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Monomeric Boron and Tin(II) Heterocyclic Derivatives of 1,8-Diaminonaphthalenes: Synthesis, Characterization and X-ray Structures

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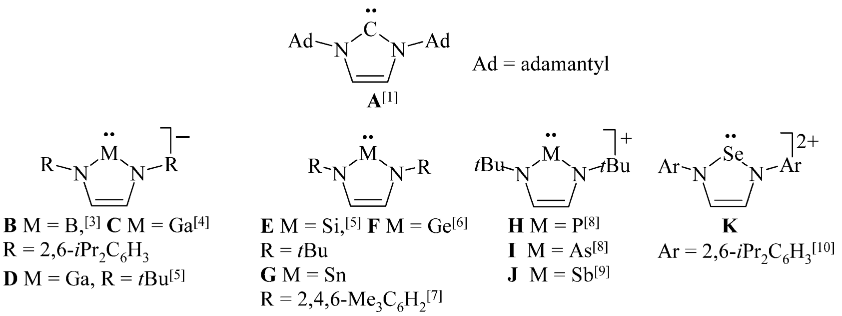
The reaction of the diaminonaphthalene dilithium salt $(THF)_2Li_2[(NSiMe_3)_2C_{10}H_6]$ with BX_3 (X = Cl, Br) in hexane provides the monomeric compounds $BX[(NSiMe_3)_2C_{10}H_6]$ [**3** (X = Cl), **4** (X = Br)] with a tricoordinate boron atom. Attempts to reduce **3** and **4** with lithium, sodium, potassium or sodium/potassium alloy with the intention to isolate a boranide resembling a carbene were unsuccessful. However, the diaminonaphthalene dilithium salt $(THF)_2Li_2[(NSi\text{-}i\text{Pr}_3)_2C_{10}H_6]$ (**2**) reacts with $SnCl_2$ in THF to provide the carbene analog **5**. Compounds **2**, **3** and **5** were characterized by single-crystal X-ray structure analysis. The structures of **3** and **5** show the naphthalene backbone to be nearly planar, while the heterocycles in **3** and **5** containing boron and tin atoms, respectively, have torsion angles (**3**: 30.06°; **5**: 37.27°) with respect to the naphthalene plane. The boron atom has a trigonal-planar environment, and the stannylene tin–nitrogen bonds form a very acute N–Sn–N angle of 92.2°.

Introduction

Since the report in 1991 of the first solid-state[1] stable carbene (Scheme 1; compound **A**), the synthesis and characterization of compounds of *p*-block elements analogous to singlet carbenes has rapidly increased in the last decade.[2] Interest in groups 13–16 diazabutadiene (DAB) compounds has been initiated largely by their isoelectronic relationship to the corresponding carbenes. Especially heterocyclic derivatives with boron (**B**),[3] gallium (**C** and **D**),[4] silicon (**E**),[5] germanium (**F**),[6] tin (**G**),[7] phosphorus (**H**),[8] arsenic (**I**),[8] antimony (**J**),[9] and selenium (**K**)[10] have been reported (Scheme 1). Moreover, the β-diketiminato ligands proved to be very effective ligands for elements of group 13.[11] These bidentate ligands have been employed for the stabilization of novel monovalent group 13 elements like those of aluminum (**L** and **P**),[12] gallium (**M**),[13] indium (**N**, **Q** and **R**)[14] and thallium (**O**,[14b] **S** and **T**)[15] (Scheme 2).



Scheme 1. Heterocyclic carbene and heteroelement analogs of diazabutadienes.

Recently, the synthesis and the crystal structure of the boryl anion and its reactivity toward electrophilic groups have been reported (Scheme 3). It is known that in order to

