first benzannulated germylene of type **C2** was reported in 1989,<sup>12</sup> 10 years before the synthesis of benzannulated carbene **C1**.<sup>13</sup> Stannylenes of type **C3** were first prepared and completely characterized in 1994.<sup>14</sup> Today, various types of benzannulated



Figure 1. N-Heterocyclic carbenes, germylenes, and stannylenes.

N-heterocyclic germylenes<sup>1,7,15</sup> and stannylenes<sup>1,7,16</sup> including some chiral derivatives<sup>16c</sup> are known.

A number of polydentate germylenes and stannylenes have been described.<sup>17</sup> We prepared bidentate bisgermylenes<sup>18</sup> and bisstannylenes<sup>19</sup> of type **D**, which are capable of forming chelate complexes **E** with selected transition metals. In analogy to the known rigid dicarbene ligands of type **F1** (Figure 2),<sup>4,20</sup> we have now studied the preparation of rigid ditopic digermylenes (**F2**) and distannylenes (**F3**). Like the dicarbenes **F1**,<sup>6e-g</sup> the rigid ditopic digermylenes and distannylenes are

Received: January 25, 2012 Published: February 29, 2012 potential building blocks for tetranuclear molecular squares and additional metallosupramolecular structures.



Figure 2. Linear rigid dicarbenes and their heavier analogues.

#### 2. RESULTS AND DISCUSSION

Benzannulated N-heterocyclic germylenes and stannylenes are conveniently obtained by transamination of suitable N,N'dialkylated *o*-phenylenediamines with  $M[N(SiMe_3)_2]_2$  (M = Ge, Sn).<sup>18,19</sup> The same protocol can be applied for the synthesis of benzobisgermylenes and benzobisstannylenes of types F2 and F3 provided suitable 1,2,3,4-tetra(alkylamine)benzenes are available. We have prepared the asymmetrically substituted 1,2,3,4-tetra(alkylamine)benzene 3a (Scheme 1) by

Scheme 1. Synthesis of the Asymmetrical 1,2,3,4-Tetra(alkylamine)benzene 3a



reaction of the known compound  $1^{21}$  with acetyl chloride to give the 1,2,3,4-tetraamidobenzene 2. Subsequent reduction of the amido groups with AlH<sub>3</sub> (generated *in situ*<sup>18a</sup>) gave 3a in good yield.

The symmetrically substituted 1,2,4,5-tetra(alkylamine)benzenes  $3b,c^{20,22}$  (Scheme 2) were prepared following described procedures. As previously noticed,<sup>22</sup> the tetra-(alkylamine)benzenes 3a-c are very sensitive toward oxidation, and exposure of them to aerial oxygen leads to the formation of *N*-alkyl-2-(alkylamine)-*N*'-alkyl-5-(alkylamine)-1,4-benzoquinonediimines. We have, however, isolated 1,2,4,5-tetra(neopentylamine)benzene **3b** and crystallized the compound at ambient temperature from a toluene solution.

The X-ray diffraction analysis confirms the formation of the tetramine **3b** (Figure 3). Bond parameters of **3b** fall in the expected range. The aromatic ring is undisturbed, with C–C bond lengths in the range 1.391(2)-1.405(2) Å.

Scheme 2. Transamination Reactions of the 1,2,3,4-Tetra(alkylamine)benzenes 3a-c with  $Ge[N(SiMe_3)_2]_2$  and  $Sn[N(SiMe_3)_2]_2$ 



Figure 3. Molecular structure of 3b (50% displacement ellipsoids, hydrogen atoms have been omitted, the molecule resides on a crystallographic inversion center). Selected bond lengths (Å) and angles (deg): N1-C3 1.406(2), N1-C4 1.449(2), N2-C1 1.419(2), N2-C9 1.449(2), C1-C2 1.391(2), C1-C3\* 1.405(2), C2-C3 1.400(2); C3-N1-C4 119.99(14), C1-N2-C9 121.21(14).

