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Protic N-Heterocyclic Germylenes and Stannylenes: Synthesis and Reactivity

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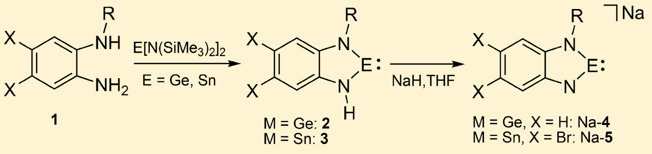
Supporting Information

ABSTRACT: The monoalkylated or monoarylated *o*-phenylenediamines **1a**−**d** (**1a**, R = *t*-Bu; **1b**, R = adamantyl; **1c**, R = phenyl; **1d**, R = mesityl) react via transamination with $Ge[N(SiMe_3)_2]_2$ or $Sn[N(SiMe_3)_2]_2$ to give the protic benzimidazolin-2-germylenes **2a**−**d** or the benzimidazolin-2-stannylenes **3a**,**b**. Germylenes **2a**,**b** can be deprotonated to give the salts Na-**4a** and Na-**4b**, each containing an anionic N-deprotonated N-heterocyclic germylene. The protic stannylenes **3a**,**b** react with NaH presumably via reduction of the tin(II) center by the deprotonated electron-rich *o*-phenylenediamine ligand and release of elemental tin. To prevent this reduction, the electron-poor *N*-H,*N*′-H-5,6-dibromobenzimidazolin-2-stannylene (**5**) was prepared and successfully N-deprotonated to give an anionic stannylene in Na-**6**. The molecular structures of **2a**, **3a**, and Na-**4a** were established by X-ray diffraction studies.



INTRODUCTION

The heavier group 14 analogues of carbenes (R_2C:), the silylenes, germylenes, stannylenes, and plumbylenes of the general formula R_2E: (generically named tetrylenes) feature an electron-deficient group 14 element (E:) with only six electrons in the valence shell. The first examples for stable stannylenes and plumbylenes of type $M[CH(SiMe_3)_2]_2$ were described by Lappert more than 40 years ago.[1] Subsequently, a large number of tetrylenes bearing different substituents R at the R_2E: center have been reported.[2] In contrast to the subvalent carbon derivatives R_2C:, where depending on the substituents both the singlet and triplet ground states can be observed,[3] the heavier tetrylenes occur exclusively in the diamagnetic singlet ground state with two nonbonding paired electrons.[2,4] Normally, tetrylenes feature a bent geometry. The electronic situation is best described by sp^2 hybridization at the E atom with the electron pair residing in one of the sp^2 orbitals and the p orbital remaining empty. However, excitation to the triplet state can occur, and this is thought to play a role in the activation of dihydrogen by selected diarylstannylenes.[5]

Early on it was noted that the electronic situation in tetrylenes can lead to amphiphilic behavior with the free electron pair acting as a Lewis base and the empty p orbital functioning as a Lewis acid.[2] Consequently, different germylenes and stannylenes have been shown to form adducts with both Lewis bases and Lewis acids.[2] These interesting properties have led to a resurgence of interest in tetrylenes and their potential for the activation of unreactive substrates.[5]

In analogy to stable N-heterocyclic carbenes, N-heterocyclic tetrylenes have been prepared, with selected compounds of this type being known even before the NHC analogues were described. After the preparation of the first benzannulated N-heterocyclic carbene **A**[6] (Figure 1), we and others became interested in the germanium, tin, and lead analogues of this NHC. The corresponding benzannulated N-heterocyclic silylene **B** has been prepared by Gehrhus and Lappert.[2c] Various benzannulated N-heterocyclic germylenes **C**,[7] stannylenes **D**,[8] and plumbylenes **E**[9] (Figure 1), including chiral germylenes and stannylenes,[7f] have been prepared and characterized. N-heterocyclic germylenes and stannylenes **C** and **D** have been used as Lewis base ligands for the synthesis of transition-metal complexes.[7c,e,8f−h] In addition, compounds of types **C**−**E** form adducts with Lewis bases which interact with the empty p orbital[7c,d,h,8c−h,9,9c] (Figure 1, **F**).

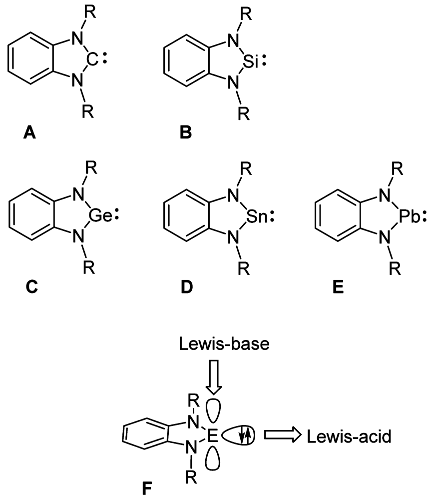


Figure 1. Benzannulated N-heterocyclic carbenes **A** and tetrylenes **B**−**E**.

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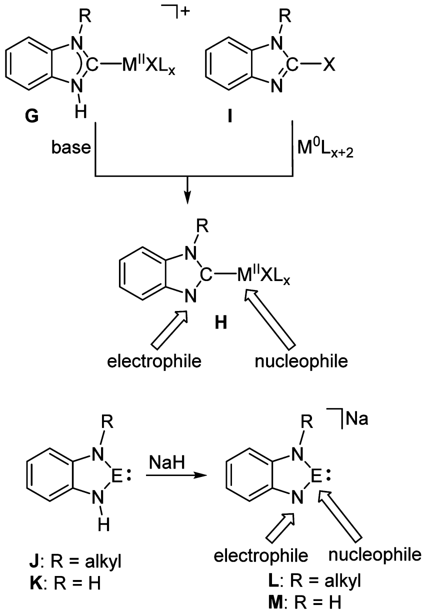
We have unsuccessfully tried to utilize the amphiphilic properties of the heavier tetrylenes for the cooperative activation of less reactive substrates such as dihydrogen. Such activation was, however, performed with diarylstannylenes[5] and with selected cyclic alkylaminocarbenes (CAACs).[10] We therefore decided to generate nucleophilic and electrophilic reaction sites at different positions of the tetrylenes. For metal complexes of protic NHCs **G**, a similar separation can be achieved by N deprotonation of the NHC ligand, generating a highly nucleophilic ring nitrogen atom in **H**.[11] Alternatively, complexes with N-deprotonated NHC ligands of type **H** can be obtained by the oxidative addition of 2-halogeno-*N*-alkylbenzimidazoles[12] **I** or 2-halogenobenzimidazoles[13] to selected transition-metal complexes (Scheme 1, top). Similarly to the lighter NHC homologues, it should also be possible to deprotonate the heavier protic tetrylenes (Ge, Sn). Here we describe the preparation of novel monoprotic (**J**) and diprotic (**K**) N-heterocyclic germylenes and stannylenes and their deprotonation to give the sodium salts **L** and **M**, respectively (Scheme 1, bottom).