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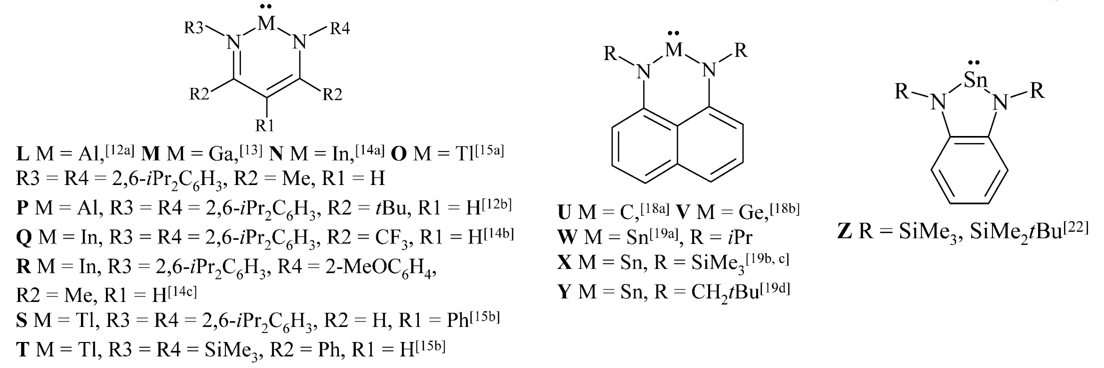


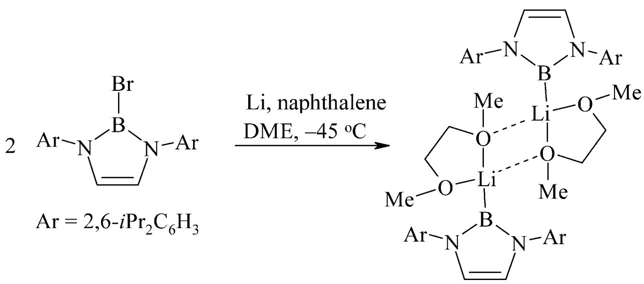
L M = Al,[12a] **M** M = Ga,[13] **N** M = In,[14a] **O** M = Tl[15a]
R3 = R4 = 2,6-iPr$_2$C$_6$H$_3$, R2 = Me, R1 = H
P M = Al, R3 = R4 = 2,6-iPr$_2$C$_6$H$_3$, R2 = tBu, R1 = H[12b]
Q M = In, R3 = R4 = 2,6-iPr$_2$C$_6$H$_3$, R2 = CF$_3$, R1 = H[14b]
R M = In, R3 = 2,6-iPr$_2$C$_6$H$_3$, R4 = 2-MeOC$_6$H$_4$,
R2 = Me, R1 = H[14c]
S M = Tl, R3 = R4 = 2,6-iPr$_2$C$_6$H$_3$, R2 = H, R1 = Ph[15b]
T M = Tl, R3 = R4 = SiMe$_3$, R2 = Ph, R1 = H[15b]

U M = C,[18a] **V** M = Ge,[18b]
W M = Sn[19a], R = iPr
X M = Sn, R = SiMe$_3$[19b, c]
Y M = Sn, R = CH$_2$$t$Bu[19d]

Z R = SiMe$_3$, SiMe$_2$$t$Bu[22]

Scheme 2. Low-valent group 13 and 14 derivatives of β-diketiminates, N,N'-disubstituted naphthalenes, and o-phenylenediamines.

obtain this kind of carbene analog, there is a need for ligands that possess some specific features. For instance, N-based ligands with delocalized heterocyclic π-systems that improve the stability of these derivatives.[16] Moreover, bulky groups bonded directly to the nitrogen atoms have two important functions: (i) to restrict the environment at the nitrogen atom to a planar geometry in order to improve the π-delocalization and (ii) to avoid molecular aggregation.[17] Indeed, carbene analogs of group 14 elements with 1,8-diaminonaphthalene ligands have been reported (Scheme 2; **U**–**Y**).[18,19] Despite the exceptional high basicity of the "proton sponge", there are a few reports that describe the preparation of carbene analogs derived from main group elements. This kind of bulky nitrogen-based ligand currently attracts growing interest due to specific steric and electronic properties to control efficiently the geometry at the metal atom. For this reason and in continuation of our research on this subject we report on the synthesis and characterization of two new diaminonaphthalene boron halides and one stannylene derivative.