The 1,2,3,4-tetra(alkylamine)benzene **3a** was reacted with Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>23</sup> to yield via transmetalation the rigid ditopic benzobisgermylene **4a**, featuring two differently substituted N-heterocyclic diaminogermylene subunits (Scheme 2). Benzobisgermylene **4a** was isolated as a yellow air-sensitive solid that is soluble in THF, benzene, and toluene but almost insoluble in aliphatic hydrocarbons such as *n*-hexane.

The benzobisgermylene **4a** was characterized by NMR spectroscopy and mass spectrometry. The <sup>1</sup>H NMR spectrum shows the resonances for the aromatic protons at  $\delta$  6.86 ppm and for the methylene protons of the N-substituents at  $\delta$  3.84–4.08 ppm. Compared to the free tetramine ( $\delta$  6.45 ppm and 2.89–3.01 ppm), equivalent resonances are shifted downfield in the benzobisgermylene, reflecting a decrease of the electron density in the organic scaffold upon formation of the germanium(II) compound.

Compound 4a was crystallized from a THF/*n*-hexane solution at -18 °C. The X-ray diffraction structure analysis confirmed the formation of the benzobisgermylene (Figure 4, top). The two diaminogermylene subunits feature essentially



Figure 4. Molecular structure of 4a (top, 50% displacement ellipsoids) and plot of the intermolecular interaction between the benzobisgermylenes (bottom). Selected bond lengths (Å) and angles (deg): Ge1– N1 1.862(3), Ge1–N2 1.877(3), Ge2–N3 1.856(3), Ge2–N4 1.865(3), N1–C1 1.393(4), N1–C7 1.450(4), N2–C2 1.386(4), N2–C9 1.454(4), N3–C5 1.391(4), N3–C11 1.471(4), N4–C4 1.393(4), N4–C16 1.456(4); N1–Ge1–N2 84.41(11), N3–Ge2–N4 84.77(11).

identical metric parameters in spite of the differences in the N-substituents. The Ge–N and N–C bond distances as well as the N–Ge–N bond angles fall in the range previously reported for benzannulated N-heterocyclic germylenes.<sup>12a,18</sup> The five-membered heterocycles are planar, with each containing two trigonal-planar nitrogen atoms (range for the sum of angles at the nitrogen atoms N1–N4 359.8–360.0°).

In the solid state the benzobisgermylene **4a** forms infinite polymeric chains via interactions of the germanium atoms of one molecule with the aromatic rings of neighboring molecules (Figure 4, bottom). The shortest intermolecular Ge…C distances measure 3.441–3.663 Å. Similar interactions have been observed in the solid-state structures of related benzannulated N-heterocyclic germylenes, confirming the electrophilic nature of the empty p-orbital at the germylene germanium atom.<sup>24</sup>

The reaction of the 1,2,3,4-tetra(alkylamine)benzenes **3b**,c with Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>23a</sup> yielded unexpected results (Scheme 2). Instead of the expected benzobisstannylenes analogous to **4a**, the noncyclic diimine-stabilized distannylenes **6b**,c featuring a *p*-benzoquinonediimine backbone and elemental tin were obtained. The distannylenes **6b**,c have been identified by NMR spectroscopy. The spectra show the characteristic resonances for the SiMe<sub>3</sub> groups, while the signal for the aromatic protons of the backbone has been replaced by resonances of the *p*-benzoquinonediimine moiety, which appear in the range  $\delta$  5.13–5.52 ppm.

The formation of **6b**,**c** was surprising since it has been shown multiple times that 1,2-di(alkylamine)benzenes react smoothly with  $Sn[N(SiMe_3)_2]_2$  to yield the benzannulated N-heterocyclic stannylenes, <sup>14,16</sup> and no oxidation of the 1,2-di(alkylamine)-benzene precursors was observed in these reactions. We attribute the different reactivity of the 1,2,4,5-tetra(alkyamine)benzenes **3b**,**c** to the possibility of two one-electron oxidations proceeding at each of the two *o*-phenylenediamine sites of the tetramine

molecules, leaving one secondary amine at each side of the molecule unchanged for the subsequent reaction with Sn[N- $(SiMe_3)_2]_2$ . The reasons for this partial oxidation of 1,2,3,4-tetra(alkylamine)benzenes to *p*-benzoquinonediimines have been discussed on the basis of DFT calculations.<sup>22</sup> A two-electron oxidation of 1,2-di(alkylamine)benzenes would lead to 1,2-benzoquinonediimines, which subsequently cannot undergo any transamination reaction with Sn[N(SiMe\_3)\_2]\_2.