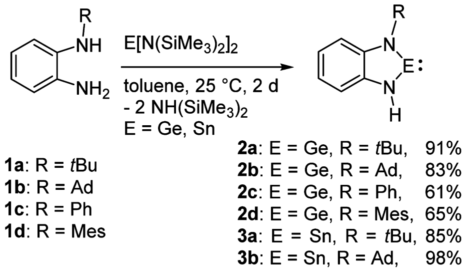
Scheme 1. Deprotonation of Coordinated Protic NHCs and of Free Protic Tetrylenes



RESULTS AND DISCUSSION

The monosubstituted *o*-phenylendiamine derivatives **1a−d** (Scheme 2) have been prepared following published procedures.[14] A subsequent transamination reaction of **1a−d** with M[N(SiMe$_3$)$_2$]$_2$ (M = Ge, Sn)[15] in dry toluene at room temperature led to the protic benzimidazolin-2-germylenes **2a−d** and stannylenes **3a,b** (Scheme 2). The protic tetrylenes have been isolated as orange or yellow solids or brown oils in good yields.

Scheme 2. Synthesis of the Germylenes 2a−d and the Stannylenes 3a,b



In analogy to the N,N′-dialkylated derivatives **C−E** (Figure 1), the monoprotic N-heterocyclic germylenes and stannylenes are sensitive toward air and moisture. Germylenes **2a−d** exhibit a solubility in organic solvents which depends on the N,N′-substitution pattern. For example, **2a** dissolves rather well in nonpolar solvents such as *n*-hexane, while germylene **2b** shows a poor solubility in this nonpolar solvent but dissolves well in ethers or aromatic hydrocarbons. The protic *N*-adamantyl-substituted stannylene **3b** shows poor solubility even in a polar solvent such as THF.

Formation of the germylenes **2a−d** and the stannylenes **3a,b** was monitored by ^{1}H NMR spectroscopy. For all tetrylenes, the NH resonance was detected with a relative intensity of 1 and this resonance was shifted downfield in comparison to the corresponding *o*-phenylenediamine starting material. For example, the resonance δ(NH$_2$ and NH*t*Bu) 3.03 ppm for **1a** shifted upon formation of the germylene **2a** to δ(NH) = 7.40 ppm (both measured in C_6D_6). NMR spectra for the germylene **2b** and the stannylene **3a** were measured both in C_6D_6 and in THF-d_8. In the ^{1}H NMR spectra, the chemical shift for the NH resonances depended strongly on the solvent used. The N−H signal for the protic germylene **2b** in C_6D_6 (δ 7.48 ppm) appears at $\Delta\delta \approx 2$ ppm shifted to higher field in comparison to the N−H resonance detected in the polar solvent THF-d_8 (δ 9.47 ppm). A similar observation was made for stannylene **3a** (δ 5.44 ppm in C_6D_6 and δ 7.40 ppm in THF-d_8). A likely reason for these observations is the formation of hydrogen bonds (N−H···O) between the N−H groups of the tetrylenes and the oxygen atoms of THF molecules. Such hydrogen bonds cannot form in C_6D_6.

In addition, the ^{119}Sn{^{1}H} NMR spectra also reveal a strong solvent dependence of the resonance for the stannylene tin atoms. The ^{119}Sn{^{1}H} NMR signal for **3a** in C_6D_6 (δ 223 ppm) is shifted downfield ($\Delta\delta \approx 46$ ppm) in comparison to the resonance observed in THF-d_8 (δ 177 ppm). This difference in chemical shift can be explained by THF coordination to the tin center with a concurrent increase of electron density at the metal, causing the observed high-field shift of the ^{119}Sn{^{1}H} resonance in THF-d_8. This observation is consistent with previous ^{119}Sn{^{1}H} NMR studies on *N,N*′-dialkylbenzimidazolin-2-stannylenes, where also a high-field shift of the ^{119}Sn{^{1}H} resonance in ether solvents in comparison to hydrocarbon solvents was observed.[8d] In addition to the NMR studies, all new tetrylenes were analyzed by mass spectrometry. All germylenes **2a−d** and stannylenes **3a,b** exhibit strong peaks for the molecular ions and for typical fragmentation products [M − (Ge or Sn)]$^+$ with the correct isotope distribution.

Single crystals suitable for an X-ray diffraction study were obtained by cooling of a saturated *n*-hexane solution of compound **2a** to −30 °C. Germylene **2a** crystallizes as transparent yellow prisms. The asymmetric unit contains eight essentially identical molecules of **2a**. One molecule of **2a** is depicted in Figure 2.

In the solid state, germylene **2a** exists as monomers which do not maintain any intermolecular interactions. This behavior differs from that of various other benzannulated N-heterocyclic germylenes, which have been shown to form higher oligomers in the solid state by interaction of the ring nitrogen atoms with neighboring Lewis acidic germanium(II) centers.[7c,d,h] The Ge1−N1

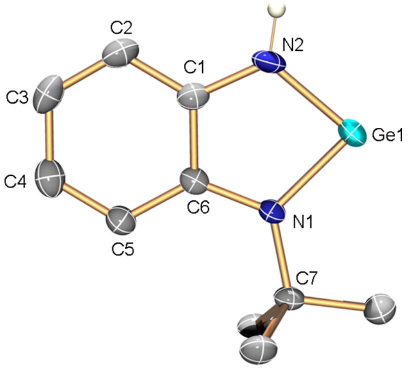


Figure 2. Molecular structure of one molecule of germylene **2a** in the asymmetric unit (50% displacement ellipsoids, hydrogen atoms, except for the N−H hydrogen atom, omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge1−N1 1.878(2), Ge1−N2 1.836(3), N1−C6 1.397(4), N1−C7 1.488(4), N2−C1 1.380(4); N1−Ge1−N2 84.39(11), Ge1−N1−C6 114.0(2), Ge1−N2−C1 114.5(2).

distance involving the alkylated ring nitrogen atom measures 1.878(2) Å and falls in the range observed for equivalent bonds in *N,N′*-dialkylbenzimidazolin-2-germylenes.[7] The bond distance Ge1−N2 involving the protonated ring nitrogen atom is slightly shorter (1.836(3) Å). The N1−Ge1−N2 angle (84.39(11)°) also falls in the range observed previously for *N,N′*-dialkylbezimidazolin-2-germylenes,[7] confirming that the substitution of one *N*-alkyl substituent for a hydrogen atom does not change the overall geometry of the germylene significantly. Both ring nitrogen atoms are surrounded in a trigonal-planar fashion.