Scheme 3. Synthesis of a boryllithium compound.[3]

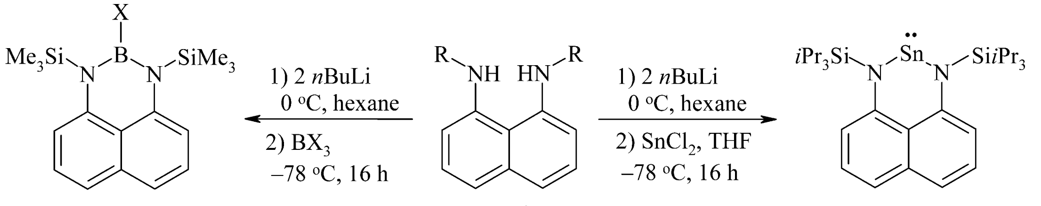
Results and Discussion

Syntheses

The starting material **2** was prepared according to the literature.[20] Herein we report its crystal structure. The reaction of the diaminonaphthalene dilithium salt (THF)$_2$Li$_2$-[(NSiMe$_3$)$_2$C$_{10}$H$_6$] with BX$_3$ (X = Cl, Br) in hexane provided the monomeric compounds MX[(NSiMe$_3$)$_2$C$_{10}$H$_6$] [M = B; **3** (X = Cl), **4** (X = Br)] in good yields (Scheme 4). Compounds **3**–**5** could be isolated as colorless, yellow or deep-red solids, respectively. Compounds **3** and **5** were purified by crystallization at 26 °C from pentane and hexane, respectively, to give single crystals, which were suitable for X-ray diffraction (Table 1).

NMR Spectroscopic Results

Compounds **3**–**5** were characterized by multinuclear (^{1}H, ^{11}B, ^{13}C, and ^{119}Sn) NMR spectroscopy. The ^{1}H NMR spectra of compounds **3** and **4** exhibit resonances in the range from δ = 7.12 to 6.73 and 0.36 ppm in a ratio of 6:18, assigned to the C$_{10}$$H_6$ and Si(CH_3)$_3$ protons, respectively, thus confirming the existence of the 1,8-bis(trialkylsilylamino)naphthalenediyl group. Compound **5** exhibits one doublet and one multiplet (δ = 1.01 and 1.36 ppm) due to SiiPr_3 protons. The signal for the carbon atoms that are linked to nitrogen atoms in compound **5** is shifted to higher frequencies compared to those of **3** and **4**. The ^{11}B NMR shifts of **3** (δ = 32.1 ppm) and **4** (δ = 28.04 ppm) are found in a narrower range as expected[21] for an environment where the boron atom is bonded to two nitrogen atoms in



3 X = Cl, **4** X = Br

1 R = SiMe$_3$
2 R = SiiPr$_3$

5

Scheme 4. Synthesis of boron and stannylene compounds derived from diaminonaphthalenes.

Table 1. X-ray crystallographic data for **2**, **3**, and **5**.

	2	**3**	**5**
Empirical formula	$C_{28}H_{50}N_2Si_2$	$C_{16}H_{24}BClN_2Si_2$	$C_{28}H_{48}N_2Si_2Sn$
Formula mass	470.88	346.81	587.55
Temperature [K]	293(2)	100(2)	100(2)
Wavelength [Å]	0.71073	1.54178	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P1$	$P2_1/n$	$C2/c$
a [Å]	8.474(1)	6.953(2)	21.503(2)
b [Å]	11.728(1)	13.698(2)	9.709(1)
c [Å]	16.352(1)	19.224(2)	14.291(1)
α [°]	90.58(1)	90	90
β [°]	103.78(1)	94.56(2)	101.30(1)
γ [°]	110.47(1)	90	90
V [Å^3]	1470.87(3)	1825.1(6)	2925.6(5)
Z	2	4	4
$D_{calcd.}$ [Mg/m^3]	1.063	1.262	1.334
Absorption coefficient [mm^{-1}]	0.138	3.073	0.974
$F(000)$	520	736	1232
θ range for data collection [°]	3.19–27.46	3.98–59	1.93–26.38
Index ranges	$-10 \leq h \leq 10$	$-7 \leq h \leq 6$	$-26 \leq h \leq 26$
	$-13 \leq k \leq 15$	$-15 \leq k \leq 15$	$0 \leq k \leq 12$
	$-21 \leq l \leq 21$	$-21 \leq l \leq 21$	$0 \leq l \leq 17$
Reflections collected	21319/6586	18324/2612	15793/2987
R(int)	0.0496	0.0313	0.0228
Data/restraints/parameters	6586/0/480	2612/0/206	2987/0/157
Goodness-of-fit on F^2	1.005	1.045	1.095
Final Rint [$I > 2\sigma(I)$]	$R1 = 0.0524$	$R1 = 0.0267$	$R1 = 0.0305$
	$wR2 = 0.1228$	$wR2 = 0.0712$	$wR2 = 0.0860$
Rint (all data)	$R1 = 0.0809$	$R1 = 0.0271$	$R1 = 0.0340$
	$wR2 = 0.1387$	$wR2 = 0.00715$	$wR2 = 0.0880$
Largest difference peak/hole [e Å^{-3}]	0.341/–0.373	0.281/–0.215	0.550/–0.691
CCDC-	-665740	-665300	-665299