To test this hypothesis, we have carried out the aerial oxidation of the 1,2,3,4-tetra(alkylamine)benzenes **3b**,**c** in THF and obtained the expected *N*-alkyl-2-(alkylamino)-*N*'-alkyl-5-(alkylamino)-1,4-benzoquinonediimines **5b**,**c** as yellow, air-stable solids in essentially quantitative yield (Scheme 3).

# Scheme 3. Oxidation of the 1,2,4,5-Tetra(alkylamine)benzenes 3b,c with Aerial Oxygen and Subsequent Transamination with $Sn[N(SiMe_3)_2]_2$



The oxidation of 1,2,3,4-tetra(alkylamine)benzenes with loss of the aromatic character in favor of the 1,4-quinoid structure has been reported previously.<sup>21</sup>

Reaction of the compounds **5b**,**c** with Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> proceeds under mono-transamination at each side of the molecule and formation of the distannylenes **6b**,**c** in yields of 67% and 57%, respectively. The <sup>1</sup>H NMR spectra of the distannylenes **6b**,**c** feature a characteristic resonance for the quinoid CH group<sup>21</sup> at  $\delta$  5.52 ppm (**5b**) and  $\delta$  5.14 ppm (**5c**) and at around  $\delta$  0 ppm for the SiMe<sub>3</sub> groups. The <sup>29</sup>Si{<sup>1</sup>H}, the <sup>119</sup>Sn{<sup>1</sup>H}, and in part the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra exhibit a doubling of all signals (for example <sup>119</sup>Sn{<sup>1</sup>H} NMR:  $\delta$ -21.8, -33.0 ppm for **6b**;  $\delta$  -31.0, -42.4 ppm for **6c**). We assume that two isomers (*syn* and *anti*, Scheme 3) exist in solution. At ambient temperature, these isomers do not interconvert due to the steric crowding at the tin atoms.

Red to purple crystals of the air-sensitive *anti* isomers of **6b** and **6c** were obtained from THF solutions of the compounds after slow evaporation of the solvent over one week at ambient temperature. Both distannylenes (Figure 5) feature an essentially planar structure. The Sn–N bond lengths within the heterocycles of **6b**,**c** differ only marginally and fall in the range



Figure 5. Molecular structures of 6b (top, 50% displacement ellipsoids) and 6c (bottom, 50% displacement ellipsoids). Both molecules reside on crystallographic inversion centers located at the midpoint of the *p*-benzochinonediimine ring. Selected bond lengths (Å) and angles (deg) for 6b [6c]: Sn–N1 2.2056(14) [2.206(2)], Sn–N2 2.1917(13) [2.170(2)], Sn–N3 2.1340(14) [2.124(2)], Si1–N3 1.7315(15) [1.730(2)], Si2–N3 2.7370(14) [1.734(2)], N1–C3 1.321(2) [1.328(2)], N1–C4/C8 1.469(2) [1.471(3)], N2–C2 1.329(2) [1.325(2)], N2–C9/C4 1.466(2) [1.468(3)], C1–C2 1.397(2) [1.401(3)], C2–C3 1.507(2) [1.491(3)], C3–C1\* 1.394(2) [1.397(3)]; N1–Sn–N2 73.96(5) [74.35(6)], N1–Sn–N3 92.06(5) [104.58(7)], N2–Sn–N3 102.88(5) [93.44(7)], sum of angles at nitrogen atoms 358.12–359.92°.

previously found for benzannulated N-heterocyclic stannylenes.<sup>16</sup> This observation indicates electron delocalization within the fivemembered stannylene heterocycles. The quinone structure of the central six-membered ring manifests itself with short C1\*–C3 and C1–C2 bond lengths (range 1.394(2)–1.401(3) Å) and elongated C2–C3 bonds (range 1.491(3)–1.507(2) Å). These features are consistent with experimental data and DFT calculations on the free [*N*-neopentyl-2-(neopentylamino)-*N*'-neopentyl-5-(neopentylamino)-1,4-benzoquinonediimine (**5b**) which had been previously characterized by X-ray crystallography.<sup>22</sup>