Next we determined the molecular structure of stannylene **3a** (Figure 3). Single crystals of **3a** were obtained from a saturated THF solution of the compound by cooling to −30 °C. In contrast to the identical NH-N*t*Bu-substituted germylene **2a**, stannylene **3a** forms a dimer in the solid state, which cocrystallizes with one molecule of THF. Dimerization of two molecules of **3a** is achieved by two intermolecular Sn···N interactions involving the protonated ring nitrogen atoms. The intramolecular Sn−N distances (Sn1−N1 2.1510(11) Å, Sn1−N2 2.1194(11) Å, Sn2−N3 2.1838(10) Å, Sn2−N4 2.1464(10) Å) fall in the range normally observed for N,N′-dialkylated benzimidazolin-2-stannylenes[8] and are only about 0.2 Å shorter than the intermolecular Sn−N separations (Sn1−N3 2.3266(11) Å, Sn2−N1 2.3471(11) Å). We take this as an indication of the presence of strong intermolecular interactions between the stannylenes. While the nonaggregated germylene **2a** features a short N(H)−Ge and a longer N(*t*Bu)−Ge bond, the opposite situation was found for the dimerized stannylene **3a** (long N(H)−Sn and short N(*t*Bu)−Sn bonds). Intermolecular coordination of the N(H) ring nitrogen atoms apparently leads to a lengthening of the intramolecular Sn−N bond lengths. In addition, a pyramidalization is observed for those ring nitrogen atoms, which coordinate to two Sn^{II} centers. Similar structural features have been observed for dimers formed from two N,N′-dialkylated benzimidazolin-2-stannylenes.[8d] Some additional intermolecular interactions between the dimer $(\mathbf{3a})_2$ with the aromatic π system of a neighboring dimer (Sn···centroid distances of the phenyl group of a neighboring dimer 3.492−3.583 Å) have also been noted, in accord with previous observations for benzimidazolin-2-stannylenes.[8b]

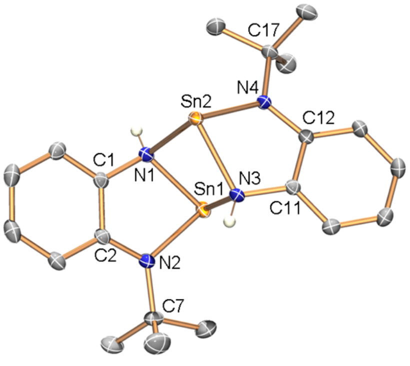
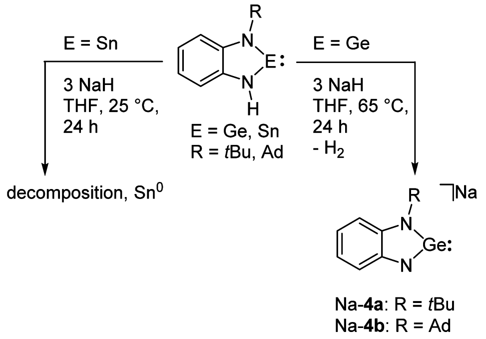


Figure 3. Molecular structure of the dimer $(\mathbf{3a})_2$ in $(\mathbf{3a})_2\cdot$THF (50% displacement ellipsoids, hydrogen atoms, except for the N−H hydrogen atom, omitted for clarity). Selected bond lengths (Å) and angles (deg): Sn1−N1 2.1510(11), Sn1−N2 2.1194(11), Sn1−N3 2.3266(11), Sn2−N3 2.1838(10), Sn2−N4 2.1464(10), Sn2−N1 2.3471(11), N1−C1 1.432(2), N2−C2 1.387(2), N2−C7 1.479(2), N3−C11 1.421(2), N4−C12 1.390(2), N4−C17 1.477(2); N1−Sn1−N2 79.13(4), N1−Sn1−N3 88.59(4), N3−Sn2−N4 79.13(4), N3−Sn2−N1 88.59(4), Sn1−N1−C1 111.49(8), Sn1−N2−C2 114.68(8), Sn2−N3−C11 110.53(8), Sn2−N4−C12 113.34(7).

Next the deprotonation of protic benzimidazolin-2-germylenes and stannylenes was attempted. Germylenes **2a**,**b** and stannylenes **3a**,**b** were selected for the deprotonation reaction, since they could be prepared in high yields. Germylenes **2a**,**b** react with NaH as a base in THF at 65 °C to give the germylenes Na-**4a** and Na-**4b** as gray-yellow salts, each featuring an N-deprotonated germylenide anion (Scheme 3).

Scheme 3. Deprotonation of Protic Benzimidazolin-2-germylenes and -stannylenes



However, the same reaction performed with stannylenes **3a**,**b** (at slightly lower temperature to prevent decomposition of the temperature-sensitive stannylenes) did not yield the anionic stannylenes but led to decomposition of the starting materials **3a**,**b** with release of elemental tin. We have noticed previously that otherwise identical Ge^{II} and Sn^{II} compounds react differently under reducing conditions, as observed in the reaction of $M[N(SiMe_3)_2]_2$ (M = Ge^{II}, Sn^{II}) with electron-rich 1,2,4,5-tetrakis(alkylamine)benzenes. In this reaction, the Ge^{II} precursor yielded the expected benzobis(germylene), while the Sn^{II} precursor reacted with oxidation of the electron-rich ligand.[7g] A similar oxidation of the deprotonated *o*-phenylenediamine ligand might also be responsible for the instability of the deprotonated stannylenes.