a trigonal-planar geometry. The first attempt to reduce **4** in 1,2-dimethoxyethane by adding finely divided sodium at – 78 °C for 12 h, resulted in a deep red solution after 6 h at –78 °C. The ^{11}B NMR spectrum showed two broad resonances (δ = 28.81 and 37.8 ppm in a ratio of 3:1). It was not possible to determine the half-width of the signals because both resonances were strongly overlapping. In the second experiment after 2 d, the ^{11}B NMR spectrum exhibited three broad signals (δ = 0.5, 28.58, and 37.7 ppm in a ratio of 1:1:0.5). Finally, in the latter case after 3 d, most of the sodium was consumed, and the ^{11}B NMR spectrum exhibited only two broad resonances (δ = 0.5 and 38.0 ppm in a ratio of 1:1). The latter ^{11}B chemical shift was displaced at higher frequencies, this indicates a higher electron density on the boron atom, comparable to that of the boranide.[3] The ^{119}Sn NMR spectrum of compound **5** exhibits a resonance at δ = 513.6 ppm indicative of a dicoordinate tin atom in solution.[22] In comparison, the phenylene derivatives Sn[(NR)$_2$C$_6$H$_4$] (R = SiMe$_3$, SiMe$_2$*t*Bu; **Z**; Scheme 2) [23] give rise to resonances at δ = 415 and 456 ppm, respectively, and Sn[(NR)$_2$C$_{10}$H$_6$] (**W**: R = *i*Pr; **X**: R = SiMe$_3$; **Y**: R = CH$_2$*t*Bu; Scheme 2) at δ = 330, 144, and 183 ppm.

Molecular Structures of Compounds 2, 4, and 5

Compounds **2** (Figure 1), **4** (Figure 2), and **5** (Figure 3) crystallize in the triclinic space group $P\bar{1}$ and in the monoclinic space groups $P2_1/n$ and $C2/c$, respectively. Selected bond lengths, bond angles and torsion angles are given in Figures 1, 2 and 3. The molecular structures of **2**, **4**, and **5** adopt all local C_2 symmetry. Due to the steric demand of the SiMe$_3$ and Si*i*Pr$_3$ groups they adopt a *trans* arrangement, and the C–N bonds are twisted slightly out of the naphthalene plane by ca. 4° (**2**), ca. 12.5° (**4**) and ca. 14.8° (**5**) respectively. In compound **2** the non-bonding N–N distance (2.800 Å) is rather long, compared to other "proton sponges".[24] Compound **3** is the first example of a monomeric 1,8-bis(trimethylsilylamino)naphthalenediylborane. The bis(amino)naphthalenediyl group is bonded in an *N*,*N′*-chelating fashion to the boron atom which has a trigonal-planar geometrical environment. The B–N bond lengths [1.424(4) Å and 1.419(4) Å] are in the usual range for B–N compounds,[25] comparable to the B–N bonds found in 1,3,2-diazabora[3]ferrocenophanes with Me$_3$Si–N–B–F moieties [1.41.6(6) Å and 1.418(6) Å] and Me$_3$Si–N–B–Cl units [1.417(11) Å]. The B–Cl bond length [1.792(3) Å] is almost the same as those found in the literature [1.816(8) Å].[26] Compound **5** exists in the solid state as a stable monomer due to the sterically demanding N(Si*i*Pr$_3$)$_2$ groups and also due to the interaction of the vacant *p*-orbital at the tin atom with the unshared electron pairs of the trigonal-planar nitrogen atoms. The tin atom has a pseudotrigonal-planar geometry in which the tin atom is surrounded by two nitrogen atoms, and the third position is occupied by a lone pair of electrons that is stereochemically active. The Sn–N and Si–N bond lengths [2.066(2) Å and 1.766(2) Å] are comparable to those given in Scheme 2 [carbene **X**; Sn–N 2.100(5) and 1.746(2) Å]. The N1–Sn–N2 bite angle (92.17°) is larger compared with that of $\mathrm{Sn[(NR)_2C_6H_4]}$ [85.6(3)° for R = *i*Pr; 87.3(2)° for R = $\mathrm{SiMe_3}$; 86.9°(2) for R = $\mathrm{CH_2}$*t*Bu]. The conformation of the bulky groups bonded to the nitrogen atoms in compounds **3** and **5** is *transoid*.