# 3. CONCLUSIONS

We have prepared symmetrically and unsymmetrically substituted 1,2,3,4-tetra(alkylamine)benzenes. The unsymmetrically tetramine **3a** reacts with Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> to yield the ditopic digermylene **4a** featuring two differently N,N'-substituted N-heterocyclic germylene moieties. Reaction of the symmetrically substituted tetramines **3b,c** with Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> did not yield the expected distannylene but elemental tin and distannylenes **6b,c**, featuring an N-alkyl-2-(alkylamino)-N'-alkyl-5-(alkylamino)-1,4-benzoquinonediimine backbone and an additional N(SiMe<sub>3</sub>)<sub>2</sub> ligand per tin(II) center. The reasons for the differences in the reactivity of the 1,2,3,4-tetra(alkylamine)benzenes with the Ge<sup>II</sup> and Sn<sup>II</sup> precursors and particularly for the facile oxidation of the tetramines **3b,c** yields the free N-alkyl-2-(alkylamino)-N'alkyl-5-(alkylamino)-1,4-benzoquinonediimes, which react with  $Sn[N(SiMe_3)_2]_2$  to yield the stannylenes **6b,c**. Like its lighter benzobiscarbene analogues,<sup>6</sup> benzobisgermylene **4a** is a potential building block for larger metallosupramolecular structures.

# 4. EXPERIMENTAL SECTION

General Procedures. If not noted otherwise, all reactions were carried out under an argon atmosphere using conventional Schlenk techniques or in a glovebox. Solvents were dried and freshly distilled by standard procedures prior to use. NMR spectra were recorded on Bruker AC 200, Bruker AVANCE I 400, or Bruker AVANCE III 400 spectrometers. Chemical shifts ( $\delta$ ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent (<sup>1</sup>H NMR), Me<sub>4</sub>Si (<sup>29</sup>Si NMR), or Me<sub>4</sub>Sn as an internal standard. EI mass spectra were obtained with a Finnigan MAT 95 spectrometer. Di[bis-(trimethylsilyl)amino]tin(II), di[bis(trimethylsilyl)amino]germanium-(II),<sup>23</sup> and compound  $1^{21}$  were prepared by published procedures. Compound 3b.2HCl, but not the free tetramine 3b, was previously isolated.<sup>22</sup> We prepared **3b**,c by AlH<sub>3</sub> reduction of the corresponding tetramides in analogy with the procedure used for the synthesis of 3a. The tetramines (related compounds are used as oxygen sensors) as well as the germylens and stannylenes are highly sensitive toward oxygen. Satisfactory microanalytical data could not be obtained. Instead, MS data are given in the Experimental Section, and detailed NMR spectra have been deposited as Supporting Information.



**1,2-Bis(2,2-dimethylpropanamido)-4,5-di(ethylamido)benzene (2).** Compound  $1^{21}$  (0.75 g, 2.5 mmol) was dissolved in THF (50 mL) at 0 °C under an argon atmosphere. To this solution was added dropwise under an argon atmosphere 0.7 g (8.9 mmol) of acetyl chloride. The reaction mixture was stirred for 3 d at ambient temperature. Over the reaction time the tetramide **2** precipitated from the solution. It was isolated by filtration and recrystallized from methanol. Yield: 0.81 g (2.07 mmol, 85%) of colorless crystals. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$  9.34 (s, br, 2H, H8), 9.02 (s, br, 2H, H4), 7.64 (s, 2H, H6), 2.06 (s, 6H, H10), 1.21 ppm (s, 18H, H1). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, [D<sub>6</sub>]DMSO):  $\delta$  176.7 (C9), 168.6 (C3), 127.7 (C7), 127.5 (C5), 121.1 (C6), 39.4 (C2), 27.2 (C10), 23.6 ppm (C1). MS (EI): *m/z* (%) = 390 (100) [M]<sup>+</sup>. C<sub>20</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>, M = 390.48.