The ^1H NMR spectra of the protic germylene **2b** (in red) and the product of deprotonation Na-**4b** (in green), both measured in THF-d_8, are depicted in Figure 4 for comparison. The NH resonance at δ 9.47 ppm is clearly visible in the spectrum

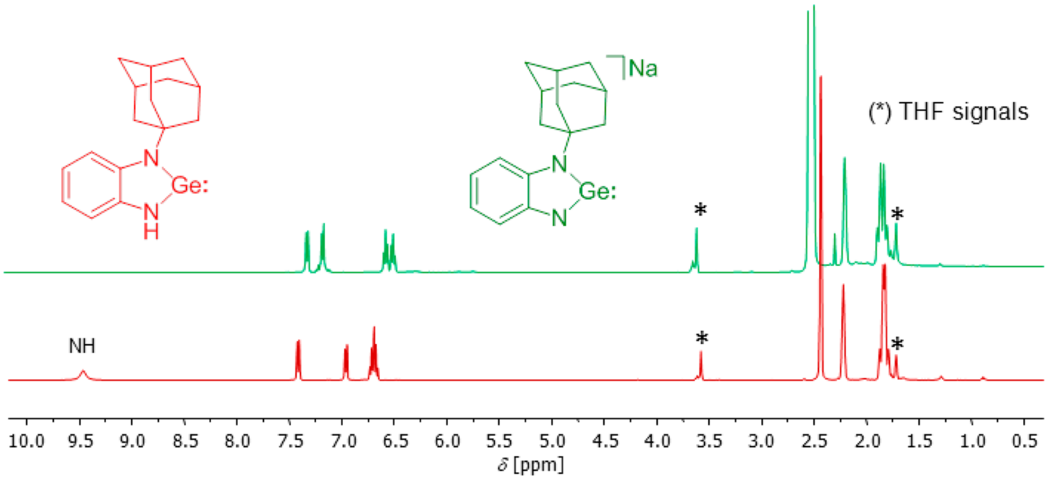
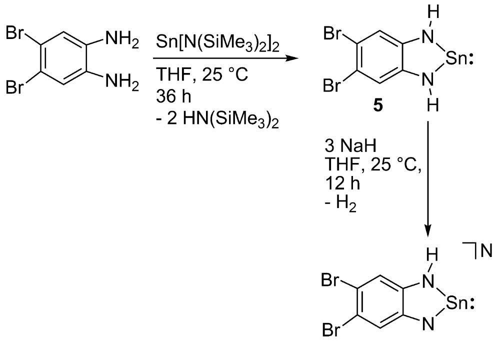


Figure 4. ^{1}H NMR spectra of **2b** (in red) and Na-**4b** (in green) measured in THF-d_8.

of **2b**, but no resonance in this region can be detected in the spectrum of Na-**4b**, confirming the successful deprotonation. In addition, the aromatic signals are shifted to high field upon deprotonation, obviously a consequence of the increased electron density in the ligand scaffold. In addition, the ^{13}C{^{1}H} NMR spectrum of compound Na-**4b** shows a noteworthy downfield shift of both ipso carbon signals (*δ* 158.8, 145.6 ppm in THF-d_8) in comparison to the signals for **2b** (*δ* 145.4, 139.9 ppm in THF-d_8).

In order to stabilize a deprotonated benzimidazolin-2-stannylene, electron-withdrawing bromide substituents were introduced to the aromatic ring. The compound 5,6-dibromobenzimidazolin-2-stannylene (**5**) was synthesized from the known 4,5-dibromo-*o*-phenylenediamine[16] by a transamination reaction with $Sn[N(SiMe_3)_2]_2$ (Scheme 4).

Scheme 4. Synthesis of Stannylene 5 and Deprotonation of 5 To Give Na-6



5

Na-**6**

Stannylene **5** was obtained as a yellow solid which is insoluble in *n*-hexane and toluene and only sparingly soluble in THF.

In contrast to the decomposition observed during the deprotonation of **3a**,**b** with NaH, the reaction of **5** with NaH in THF gave the monodeprotonated stannylene Na-**6**·THF as an extremely air sensitive gray powder in 61% yield. As intended, the introduction of the electron-withdrawing bromide substituents stabilized the deprotonated stannylene. The salt Na-**6** was completely characterized by NMR spectroscopy and microanalytical data. In the ^{1}H NMR spectrum of Na-**6** only one signal for the aromatic protons was observed. This would indicate a fast exchange of the remaining NH proton between the two nitrogen atoms on the NMR time scale. The resonance for the NH proton was observed upfield at *δ* 3.59 ppm in comparison to the NH resonance for **5** (*δ* 4.20 ppm). The deprotonation of **5** leads to a drastic change in the ^{119}Sn{^{1}H} NMR spectrum. Upon deprotonation, the resonance for the tin atom shifts from *δ* 57 ppm in **5** to *δ* −326 ppm in Na-**6**. This drastic shift clearly illustrates the electron-rich nature of the anion **6**$^-$ and a delocalization of the negative charge over the N−Sn−N moiety.

Crystals of (Na-**4a**)$_2$·4THF were obtained for a concentrated THF solution of Na-**4a** at ambient temperature. The molecular structure (Figure 5) shows a centrosymmetric dimer linked by a four-membered N_2Na_2 ring. The sodium atoms of the central four-membered ring are coordinated in a tetrahedral fashion by the deprotonated nitrogen atoms of two germylenes and by the oxygen atoms of two THF molecules. After N-deprotonation the Ge−N2 bond becomes significantly shorter (1.810(2) Å) than the Ge−N1 bond (1.905(2) Å), in spite of the fact that

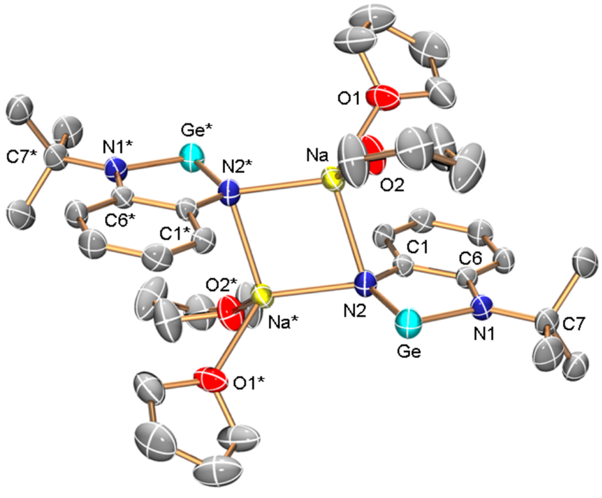


Figure 5. Molecular structure of (Na-**4a**)$_2$·4THF (50% displacement ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge−N1 1.905(2), Ge−N2 1.810(2), N2−Na 2.450(2), N2−Na* 2.337(2), N1−C6 1.387(3), N1−C7 1.479(3), N2−C1 1.374(3); N1−Ge−N2 88.80(8), Ge−N1−C6 110.46(14), Ge−N1−C7 126.66(14), Ge−N2−C1 110.74(14), Na−N2−Na* 82.86(7).