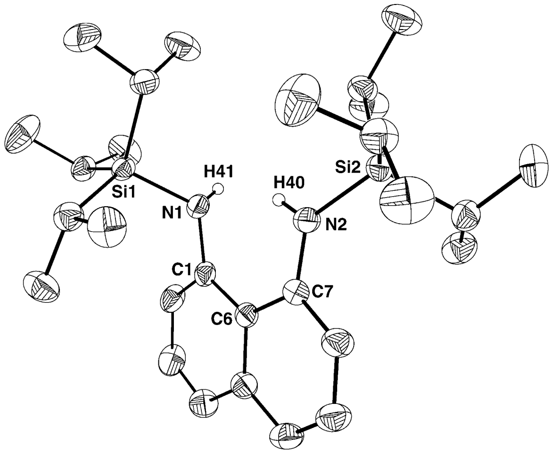


Figure 1. Solid-state structure of compound **2**. Anisotropic displacement parameters are depicted at the 50% probability level with hydrogen atoms except of those bound to nitrogen atoms omitted for clarity. Selected bond lengths [Å], bond angles [°] and torsion angles [°]: C(1)–N(1) 1.445(2), C(7)–N(2) 1.395(2), Si(1)–N(1) 1.7517(17), Si(2)–N(2) 1.7356(17), N(2)–N(1) 2.800; N(2)–H40···N(1) 2.141; C(7)–N(2)–H(40) 110.8, C(1)–N(1)–H(41) 114.8; C(7)–N(2)–Si(2) 133.29, C(1)–N(1)–Si(2) 123.0; C(7)–C(6)–C(1)–N(1) 7.57(5), C(1)–C(6)–C(7)–N(2) 5.44(5), C(1)–C(6)–C(7)–C(8) 176.05.