1,2-Di(ethylamine)-4,5-di(neopentylamine)benzene (3a). Concentrated sulfuric acid (0.82 mL, 15.4 mmol) was cautiously and dropwise added at 0 °C to a suspension of 1.17 g (30.8 mmol) of lithium aluminum hydride in 100 mL of argon-saturated THF. After the initial development of hydrogen gas ceased the resulting white suspension was stirred for 1 h at ambient temperature. Subsequently, 0.4 g (1.02 mmol) of tetramide 2 was slowly added. The resulting orange suspension was stirred for 3 d at ambient temperature. Excess lithium aluminum hydrides and AlH3 was then destroyed with degassed water at 0 °C. The aqueous suspension was extracted with diethyl ether (5  $\times$  15 mL). The combined ether extracts were dried over magnesium sulfate, and the solvent was removed in vacuo, leaving compound 3a as an orange solid. Yield: 0.33 g (0.98 mmol, 95%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  6.45 (s, 2H, H6), 3.16 (s, br, 4H, H4 and H8), 3.01 (s, 4H, H3), 2.89 (q,  ${}^{3}J$  = 7.0 Hz, 4H, H9), 1.09 (t,  ${}^{3}J$  = 7.0 Hz, 6H, H10), 1.01 ppm (s, 18H, H1). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,

C<sub>6</sub>D<sub>6</sub>): δ 132.6 (C7), 132.1 (C5), 103.9 (C6), 58.8 (C3), 40.4 (C9), 31.8 (C2), 28.0 (C1), 15.5 ppm (C10). MS (EI): m/z (%) = 334 (100), [M]<sup>+</sup>. C<sub>20</sub>H<sub>38</sub>N<sub>4</sub>, M = 334.55.



1,2,4,5-Tetra(neopentylamine)benzene (3b) and 1,2,4,5-Tetra(isobutylamine)benzene (3c). Compounds 3b,c were prepared as described for 3a by reduction of the corresponding tetra-mides. Selected analytic date for 3b: Yield 46%. <sup>1</sup>H NMR (400 MHz, [D<sub>8</sub>]toluene): δ 6.22 (s, 2H, H2), 3.40 (s, 4H, NH), 2.73 (s, 8H, H3), 1.01 ppm (s, 36H, H5). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, [D<sub>8</sub>]toluene): δ 137.5 (C1), 133.0 (C2), 58.9 (C3), 31.8 (C4), 28.0 ppm (C5). MS (EI): m/z (%) = 418.0 (100) [M<sup>+</sup>]. C<sub>26</sub>H<sub>50</sub>N<sub>4</sub>, M = 418.71. The tetramine 3c could not be isolated in pure form. The *p*-benzoquino-nediimine 5c obtained by oxidation of 3c, however, was fully characterized. Crystals of 3b have been obtained from a toluene solution at ambient temperature.



**1,2-Di(ethylamino)-4,5-di(neopentylamino)digermanium(II)** (**4a).** A dried Schlenk flask was charged in the glovebox with 64 mg (0.192 mmol) of tetramine **3a** and 3 mL of dry THF. To the resulting solution was added 0.159 g (0.403 mmol) of Ge[N(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub><sup>23</sup> at ambient temperature. The reaction mixture was stirred at 65 °C for 36 h. Subsequently the solvent and volatile products were removed *in vacuo*. A yellow solid was obtained, which was dissolved in THF (as little as possible), and the solution was layered with *n*-hexane. After cooling to -18 °C for 3 d red-orange crystals of the benzobisgermylene **4a** were obtained. Yield: 82 mg (0.173 mmol, 90%). <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.86 (s, 2H, H5), 4.08–3.84 (m, 8H, H3, H7), 1.49 (t, 6H, H8), 1.03 ppm (s, 18H, H1). <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  138.1 (C6), 137.1 (C4), 91.0 (C5), 57.4 (C3), 41.6 (C7), 33.3 (C2), 29.0 (C1), 18.2 ppm(C8). MS (EI): *m/z* (%) = 476 (100) [M<sup>+</sup>] (correct isotope pattern). C<sub>20</sub>H<sub>34</sub>N<sub>4</sub>Ge<sub>2</sub>, M = 475.70.