N1 binds to four partners while N2 only maintains three bonds. Electrostatic interactions between the deprotonated ring nitrogen atom and the Ge^{II} center appear responsible for this bond shortening. Ring nitrogen atom N1 adopts a trigonal-planar geometry. The N1−Ge−N2 angle is 88.80(8)° and is slightly larger than that in the protonated N-heterocyclic germylene **2a** (N1−Ge1−N2 84.39(11)°). Upon deprotonation, the intra-ring Ge−N−C angle at the deprotonated ring nitrogen atom (Ge−N2−C1 110.74(14)°) does not significantly differ from the intra-ring Ge−N−C angle at the alkylated ring nitrogen atom (Ge−N1−C6 110.46(14)°).

Given the presence of a basic deprotonated ring nitrogen atom and a Lewis acidic Ge^{II} center in Na-**4a**, it appeared attractive to utilize deprotonated N-heterocyclic tetrylenes as frustrated Lewis pairs. This would, however, require the liberation of the basic nitrogen center by removal of the sodium cation. All attempts to prepare a free anionic N-heterocyclic germylene by the reaction of Na-**4a** with crown ethers or cryptands have so far led to decomposition of the compound. Preliminary DFT calculations (B3LYP/6-31G(d) level) on the anion **4a**$^-$ (without an Na atom) have shown that an anionic tetrylene of type **4a**$^-$ would feature negatively charged ring nitrogen atoms. The LUMO in compounds of type **4a**$^-$ is the electrophilic empty p orbital at the Ge^{II} center, which is still available in spite of the increased electron density in the heterocycle due to N-deprotonation.

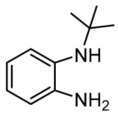
■ CONCLUSIONS

We have prepared the protic N-heterocyclic germylenes **2a**−**d** and stannylenes **3a**,**b**. The deprotonation of protic germylenes with NaH leads to compounds containing new anionic germylenes in the salts Na-**4a** and Na-**4b**. While a similar N-deprotonation with the protic stannylenes **3a**,**b** gave only decomposition products and elemental tin, the use of electron-poor 5,6-dibromo-substituted benzannulated N-heterocyclic stannylenes such as **5** allowed the N-deprotonation and yielded the salt Na-**6**. Deprotonated N-heterocyclic germylenes and stannylenes might lead to new FLPs with a Lewis basic site located at the one of the ring nitrogen atoms and a Lewis acidic site at the E^{II} atom, provided that the anionic tetrylene can be separated from the cation present. Corresponding investigations are in progress.

■ EXPERIMENTAL SECTION

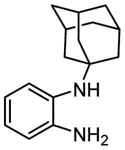
General Procedures. If not noted otherwise, all reactions were carried out under an argon atmosphere using conventional Schlenk techniques or in a glovebox. Solvents were dried and freshly distilled by standard procedures prior to use. NMR spectra were recorded at ambient temperature with Bruker AC 200, Bruker AVANCE I 400, and Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent (^{1}H NMR) or Me_4Sn (^{119}Sn NMR) as an internal standard. EI mass spectra were obtained with a Finnigan MAT 95 spectrometer. Bis[bis(trimethylsilyl)amido]tin(II),[15] bis[bis(trimethylsilyl)-amido]germanium(II),[15] and 5,6-dibromo-*o*-phenylenediamine[16] were prepared by published procedures. Compounds **1a**,[14a,b] **1c**,[14d,e] and **1d**[14f,g] were prepared by the reaction of 1-fluoro-2-nitrobenzene with the suitable primary amine and subsequent reduction of the nitro group with Raney Ni[14a] and hydrazine in methanol. Compound **1b** was prepared from *N*-(1-adamantyl)-2-nitroaniline, followed by reduction with hydrazine and Raney Ni in dry methanol. The preparation and spectroscopic data for the precursor compound *N*-(1-adamantyl)-2-nitroaniline have been previously reported.[14c] Satisfactory elemental analyses of compounds **2b**,**d**, **3a**,**b**, and **5** were difficult to obtain due to the sensitivity of the compounds toward oxygen and moisture. A complete set of NMR spectra is provided in the Supporting Information instead.

Synthesis of *N*-(*tert*-Butyl)-1,2-diaminobenzene (1a).



The preparation of compound **1a** has been described in the literature,[14a,b] but no NMR spectroscopic data are available. Therefore, we report here the ^{1}H NMR spectrum of **1a**. ^{1}H NMR (400 MHz, C_6D_6): δ 6.91−6.83 (m, 2H, Ar-H), 6.80−6.75 (m, 1H, Ar-H), 6.53−6.50 (m, 1H, Ar-H), 3.03 (s br, 3H, NH), 1.10 ppm (s, 9H, CH_3)).

Synthesis of *N*-(1-Adamantyl)-1,2-diaminobenzene (1b).

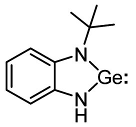


A suspension of 1-fluoro-2-nitrobenzene (1.5 g, 10.6 mmol), KF (0.7 g, 12.0 mmol), and 1-adamantylamine (1.6 g, 10.6 mmol) in dry DMF (3 mL) was sealed in a Young tube under argon and heated to 170 °C for 12 h. Subsequently, the orange reaction mixture was poured into a saturated aqueous NH_4Cl solution (40 mL) and extracted with ethyl acetate (3 × 40 mL). The organic layer was washed twice with H_2O and then dried over $MgSO_4$. Evaporation of the solvent gave orange crystals of *N*-(1-adamantyl)-2-nitroaniline (2.73g, 10.0 mmol, 94%). The spectroscopic data were identical with those reported in the literature.[14c]

A sample of *N*-(1-adamantyl)-2-nitroaniline (1.1 g, 4.04 mmol) and hydrazine hydrate (1.0 mL, 16.1 mmol) were dissolved in dry methanol (20 mL) under argon at 0 °C. Then a catalytic amount of Raney Ni was added (100 mg). At this point a vigorous dihydrogen evaluation was observed. The reaction mixture was slowly brought to room temperature, and the stirring was continued for 24 h. Then all solids were removed by filtration. Removal of the solvent in vacuo gave analytically pure **1b**. Yield: 0.96 g (3.96 mmol, 98%) of colorless crystals. ^{1}H NMR (400 MHz, C_6D_6): δ 6.93 (td, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.4 Hz, 1H, Ar-H5), 6.88 (dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.4 Hz, 1H, Ar-H6), 6.76 (td, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.4 Hz, 1H, Ar-H4), 6.55 (dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.4 Hz, 1H, Ar-H3), 3.14 (s br, 3H, NH-Ad and NH_2), 1.94−1.88 (m, 3H, Ad-H), 1.72−1.68 (m, 6H, Ad-H), 1.54−1.42 ppm (m, 6H, Ad-H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 143.27, 131.72 (Ar-C_{ipso}), 126.27, 123.75, 118.19, 115.99 (Ar-C), 53.11 (Ad-C_q), 43.40, 36.55, 29.91 ppm (Ad-C). MS (EI): m/z (%) 242 (100) [**1b**]$^+$.