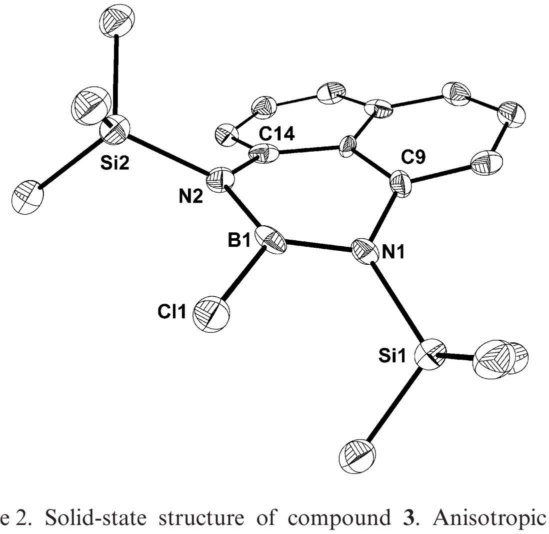


Figure 2. Solid-state structure of compound **3**. Anisotropic displacement parameters are depicted at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths [Å], bond angles [°] and torsion angles [°]: B(1)–Cl(1) 1.792(3), B(1)–N(1) 1.424(4), B(1)–N(2) 1.419(4), N(1)–Si(1) 1.782(2), N(2)–Si(2) 1.783(2), N(1)–C(9) 1.431(3), N(2)–C(14) 1.432(3); Cl(1)–B(1)–N(1) 117.6(2), Cl(1)–B(1)–N(2) 119.0(2), N(1)–B(1)–N(2) 123.4(2), B(1)–N(1)–C(9) 114.3(2), B(1)–N(2)–C(14) 114.3(2); C(9)–C(13)–C(14)–N(2) 16.05, C(14)–C(13)–C(9)–N(1) 15.51, C(9)–C(13)–C(14)–C(15) 167.45, C(15)–C(14)–N(2)–Si(2) 35.73.

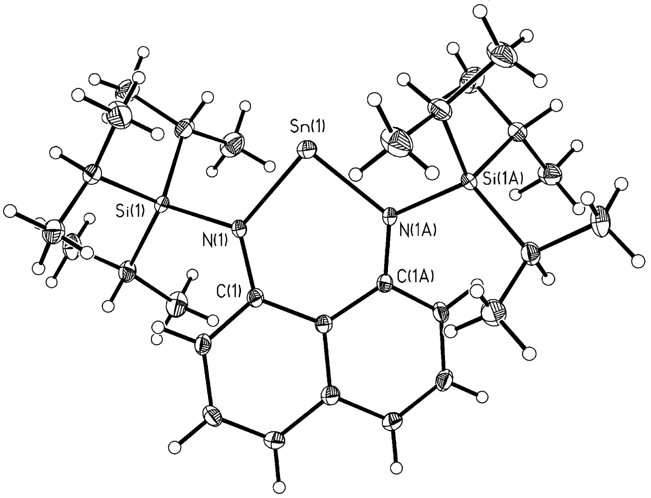


Figure 3. Solid-state structure of compound **5**. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [Å], bond angles [°] and torsion angles [°]: Sn(1)–N(1) 2.066(2), Sn(1)–N(1A) 2.066(2), N(1)–Si(1) 1.766(2), N(1)–C(1) 1.413(3); N(1)–Sn(1)–N(1A) 92.17(12), Sn(1)–N(1)–C(1) 121.86(16), Sn(1)–N(1)–Si(1) 115.31(11); Sn(1)–N(1)–C(1)–C(6) 37.27, N(1)–C(1)–C(6)–C(1°) 20.36, C(1)–C(6)–C(1°)–C(2) 165.17, C(2)–C(1)–N(1)–Si(1) 30.44.

Conclusions

Herein we describe the synthesis, characterization and X-ray structures of the first example of a monomeric 1,8-bis(trimethylsilylamino)naphthalenediylborane and of a stannylene supported by the 1,8-bis(triisopropylsilylamino)naphthalenediyl group. The latter can act as precursor for the preparation of Sn-transition metal complexes. Probably the trimethylsilyl groups cannot stabilize the boryl anion, when compared with the NacNac supported by the 2,6-$i\mathrm{Pr_2C_6H_3}$ groups of the monomeric $\mathrm{Al^I}$ compound.[27]

Neither the steric requirement is high enough nor the donor capacity is sufficient. Currently, we continue our research for suitable substituents providing both features.

Experimental Section

General: All manipulations were performed under dried nitrogen in standard Schlenk glassware. Solvents were dried according to known procedures and saturated with N_2. The deuterated solvents used for the NMR measurements, *n*-pentane and *n*-hexane for the crystallization were distilled from Na/K alloy prior to use. Commercially available chemicals were purchased from Aldrich or Fluka and used as received. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ^{1}H (200.13 and 300.13 MHz), ^{11}B (96.29 MHz), ^{13}C (75.46 MHz), ^{29}Si (59.62 MHz) and ^{119}Sn (111.97 MHz) NMR spectra were recorded with Bruker Avance 200 and Avance 300 spectrometers. EI mass spectra were recorded with a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi B540 melting-point apparatus.