*N*-Neopentyl-2-(neopentylamino)-*N*′-neopentyl-5-(neopentylamino)-1,4-benzoquinonediimine (5b). Tetramine 3b 0.80 g (1.92 mmol) was dissolved in THF (20.0 mL), and the solution was stirred in air for 12 h. Subsequently the solvent was removed *in vacuo*, giving 5b as a yellow solid. Yield: 780 mg (1.88 mmol, 98%). <sup>1</sup>H NMR (400.0 MHz, CDCl<sub>3</sub>): δ 6.75 (s, 2H, NH), 5.17 (s, 2H, H2), 2.96 (s, 8H, H3), 1.01 ppm (s, 36H, H5). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 135.8 (C1), 84.0 (C2), 32.2 (C3), 30.3 (C4), 27.9 ppm (C5). MS (MALDI): m/z (%) = 418 (100) [M + 2H]<sup>+</sup>. C<sub>26</sub>H<sub>48</sub>N<sub>4</sub>, M = 416.69.

*N*-Isobutyl-2-(isobutylamino)-*N*'-isobutyl-5-(isobutylamino)-1,4-benzoquinonediimine (5c). Compound 5c was synthesized as described for 5b from 0.60 g (1.67 mmol) of tetramine 3c. Yield: 590 mg (1.64 mmol, 98%) of a red solid. <sup>1</sup>H NMR (400.0 MHz, CDCl<sub>3</sub>):  $\delta$  6.53 (s, 2H, NH), 5.19 (s, 2H, H2), 3.29–2.66 (m, 8H,



H3), 1.97 (m, 4H, H4), 0.99 ppm (d,  ${}^{3}J$  = 6.7 Hz, 24H, H5).  ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  135.8 (C1), 84.5 (C2), 34.2 (C3), 30.3 (C4), 20.7 ppm (C5).



[N-Neopentyl-2-(neopentylamino)-N'-neopentyl-5-(neopentylamino)-1,4-benzoquinonediimine]di[bis(trimethylsilyl)aminotin(II)] (6b). An oven-dried Schlenk flask was cooled under argon and charged with *p*-benzoquinonediimine **5b** (100 mg, 0.24 mmol) and THF (20.0 mL). To this was added Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (210 mg, 0.48 mmol). The reaction mixture was stirred for 24 h at ambient temperature. Subsequently the solvent and the volatile byproduct HNSiMe<sub>3</sub> were removed in vacuo. The resulting solid residue was taken up in n-hexane, and the slurry was filtered. Removal of the solvent from the filtrate gave compound 6b as a purple solid. Yield: 156 mg (0.16 mmol, 67%). Crystals of 6b were obtained from a THF solution of the compound by slow evaporation of the solvent at ambient temperature over 1 week. Most resonances in the NMR spectra are doubled due to the presence of two isomers (syn and anti) of compound 6b, which are present in a 1:1 ratio in solution. <sup>1</sup>H NMR (400.0 MHz, [D<sub>8</sub>]THF): δ 5.52 (s, 2H, H2), 5.51 (s, 2H, H2), 3.52-3.31 (m, 16H, H3, both isomers), 1.10 (s, 36H, H5), 1.09 (s, 36H, H5), 0.06 (s, 18H, H6), 0.05 ppm (s, 18H, H6).  ${}^{13}C{}^{1}H$  NMR (100 MHz,  $[D_8]$ THF):  $\delta$ 163.7 (C1), 163.5 (C1), 90.6 (C2), 90.3 (C2), 60.0 (C3), 35.6 (C3), 35.5 (C4), 34.1 (C4), 30.3 (C5), 30.2 (C5), 6.6 (C6), 6.5 ppm (C6). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz,  $[D_8]$ THF):  $\delta$  0.09, -0.27 ppm. <sup>119</sup>Sn{<sup>1</sup>H} NMR (149.2 MHz,  $[D_8]$ THF):  $\delta$  -21.8, -33.0 ppm. MS (EI): m/z(%): 972 (1)  $[M]^+$ , 812 (11)  $[M - N(SiMe_3)_2]^+$ .  $C_{38}H_{82}N_6Si_4Sn_2 M =$ 972.82.