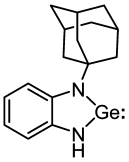
General Procedure for the Preparation of the Germylenes 2a−d and Stannylenes 3a,b. A sample of bis[bis(trimethylsilyl)amido]-germanium(II) ($Ge[N(SiMe_3)_2]_2$; 0.393 g, 1.0 mmol), or bis[bis-(trimethylsilyl)amido]tin(II) ($Sn[N(SiMe_3)_2]_2$; 0.439 g, 1.0 mmol) was added to a solution of one of the *N*-aryl- or *N*-alkyldiamines **1a**−**d** (1.0 mmol) in dry toluene (10 mL). The reaction mixture was stirred for 48 h at ambient temperature. Subsequently, the solvent and the volatile $HN(SiMe_3)_2$ were removed in vacuo. For compounds **2b**,**d** and **3a**,**b**, solids were obtained which were each washed three times with *n*-hexane (2 mL) and recrystallized from toluene (**2b**,**d**) or THF (**3a**,**b**). Compounds **2a**,**c** were isolated as brown oils, and **2a** was recrystallized from *n*-hexane at −30 °C.

*Synthesis of N-H,N′-tert-Butylbenzimidazolin-2-germylene (**2a**).*



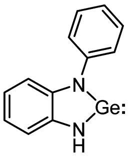
The crude reaction product was recrystallized from *n*-hexane (3 mL) at −30 °C. Yield: 0.214 g (0.91 mmol, 91%) of orange-yellow crystals. ^{1}H NMR (400 MHz, C_6D_6): δ 7.40 (s br, 1H, NH), 7.31−7.27 (m, 1H, Ar-H), 7.02−6.93 (m, 2H, Ar-H), 6.84−6.80 (m, 1H, Ar-H), 1.54 ppm (s, 9H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 144.3, 139.9 (Ar-C_{ipso}), 118.1, 117.9, 114.3, 113.8 (Ar-C), 56.2 ($C(CH_3)_3$), 32.3 ppm ($C(CH_3)_3$). MS (EI): *m*/*z* (%) 236 (83) [**2a**]$^+$, 221 (65) [**2a** − CH_3]$^+$, 180 (28) [**2a** − *t*Bu + H]$^+$, 164 (100) [**2a** − Ge + 2H]$^+$. Anal. Calcd for **2a** ($C_{10}H_{14}N_2Ge$): C, 51.14; H, 6.01; N, 11.93. Found: C, 50.94; H, 6.03; N 11.87.

*Synthesis of N-H,N′-Adamantylbenzimidazolin-2-germylene (**2b**).*



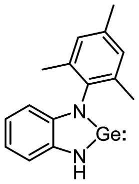
Yield: 0.260 g (0.83 mmol, 83%) of orange crystals. ^1H NMR (400 MHz, C_6D_6): δ 7.54−7.51 (m, 1H, Ar-H), 7.48 (s br, 1H, NH), 7.03−6.95 (m, 2H, Ar-H), 6.87−6.83 (m, 1H, Ar-H), 2.32−2.29 (m, 6H, Ad-H), 1.98 (s br, 3H, Ad-H), 1.57−1.54 ppm (m, 6H, Ad-H). ^1H NMR (400 MHz, THF-d_8): δ 9.47 (s br, 1H, NH), 7.43−7.41 (m, 1H, Ar-H), 6.97−6.95 (m, 1H, Ar-H), 6.72−6.68 (m, 2H, Ar-H), 2.44 (m, 6H, Ad-H), 2.22 (s br, 3H, Ad-H), 1.89−1.78 ppm (m, 6H, Ad-H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 144.4, 139.3 (Ar-C_{ipso}), 118.0, 117.8, 114.8, 114.1 (Ar-C), 57.8 (Ad-C_q), 45.7, 36.9, 30.5 ppm (Ad-C). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ 145.4, 139.9 (Ar-C_{ipso}), 117.9, 117.6, 114.8, 114.1 (Ar-C), 58.2 (Ad-C_q), 46.4, 37.6, 31.5 ppm (Ad-C). MS (EI): *m*/*z* (%) 314 (100) [**2b**]$^+$.

*Synthesis of N-H,N′-Phenylbenzimidazolin-2-germylene (**2c**).*



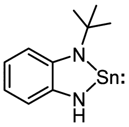
Yield: 0.155 g (0.63 mmol, 61%) of a viscous red-brown oil. ^1H NMR (400 MHz, C_6D_6): δ 7.32 (s br, 1H, NH), 7.20−7.11 (m, 5H, Ph-H), 7.05−6.99 (m, 1H, Ar-H), 6.97−6.91 (m, 1H, Ar-H), 6.90−6.84 (m, 1H, Ar-H), 6.80−6.74 ppm (m, 1H, Ar-H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 142.2, 140.9 (Ar-C_{ipso}), 129.6, 126.3, 125.7, 119.2, 119.1, 113.4, 111.1 ppm (Ar-C and Ph-C). The resonance for the *N*-phenyl-C_{ipso} carbon atom was not observed. MS (EI): *m*/*z* (%) 256 (100) [**2c**]$^+$.

*Synthesis of N-H,N′-Mesitylbenzimidazolin-2-germylene (**2d**).*



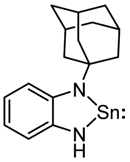
Yield: 0.193 mg (0.65 mmol, 65%) of orange needles. ^1H NMR (400 MHz, C_6D_6): δ 7.65 (s br, 1H, NH), 6.99−6.94 (m, 1H, Ar-H), 6.88 (s, 2H, Mes-H), 6.87−6.82 (m, 2H, Ar-H), 6.58−6.53 (m, 1H, Ar-H), 2.20 (s, 3H, CH_3), 1.93 ppm (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 141.5, 140.9 (Ar-C_{ipso}), 135.8, 135.3 (Mes-C-CH_3), 129.6, 119.4, 119.0, 113.0, 110.5 (Ar-C and Mes-C), 21.0, 18.1 ppm (CH_3). The resonance for the N-mesityl-C_{ipso} carbon atom was not observed. MS (EI): *m*/*z* (%) 298 (100) [**2d**]$^+$.

