Preparation of Stable Low Oxidation State Group 14 Element Amidohydrides and Hydride-Mediated Ring-Expansion Chemistry of N-Heterocyclic Carbenes

S. M. Ibrahim Al-Rafia, Robert McDonald, Michael J. Ferguson, and Eric Rivard*^[a]

Abstract: Various low oxidation state (+2) group 14 element amidohydride adducts, IPr•EH(BH₃)NHDipp (E=Si or Ge; IPr=[(HCNDipp)₂C], Dipp=2,6iPr₂C₆H₃), were synthesized. Thermolysis of the reported adducts was investigated as a potential route to Si- and Ge-based clusters; however, unexpected transmetallation chemistry occurred to yield the carbene–borane adduct, IPr•BH₂NHDipp. When a solution of IPr•BH₂NHDipp in toluene was heated to 100 °C, a rare C–N bond-activation/ring-expansion reaction involving the bound N-heterocyclic carbene donor (IPr) transpired.

Introduction

The use of electron-donating N-heterocyclic carbenes (NHCs) to stabilize reactive main-group species is a rapidly expanding area of inorganic chemistry.^[1] In many instances, the resulting coordinative NHC-element interactions are of sufficient strength to enable the isolation of complexes featuring molecular entities that only exist as fleeting intermediates or were previously unknown altogether. For example, the recent isolation of stable molecular adducts of the parent compounds borylene (:BH)^[2] and disilylene (:Si=Si:)^[3] represents a synthetic breakthrough made possible by carbene coordination chemistry. In addition, NHC-BH3 adducts have recently been shown to be versatile precatalysts for the photoinduced radical polymerization of methacrylates.^[4] It is therefore important to uncover new decomposition or activation pathways involving N-heterocyclic carbene ligands due to their increasing supporting role in catalysis.

Recently, our group has prepared donor–acceptor adducts of the low-valent group 14 methylene and ethylene analogues IPr•EH₂•LA and IPr•H₂EEH₂•LA (E=Si, Ge, and Sn; IPr=[HCNDipp)₂C:]; Dipp=2,6-*i*Pr₂C₆H₃; LA=Lewis acid, such as BH₃ or W(CO)₅).^[5,6] These hydride complexes are promising precursors for the controlled synthesis of clusters and nanoparticles, as demonstrated by the clean formation of Ge metal from the solution-phase thermolysis of the germanium(II) dihydride adduct, IPr•GeH₂•BH₃.^[5a,7] The synthesis of Group 14 element clusters is highly desirable because they often contain new structural and bonding fea**Keywords:** amides • carbenes • hydrides • main-group elements • ring expansion

tures, while concurrently serving as models for the chemical transformations that occur at or near the surface of bulk materials.^[8] In addition, group 14 (tetrel) element particles of nanometer dimensionality have been shown to display useful electronic properties, such as tunable luminescence.^[9]

Over the years, a number of tetrel element clusters have been reported, and their syntheses have generally involved the reduction of RECl (R = aryl or amide group) precursors with alkali-metal-based reagents (e.g., KC₈).^[10] Power, Lappert, and co-workers have devised an alternate route to novel Sn₁₇ or Sn₇ clusters by the thermolysis of either in situ generated or isolable Sn^{II} hydrides, such as the metastable amide [(Me₃Si)NDipp]SnH or the room-temperature-stable species, $[Ar'Sn(\mu-H)]_2$ $(Ar'=(2,6-Dipp)_2C_6H_2).^{[11a,b]}$ In addition, Klinkhammer et al. have generated Pb clusters from the decomposition of putative PbII hydride intermediates.[11c] Drawing inspiration from this chemistry, we explored the preparation of N-heterocyclic carbene stabilized amidohydride complexes of the general form IPr•EHNHDipp (E= Si, Ge, or Sn) in order to access new clusters by mild and controllable thermolytic reaction pathways. In pursuit of this goal, we uncovered a new decomposition pathway involving the carbene-borane adduct IPr•BH₂NHDipp, which led to C-N bond activation and ring expansion of the generally inert donor, IPr. This discovery has widespread implications because IPr and related NHCs are often used as supporting ligands in catalysis.

Results and Discussion

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Low-valent group 14 element hydrides, REH (R=aryl or amide group) are often unstable and can readily decompose to give clusters.^[11] With this in mind, we targeted the preparation of the amidohydride–carbene adducts IPr•E(H)NH-Dipp (E=Si, Ge, and Sn) in order to access new cluster ar-

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chetypes (e.g., $IPr_x \cdot E_y$; x < y) upon controlled thermolysis. As an entry point for our studies, we synthesized the requisite E^{II} amidohalide precursors $IPr \cdot E(CI)NHDipp$ (E=Si, Ge, or Sn; **1–3**, respectively) by treating the known adducts, $IPr \cdot ECl_2$, with one equivalent of Li[NHDipp] in Et₂O [Equation (1)].