X-ray Structure Determination of 2, 3 and 5: The data for **2**, **3** and **5** were collected from shock-cooled crystals at 100(2) K.[28] The data for **2** was collected with an Enraf-Nonius Kappa-CCD, the data for **3** with a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector and a mirror-system-monochromated Cu-K_α source and for **5** with a Bruker TXS-Mo rotating anode with an APEX II detector on a D8 goniometer. The Enraf-Nonius used graphite-monochromated Mo-K_α radiation and the Bruker TXS-Mo rotating anode used INCOATEC Helios mirror optics as radiation monochromator. All three diffractometers were equipped with a low-temperature device. The data of **2**, **3** and **5** were integrated with SAINT,[29] and an empirical absorption correction (SADABS) was applied.[30] The structures were solved by direct methods (SHELXS-97)[31] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[32] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically in calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. CCDC numbers are listed in Table 1 and 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.

Synthesis of Compound 2: 1,8-Bis(triisopropylsilylamino)naphthalene was prepared according to the literature.[20] M.p. 99 °C. MS (EI): *m/z* (%) = 470 [M$^+$] (30), 314 [M$^+$ – Si(*i*Pr)$_3$] (15), 158 [M$^+$ – 2 [Si(*i*Pr)$_3$]$_2$] (100). ^{1}H NMR (200.13 MHz, CDCl$_3$, 298 K): δ = 0.35 [s, 18 H, Si(C*H*$_3$)$_3$], 5.62 (br. s, 2 H, N*H*), 6.75 (dd, $^3J_{\text{H,H}}$ = 6.8, $^4J_{\text{H,H}}$ = 1.8 Hz, 2 H, aromatic *H*), 7.29–7.34 (m, 4 H, aromatic *H*) ppm. $C_{28}H_{50}N_2Si_2$ (470.90): calcd. C 71.25, H 10.77, N 5.95; found C 71.42, H 10.70, N 5.95.

Synthesis of Compound 3: A solution of *n*-butyllithium in *n*-hexane (2.5 M, 5.5 mL, 13.8 mmol) was added drop by drop at 0 °C to a solution of 1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$ (2 g, 6.61 mmol) in *n*-hexane (40 mL). After 30 min of stirring, boron trichloride (7.27 mL, 1 M in *n*-hexane, 7.27 mmol) was added slowly at –78 °C. The reaction mixture was slowly warmed to room temperature, and stirring was continued for 16 h. After removal of all volatiles, the residue was extracted with *n*-pentane (20 mL) to give a pale-yellow solution. Storage of the extract at 2 °C for 1 d afforded colorless crystals of **3** (2.58 g, 89%). M.p. 76–78 °C. MS (EI): *m/z* (%) = 346 (77) [M$^+$], 331 (10) [M$^+$ – Me], 274 (5) [M$^+$ – Si(CH$_3$)$_3$], 238 (100) [M$^+$ – Si(CH$_3$)$_3$Cl]. ^{1}H NMR ([D$_8$]THF, 200.13 MHz, 298 K): δ = 0.36 [s, 18 H, Si(C*H*$_3$)$_3$], 6.73 (d, $^3J_{\text{H,H}}$ = 7.6 Hz, 1 H, aromatic *H*), 6.79 (d, $^3J_{\text{H,H}}$ = 7.6 Hz, 1 H, aromatic *H*), 7.12 (d, $^3J_{\text{H,H}}$ = 7.6 Hz, 4 H, aromatic *H*) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF, 75.46 MHz, 298 K): δ = 2.68 [Si(*C*H$_3$)$_3$], 114.84, 120.75, 126.19, 137.22, 142.96 (aromatic *C*) ppm. ^{11}B{^{1}H} NMR ([D$_8$]THF, 96.29 MHz, 298 K): δ = 32.1 ppm. $C_{16}H_{24}BClN_2Si_2$ (346.82): calcd. C 55.41, H 6.98, N 8.08; found C 55.76, H 6.95, N 8.18.