*Synthesis of N-H,N′-tert-Butylbenzimidazolin-2-stannylene (**3a**).*



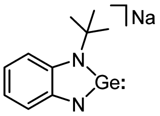
The crude reaction product was recrystallized from a saturated THF solution to give orange crystals. Yield: 239 mg (0.85 mmol, 85%). ^1H NMR (400 MHz, C_6D_6): δ 7.12−7.04 (m, 1H, Ar-H), 6.95−6.87 (m, 1H, Ar-H), 6.79−6.72 (m, 1H, Ar-H), 6.68−6.62 (m, 1H, Ar-H), 5.44 (s, br, 1H, NH) 1.45 ppm (s, 9H, CH_3). ^1H NMR (400 MHz, THF-d_8): δ 7.40 (s, br, 1H, NH), 7.00−6.96 (m, 1H, Ar-H), 6.73−6.68 (m, 1H, Ar-H), 6.57−6.51 (m, 1H, Ar-H), 6.44−6.38 (m, 1H, Ar-H), 1.72 ppm (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ 146.9, 144.1 (Ar-C_{ipso}), 116.2, 115.0, 114.4, 113.7 (Ar-C), 55.4 ($C(CH_3)_3$), 32.2 ppm ($C(CH_3)_3$). $^{119}Sn\{^1H\}$ NMR (149 MHz, C_6D_6): δ 223 ppm. $^{119}Sn\{^1H\}$ NMR (149 MHz, THF-d_8): δ 177 ppm. MS (EI): *m*/*z* (%) 282 (100) [**3a**]$^+$, 267 (34) [**3a** − CH_3]$^+$, 226 (10) [**3a** + H − *t*Bu]$^+$. 164 (59) (100) [**3a** + 2H − Sn]$^+$.

*Synthesis of N-H,N′-Adamantylbenzimidazolin-2-stannylene (**3b**).*



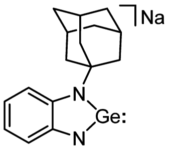
Yield: 352 mg (0.98 mmol, 98%) of a yellow solid. ^1H NMR (400 MHz, THF-d_8): δ 7.96 (s br, 1H, NH), 7.16−7.13 (m, 1H, Ar-H), 6.74−6.68 (m, 1H, Ar-H), 6.48−6.35 (m, 2H, Ar-H), 2.40−2.36 (m, 6H, Ad-H), 2.21 (s br, 3H, Ad-H), 1.86−1.75 ppm (m, 6H, Ad-H). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ 116.2, 115.8, 115.7, 115.2 (Ar-C), 57.9 (Ad-C_q), 47.2, 37.9, 31.7 ppm (Ad-C). Due to the poor solubility of **3b**, the two Ar-C_{ipso} signals could not be detected. $^{119}Sn\{^1H\}$ NMR (149 MHz, THF-d_8): δ 183 ppm. MS (EI): *m*/*z* (%) 360 (100) [**3b**]$^+$.

Synthesis of Sodium *N*,*N*′-(*tert*-Butyl)benzimidazolin-2-germylenide (Na-4a).



A Schlenk flask was flame-dried and then charged under argon with germylene **2a** (100 mg, 0.426 mmol) and an excess of NaH (0.031 g, 1.292 mmol). Subsequently dry THF (5 mL) was added and the resulting orange-yellow suspension was stirred at 65 °C for 24 h. Over that period the suspension turned to brown-black. The solvent was then removed in vacuo, and the resulting brown residue was washed with *n*-hexane (2 mL) and was then taken up in toluene (4 mL) and a small amount of THF (0.5 mL). Unreacted NaH was removed by filtration over Celite, leaving a clear dark-brown solution. Removal of solvents gave Na-**4a**·0.5THF as a yellow solid. This solid was recrystallized by slow evaporation of the solvent from a saturated THF solution at ambient temperature over 2 weeks to give $(Na\text{-}\mathbf{4a})_2\cdot 4THF$, which was subsequently characterized by an X-ray diffraction study. Yield: 57 mg of Na-**4a**·0.5THF (0.195 mmol, 46%) of yellow needles. ^1H NMR (400 MHz, THF-d_8): δ 7.15−7.03 (m, 2H, Ar-H), 6.56−6.44 (m, 2H, Ar-H), 1.76 ppm (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ 158.8, 146.3 (Ar-C_{ipso}), 117.1, 114.9, 114.0, 112.3 (Ar-C), 55.8 ($C(CH_3)_3$), 33.0 ppm ($C(CH_3)_3$). Anal. Calcd for Na-**4a**·0.5THF ($C_{12}H_{17}N_2GeNaO_{0.5}$): C, 49.21; H, 5.85; N, 9.56. Found: C, 50.32; H, 5.97, N, 9.19.

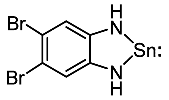
Synthesis of Sodium *N*,*N*′-Adamantylbenzimidazolin-2-germylenide (Na-4b).



Compound **Na-4b** was prepared as described for **Na-4a** from **2b** (80 mg, 0.256 mmol) and NaH (0.018 g, 0.768 mmol) in THF (5 mL). After filtration over Celite and removal of the solvents, Na-**4b** was obtained as a brown powder. This powder could also contain varying amounts of THF, depending on the lengths of drying in vacuo. Yield: 67 mg (0.200 mmol, 78% of the solvent-free compound). ^1H NMR (400 MHz, C_6D_6): δ 7.62−7.51 (m, 1H, Ar-H), 7.35−7.14 (m, 1H, Ar-H), 7.00−6.83 (m, 2H, Ar-H), 2.68 (s, 6H, Ad-H), 2.17 (s br, 3H, Ad-H), 1.86−1.65 ppm (m, 6H, Ad-H). ^1H NMR (400 MHz, THF-d_8): δ 7.31−7.27 (m, 1H, Ar-H), 7.16−7.12 (m, 1H, Ar-H), 6.57−6.44 (m, 2H, Ar-H), 2.50 (m, 6H, Ad-H), 2.21 (s br, 3H, Ad-H), 1.91−1.79 ppm (m, 6H, Ad-H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 156.8, 145.0 (Ar-C_{ipso}), 116.2, 115.1, 115.0, 113.2 (Ar-C), 57.0 (Ad-C_q), 45.8, 37.5, 31.0 ppm (Ad-C). $^{13}C\{^1H\}$ NMR (101 MHz, THF-d_8): δ

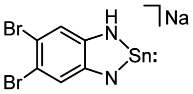
158.8, 145.6 (Ar-C_{ipso}), 117.4, 115.0, 113.9, 112.8 (Ar-C), 57.1 (Ad-C_q), 46.7, 38.2, 31.7 ppm (Ad-C). MS (EI): *m/z* (%) 314 (62) [**4b** + H]$^+$, 242 (100) [**4b** + H − Ge]$^+$.