[*N*-Isobutyl-2-(isobutylamino)-*N'*-isobutyl-5-(isobutylamino)-1,4-benzoquinonediimine]di[bis(trimethylsilyl)aminotin-(II)] (6c). Compound 6c was prepared as described for 6b from *p*-benzoquinonediimine 5c (80 mg, 0.25 mmol) and Sn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (220 mg, 0.50 mmol) in THF (20.0 mL). Yield: 130 mg (0.14 mmol, 57%) of a red solid. Crystals of 6c were obtained from a THF solution of the compound by slow evaporation of the solvent at ambient temperature over 1 week. Most resonances in the NMR spectra are doubled due to the presence of two isomers (*syn* and *anti*) of compound 6c, which are present in a 0.6:0.4 ratio in solution. <sup>1</sup>H NMR (400.0 MHz, [D<sub>8</sub>]THF):  $\delta$  5.14 (s, 2H, H2), 5.13 (s, 2H, H2), 3.40–3.18 (m, 16H, H3, both isomers), 2.26–2.13 (m, 8H, H4, both isomers), 1.07 (d, 24H, H5), 1.05 (d, 24H, H5), 0.07 (s, 18H, H6), 0.04 ppm (s, 18H, H6). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, THF-*d*<sub>8</sub>):  $\delta$  161.8 (C1), 161.7 (C1), 88.7 (C2), 88.1 (C2), 57.1 (C3), 56.6 (C3), 32.0 (C4), 31.8 (C4), 29.8 (C5), 29.7 (C5), 6.4 (C6), 6.3 ppm (C6). <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, [D<sub>8</sub>]THF):  $\delta$  0.33, 0.00 ppm. <sup>119</sup>Sn{<sup>1</sup>H} NMR (149.2 MHz, [D<sub>8</sub>]THF):  $\delta$  -31.0, -42.4 ppm. MS (EI): m/z(%): 596 (9) [M - N(SiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. C<sub>34</sub>H<sub>74</sub>N<sub>6</sub>Si<sub>4</sub>Sn<sub>2</sub> M = 916.72.

**X-ray Diffraction Studies.** X-ray diffraction data for **3b**, **4a**, **6b**, and **6c** were collected at T = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotating anode using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97<sup>25</sup> package using direct methods and were refined with SHELXL-97<sup>25</sup> against  $|F^2|$  using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models in calculated positions.

**3b.**  $C_{26}H_{50}N_4$ ,  $M = 418.70 \text{ g}\cdot\text{mol}^{-1}$ , yellow crystal,  $0.22 \times 0.04 \times 0.04 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ , Z = 2, a = 11.881(2) Å, b = 5.8206(9) Å, c = 19.9773(3) Å,  $\beta = 94.089(3)^\circ$ , V = 1378.04(4) Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.009 \text{ g}\cdot\text{cm}^{-3}$ , Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\mu = 0.059 \text{ mm}^{-1}$ ,  $\omega$ - and  $\varphi$ -scans, 12 865 measured intensities ( $3.4^\circ \leq 2\theta \leq 54.8^\circ$ ), semiempirical absorption correction ( $0.987 \leq T \leq 0.998$ ), 3146 independent ( $R_{\text{int}} = 0.0427$ ) and 2100 observed intensities ( $I \geq 2\sigma(I)$ ), refinement of 150 parameters against  $|F^2|$  of all measured intensities with hydrogen atoms in calculated positions. R = 0.0543, wR = 0.0857,  $R_{\text{all}} = 0.1355$ ,  $wR_{\text{all}} = 0.1531$ . The asymmetric unit contains 1/2 formula unit of **3b** related to the other half by a crystallographic inversion center.