Although examples of Ge^{II} and Sn^{II} amides are common in the literature,^[12] compound **1** represents a rare example of a silicon(II) amide that is stable at ambient temperature.^[13] In the absence of sterically encumbered groups at the nitrogen atom, the free, heavy group 14 chloroamines E(CI)N(H)R (E=Ge or Sn) have a tendency to spontaneously oligomerize and/or participate in further condensation chemistry.^[14] However, the presence of σ -donating carbenes in compounds **1–3** results in occupation of the initially vacant p orbitals at the group 14 centers, thereby suppressing oligomerization of the target E(CI)N(H)R units.

Compounds 1–3 (IPr·E(Cl)NHDipp; E = Si, Ge, or Sn) were isolated as air- and moisture-sensitive yellow solids in 45, 98, and 85% yields, respectively. The formation of adducts 1-3 was confirmed by elemental analysis and NMR and IR spectroscopy. The ¹H NMR data of these complexes exhibit similar spectral features, with well-resolved singlet resonances belonging to the N-H groups at $\delta = 4.14, 4.11$, and 3.82 ppm for 1-3, respectively. Moreover, each of the six $-CH_3$ groups in compounds 1-3 exists in a magnetically distinct environment, reflecting the presence of a high degree of intramolecular crowding in these chloroamide complexes. Compound 1 yields a ²⁹Si NMR signal at $\delta =$ -6.0 ppm, which is positioned upfield relative to the ²⁹Si NMR resonance of the Si^{II} precursor, IPr•SiCl₂ ($\delta =$ 19.1 ppm).^[15] The tin(II) amide IPr·Sn(Cl)NHDipp 3 displays a similar ¹¹⁹Sn NMR resonance ($\delta = -96.2$ ppm) to the related, three-coordinate Sn^{II} adduct IPr·SnCl₂ ($\delta =$ -68.7 ppm).^[5a] The IR spectra for **1-3** corroborate the abovementioned NMR assignments; stretching frequencies belonging to the N-H residues are found in the narrow range of 3357 to 3371 cm⁻¹. Conclusive evidence for the formation of IPr·E(Cl)NHDipp (E = Si, Ge, or Sn; 1–3) was obtained by single-crystal X-ray crystallography, and the refined structures are collectively shown in Figure 1.

Compounds 1–3 are isostructural with distorted trigonalpyramidal geometries at each of the three-coordinate E centers (E=Si, Ge, or Sn). This is consistent with the presence of a stereochemically active lone pair at the tetrel element centers. Furthermore, each of the E–Cl bonds in 1–3 is oriented towards the steric cradle that is created by the flanking Dipp groups of the IPr donors. The C_{IPr}–Si bond length in 1 (1.980(3) Å) is identical within experimental error to the corresponding distance in the Si^{II} adduct IPr·SiCl₂ (1.985(4) Å),^[15] but is significantly longer than the C_{IPr}–Si



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Figure 1. Molecular structures of IPr•E(Cl)NHDipp (E=Si, Ge, or Sn; 1-3) with thermal ellipsoids presented at the 30% probability level. All carbon-bound hydrogen atoms and solvate molecules have been omitted for clarity. For compound 2 only one of the two molecules in the asymmetric unit is shown; parameters for the second molecule are listed in square brackets. Selected bond lengths [Å] and angles [°]: Compound 1: Si-C(1) 1.980(3), Si-N(3) 1.765(2), Si-Cl 2.2463(11), N(3)-C(51) 1.433(3); N(1)-C(1)-N(2) 103.7(2), Cl-Si-N(3) 101.87(9), Cl-Si-C(1) 89.88(8), N(3)-Si-C(1) 98.49(11), Si-N(3)-C(51) 118.64(18). Compound 2: Ge(1A)-C(1A) 2.103(3) [2.093(3)], Ge(1A)-N(3A) 1.903(3) [1.897(2)], Ge(1A)-Cl(1A) 2.3548(9) [2.3632(9)], N(3A)-C(51A) 1.419(4) [1.420(4)]; Cl(1A)-Ge(1A)-N(3A) 99.05(8) [98.23(8)], Cl(1A)-Ge(1A)-C(1A) 88.96(8) [90.14(8)], N(3A)-Ge(1A)-C(1A) 96.14(11) [96.81(11)], Ge(1A)-N(3A)-C(51 A) 117.9(2). Compound 3: Sn-C(1) 2.3220(19), Sn-N(3) 2.1142(16), Sn-Cl(1) 2.4898(6), N(3)-C(51) 1.403(2); Cl-Sn-N(3) 95.21(5), Cl-Sn-C(1) 89.59(5), N(3)-Sn-C(1) 94.83(6), Sn-N(3)-C(51) 116.53(12).