Synthesis of *N*-H,*N*′-H-5,6-Dibromobenzimidazolin-2-stannylene (5).



Compound **5** was prepared in analogy to the synthesis of **3a**,**b** from Sn[N(SiMe$_3$)$_2$]$_2$ (0.220 g, 0.5 mmol) and 4,5-dibromo-*o*-phenylenediamine (0.133 g, 0.5 mmol) in THF (3 mL). The reaction was completed after 36 h. Yield: 182 mg (0.476 mmol, 95%) of yellow powder. ^{1}H NMR (400 MHz, THF-d_8): *δ* 6.78 (s, 2H, Ar-H), 4.20 ppm (s br, 2H, NH). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): *δ* 137.5 (Ar-C_{ipso}), 119.3 (Ar-C), 111.4 ppm (Ar-C−Br). ^{119}Sn{^{1}H} NMR (149 MHz, THF-d_8): *δ* 57 ppm. MS (EI): *m/z* (%) 382 (100) [**5**]$^+$, 266 (29) [**5** − Sn + 2H]$^+$.

Synthesis of Sodium *N*-H,*N*′-5,6-Dibromobenzimidazolin-2-stannylenide (Na-6).



A sample of stannylene **5** (0.100 g, 0.261 mmol) and an excess of NaH (0.019 g, 0.792 mmol) were mixed together in THF (5 mL) and stirred at ambient temperature under an atmosphere of argon. After a few minutes gas evolution was observed and the yellow suspension became dark. The reaction mixture was stirred for 12 h to complete the reaction. Subsequently, toluene (5 mL) was added. After filtration and removal of the solvent compound Na-**6**·THF was isolated as a gray solid. Yield: 76 mg (0.160 mmol, 61%). ^{1}H NMR (400 MHz, THF-d_8): *δ* 6.39 (s, 2H, Ar-H), 3.59 ppm (s br, 1H, NH). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): *δ* 145.6 (2 × Ar-C_{ipso}), 114.5 (2 × Ar-C), 105.9 ppm (2 × Ar-C-Br). ^{119}Sn{^{1}H} NMR (149 MHz, THF-d_8): *δ* −326 ppm. MS (EI): *m/z* (%) 266 (100) [**6** + 2H − Sn]$^+$. Anal. Calcd for Na-**6**·THF ($C_{10}H_{11}N_2Br_2NaOSn$): C, 25.19; H, 2.33; N, 5.88. Found: C, 24.84; H, 2.22; N, 6.02.

X-ray Crystallography. X-ray diffraction data for **2a**, (**3a**)$_2$·THF, and (Na-**4a**)$_2$·4THF were collected at *T* = 153(2) K with a Bruker APEX-II CCD diffractometer equipped with a rotating anode using monochromated Mo K*α* radiation (*λ* = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97[17] package using direct methods and were refined with SHELXL-97[17] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

*Crystal data and structure refinement details for **2a**:* $C_{10}H_{14}N_2Ge$, M_r = 234.82, yellow prism, 0.24 × 0.21 × 0.18 mm^3, triclinic, space group $P\bar{1}$, *Z* = 16, *a* = 15.5305(8) Å. *b* = 15.6850(8) Å, *c* = 18.5811(10) Å, *α* = 77.290(3)°, *β* = 73.985(3)°, *γ* = 89.962(3)°, *V* = 4235.3(4) Å^3, ρ_{calcd} = 1.473 g cm^{-3}, *μ* = 2.850 mm^{-1}, *ω* and *φ* scans, 74910 measured intensities (3.3° ≤ 2*θ* ≤ 62.5°), semiempirical absorption correction (0.526 ≤ *T* ≤ 0.746), 26338 independent (R_{int} = 0.0513) and 17413 observed intensities ($I \geq 2\sigma(I)$), refinement of 961 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. *R* = 0.0553, R_w = 0.1335, R_{all} = 0.0926, $R_{w,all}$ = 0.1489. The asymmetric unit contains eight molecules of **2a**. Multiple attempts to find a higher symmetry of the crystal lattice and a smaller unit cell did not yield any results.

*Crystal data and structure refinement details for (**3a**)$_2$·THF:* $C_{24}H_{36}N_4OSn_2$, M_r = 633.95, orange crystal, 0.40 × 0.17 × 0.09 mm^3, triclinic, space group $P\bar{1}$, *Z* = 2, *a* = 9.4975(2) Å, *b* = 12.3583(3) Å, *c* = 12.1682(5) Å, *α* = 72.8310(10)°, *β* = 68.3900(10)°, *γ* = 69.7310(10)°, *V* = 1267.60(5) Å^3, ρ_{calcd} = 1.661 g cm^{-3}, *μ* = 1.993 mm^{-1}, *ω* and *φ* scans, 21031 measured intensities (4.8° ≤ 2*θ* ≤ 58.3°), semiempirical absorption correction (0.503 ≤ *T* ≤ 0.841), 6807 independent (R_{int} = 0.0151) and 6533 observed intensities ($I \geq 2\sigma(I)$), refinement of 294 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. *R* = 0.0146, R_w = 0.0377, R_{all} = 0.0155, $R_{w,all}$ = 0.0383. The asymmetric unit contains two molecules of **3a** forming a dimer and one THF molecule.

*Crystal data and structure refinement details for (Na-**4a**)$_2$·4THF:* $C_{36}H_{58}N_4O_4Ge_2Na_2O_4$, M_r = 802.02, yellow crystal, 0.20 × 0.20 × 0.20 mm^3, monoclinic, space group $P2_1/m$, *Z* = 2, *a* = 8.6146(3) Å, *b* = 12.5729(4) Å, *c* = 18.9466(5) Å, *β* = 93.006(2)°, *V* = 2049.29(11) Å^3, ρ_{calcd} = 1.300 g cm^{-3}, *μ* = 1.527 mm^{-1}, *ω* and *φ* scans, 35465 measured intensities (3.9° ≤ 2*θ* ≤ 62.1°), semiempirical absorption correction (0.750 ≤ *T* ≤ 0.743), 6497 independent (R_{int} = 0.0409) and 4621 observed intensities ($I \geq 2\sigma(I)$), refinement of 269 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. *R* = 0.0413, R_w = 0.1173, R_{all} = 0.0710, $R_{w,all}$ = 0.1429. The asymmetric unit contains two molecules of Na-**4a** forming a dimer and four THF molecules coordinating to the sodium cations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR spectra of all new compounds and CIF files containg the X-ray crystallographic data for **2a**, (**3a**)$_2$·THF, and (Na-**4a**)$_2$·4THF. 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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