**4a.**  $C_{20}H_{34}N_4Ge_2$ ,  $M = 475.69 \text{ g·mol}^{-1}$ , red-orange crystal, 0.12 × 0.03 × 0.03 mm<sup>3</sup>, monoclinic, space group  $P2_1/c$ , Z = 4, a = 16.924(2) Å, b = 5.9332(6) Å, c = 22.483(2) Å,  $\beta = 102.826^{\circ}$ , V = 2201.2(4) Å<sup>3</sup>,  $\rho_{calc} = 1.435 \text{ g·cm}^{-3}$ , Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\mu = 2.742 \text{ mm}^{-1}$ ,  $\omega$ -and  $\varphi$ -scans, 19 124 measured intensities ( $2.5^{\circ} \leq 2\theta \leq 55.0^{\circ}$ ), semiempirical absorption correction ( $0.734 \leq T \leq 0.922$ ), 5059 independent ( $R_{int} = 0.0668$ ) and 3466 observed intensities ( $I \geq 2\sigma(I)$ ), refinement of 243 parameters against  $|F^2|$  of all measured intensities with hydrogen atoms in calculated positions. R = 0.0408, wR = 0.0765,  $R_{all} = 0.0770$ ,  $wR_{all} = 0.0894$ . The asymmetric unit contains one molecule of **4a**.

**6b.**  $C_{38}H_{82}N_6Si_4Sn_2$ , M = 972.84 g·mol<sup>-1</sup>, purple crystal, 0.26 × 0.13 × 0.09 mm<sup>3</sup>, triclinc, space group  $P\overline{1}$ , Z = 1, a = 9.4197(7) Å, b = 11.3455(9) Å, c = 12.6917(10) Å,  $\alpha = 80.7740(10)$ ,  $\beta = 81.3710(10)$ ,  $\gamma = 68.6430(10)^\circ$ , V = 1240.7(2) Å<sup>3</sup>,  $\rho_{calc} = 1.302$  g·cm<sup>-3</sup>, Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\mu = 1.134$  mm<sup>-1</sup>,  $\omega$ - and  $\varphi$ -scans, 15 414 measured intensities ( $3.3^\circ \leq 2\theta \leq 63.8^\circ$ ), semiempirical absorption correction ( $0.757 \leq T \leq 0.905$ ), 7765 independent ( $R_{int} = 0.0189$ ) and 6960 observed intensities ( $I \geq 2\sigma(I)$ ), refinement of 238 parameters against  $|F^2|$  of all measured intensities with hydrogen atoms in calculated positions. R = 0.0260, wR = 0.0306,  $R_{all} = 0.0615$ ,  $wR_{all} = 0.0636$ . The asymmetric unit contains 1/2 molecule of **4b** related to the other half by a crystallographic inversion center.

**6c.**  $C_{34}H_{74}N_6Si_4Sn_2$ ,  $M = 916.73 \text{ g·mol}^{-1}$ , red crystal,  $0.12 \times 0.07 \times 0.01 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ , Z = 2, a = 13.1239(5) Å, b = 11.0728(4) Å, c = 16.2589(7) Å,  $\beta = 92.1880(10)^\circ$ , V = 2361.0(2) Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.290 \text{ g·cm}^{-3}$ , Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\mu = 1.187 \text{ mm}^{-1}$ ,  $\omega$ - and  $\varphi$ -scans, 25 781 measured intensities ( $3.1^\circ \leq 2\theta \leq 58.3^\circ$ ), semiempirical absorption correction ( $0.871 \leq T \leq 0.988$ ), 6351 independent ( $R_{\text{int}} = 0.0465$ ) and 5004 observed intensities ( $I \geq 2\sigma(I)$ ), refinement of 218 parameters against  $|F^2|$  of all measured intensities with hydrogen atoms in calculated positions. R = 0.0300, wR = 0.0445,  $R_{\text{all}} = 0.06602$ ,  $wR_{\text{all}} = 0.0656$ . The asymmetric unit contains 1/2 molecule of **6c** related to the other half by a crystallographic inversion center.

## ASSOCIATED CONTENT

#### **S** Supporting Information

X-ray crystallographic files for **3b**, **4a**, **6b**, and **6c** (CIF files) and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} (and when applicable <sup>29</sup>Si{<sup>1</sup>H} and <sup>119</sup>Sn{<sup>1</sup>H}) NMR spectra for the organic precursors and all germylenes and stannylenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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