Synthesis of Compound 4: A solution of *n*-butyllithium in *n*-hexane (2.5 M, 6.1 mL, 13.8 mmol) was added drop by drop at 0 °C to a solution of 1,8-(Me$_3$SiNH)$_2$C$_{10}$H$_6$ (2 g, 6.61 mmol) in *n*-pentane (40 mL). After 30 min, boron tribromide (1.2 mL, 7.27 mmol) was added slowly at –78 °C. The reaction mixture was stirred at room temperature for 16 h, the solvent was removed in vacuo, and the residue was extracted with *n*-pentane (40 mL). The filtrate was reduced to 10 mL and stored at –35 °C to yield **4** as an orange solid (2.3 g, 82%). M.p. 119–121 °C. MS (EI): *m/z* (%) = 392 (44) [M$^+$], 318 (8) [M$^+$ – Me$_3$Si – H], 238 (100) [M$^+$ – Me$_3$Si – Br]. ^{1}H NMR ([D$_8$]THF, 200.13 MHz, 298 K): δ = 0.36 [s, 18 H, Si(C*H*$_3$)$_3$], 6.73 (d, $^3J_{\text{H,H}}$ = 7.6 Hz, 1 H, aromatic *H*), 6.79 (d, $^3J_{\text{H,H}}$ = 7.6 Hz, 1 H, aromatic *H*), 7.12 (d, $^3J_{\text{H,H}}$ = 7.6 Hz, 4 H, aromatic *H*) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF, 75.46 MHz, 298 K): δ = 2.69 [Si(*C*H$_3$)$_3$], 113.70, 119.9, 126.5, 136.4, 144.6 (aromatic *C*) ppm. ^{11}B{^{1}H} NMR ([D$_8$]THF, 96.29 MHz, 298 K): δ = 28.04 ppm. $C_{16}H_{24}BBrN_2Si_2$ (391.27): calcd. C 49.12, H 6.18, N 7.16; found C 52.85, H 6.29, N 7.54.

Synthesis of Compound 5: A solution of *n*-butyllithium in *n*-hexane (2.5 M, 4.7 mL, 11.17 mmol) was added drop by drop at 0 °C to a solution of 1,8-(*i*Pr$_3$SiNH)$_2$C$_{10}$H$_6$ (2.5 g, 5.3 mmol) in *n*-hexane (40 mL). After 2 h, a suspension of tin dichloride (1.05 g, 5.58 mmol) in dry THF (20 mL) was added slowly at –78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 16 h. After removal of all volatiles, the residue was extracted with *n*-pentane (20 mL) to yield a deep-red solution. Storage of the extract in a freezer at 2 °C for 1 week afforded deep-red crystals of **5** (2.27 g, 73%). M.p. 97–98 °C. MS (EI): *m/z* (%) = 588 (100) [M$^+$], 545 (5) [M$^+$ – *i*Pr], 503 (45) [M$^+$ – 2 *i*Pr + H], 461 (50) [M$^+$ – 3 *i*Pr], 419 (15) [M$^+$ – 4 *i*Pr + H]. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 298 K): δ = 1.01 [d, $^3J_{\text{H,H}}$ = 2.2 Hz, 36 H, CH(C*H*$_3$)$_2$], 1.36 [m, $^3J_{\text{H,H}}$ = 2.2 Hz, 6 H, C*H*(CH$_3$)$_2$], 6.78 (dd, $^3J_{\text{H,H}}$ = 7.4, $^4J_{\text{H,H}}$ = 1.3 Hz, 2 H, aromatic *H*), 7.17 (t, $^3J_{\text{H,H}}$ = 7.4 Hz, 2 H, aromatic *H*), 7.23 (d, $^3J_{\text{H,H}}$ = 7.4, $^4J_{\text{H,H}}$ = 1.3 Hz, 2 H, aromatic *H*) ppm. ^{13}C{^{1}H} NMR (75.46 MHz, C$_6$D$_6$, 298 K): δ = 14.48 [*C*H-(CH$_3$)], 18.99 [CH-(*C*H$_3$)$_2$], 116.58, 121.04, 125.08, 136.87, 146.24 (aromatic *C*) ppm. ^{29}Si{^{1}H} NMR (59.62 MHz, C$_6$D$_6$, 298 K): δ = 11.31 ppm. ^{119}Sn{^{1}H} NMR (111.97 MHz, C$_6$D$_6$, 298 K): δ = 513.6 ppm. $C_{28}H_{48}N_2Si_2Sn$ (587.57): calcd. C 57.24, H 8.27, N 4.77; found C 55.03, H 8.23, N 4.77.

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