interactions in the Robinson adducts IPr•(Cl)Si=Si(Cl)•IPr (1.934(6) Å) and IPr•SiCl₄ (1.928(2) Å).^[3] In the heavier-element congeners 2 and 3, the respective C_{IPr}-Ge (2.098(4) Å average) and C_{IPr}-Sn (2.3220(19) Å) bond lengths are very similar to values found in the progenitor GeII and SnII compounds, IPr·GeCl₂ and IPr·SnCl₂ (C_{IPr}-Ge=2.112(2), C_{IPr}-Sn = 2.341(8) Å).^[5a] The Si-N bond length in **1** (1.765(2) Å) is marginally longer than the Si-N bond lengths present in the Roesky dimeric silaisonitrile, {[(2,4,6 $iPr_{3}C_{6}H_{2})_{2}C_{6}H_{3}NSi_{2}$ (1.756(1) Å average).^[16] Similarly, the E-N (E=Ge or Sn) bond lengths in 2 and 3 are 1.900(3) Å (average) and 2.1142(16) Å, respectively, and are within the range that is expected for single bonds. For comparison, the Ge-N bonds in the acyclic GeII bisamide (Ar"NH)2Ge: $(Ar'' = 2,6-(2,4,6-Me_3C_6H_2)_2C_6H_3)$ are 1.896(2) Å, whereas



an average Sn–N separation of 2.101(3) Å exists in the tin congener $(Ar''NH)_2Sn$ ^[17] As expected, the C_{IPr}-E-N angles in **1–3** become narrower as the group 14 element becomes heavier, decreasing from a value of 98.49(1)° in **1** to 94.83(6)° in **3**.

We have recently shown that the halide substituents in the carbene-bound E^{II} dihalides, $IPr \cdot ECl_2$ (E = Si, Ge, or Sn) can undergo clean chloride/hydride metathesis chemistry with Li[BH₄] or Li[AlH₄] to yield stable adducts with E–H bonds.^[5] Inspired by these previous studies, we anticipated that the reactions of complexes **1–3** with hydride sources could provide access to the desired carbene-bound amidohydrides IPr · EHNHDipp. These could then be thermolyzed to afford low-valent group 14 element clusters [IPr_xE_y] by the loss of H₂NDipp.^[11a]

The reaction of IPr·Si(Cl)NHDipp (1) with one equivalent of Li[BH₄] in Et₂O resulted in the formation of a mixture of the new compounds IPr·SiH(BH₃)NHDipp (4) and IPr·BH₂NHDipp (6; see below), and the known compounds IPr·BH₃^[18] and IPrH₂,^[5b] as summarized in Scheme 1. The



Scheme 1. Synthesis of the silicon(II) and germanium(II) amidohydride complexes IPr-EH(BH₃)NHDipp (E=Si or Ge; **4** and **5**).

silicon(II) hydride complex 4 was isolated in pure form (34% yield) by cooling a saturated solution of the crude product mixture in Et₂O/hexanes to -35°C. Initial evidence for the formation of IPr·SiH(BH₃)NHDipp (4) was obtained by ¹H NMR spectroscopy, in which a broad SiH resonance with resolvable flanking ²⁹Si satellites (${}^{1}J_{SiH} = 160.3$ Hz) was located at $\delta = 5.13$ ppm. The proximal amide proton in the -NHDipp group was detected as a doublet resonance at $\delta =$ 1.94 ppm (${}^{3}J_{HH}$ = 5.5 Hz), with the observed pattern resulting from the coupling of an NH hydrogen atom with the adjacent silicon-bound hydride. The presence of coordinated BH₃ in **4** was confirmed by ¹¹B NMR spectroscopy, which gave a quartet resonance at $\delta = -44.1$ ppm with an expected coupling constant of ${}^{1}J_{\rm BH} = 89.5$ Hz.^[5e,19] For comparison, the previously reported Si^{II} dihydride adduct IPr•SiH₂•BH₃ has a Si H_2 resonance at $\delta = 3.76$ ppm in the ¹H NMR spectrum, and a ¹¹B NMR quartet resonance at $\delta = -46.2$ ppm (¹J_{BH}= 93.0 Hz) due to the silylene-bound BH₃ group.^[5e] Consistent with the NMR data, the IR spectrum of 4 shows an absorption band at 3559 cm⁻¹ belonging to an N-H stretching vibration, along with broadened ^{10/11}B-H stretching modes from 2326 to 2237 cm⁻¹, and a sharp Si-H stretching band at 2096 cm⁻¹. The frequency of the Si–H vibration is identical within experimental error to the $\tilde{\nu}$ (Si–H) band observed in IPr·SiH₂·BH₃.^[5e]

Similarly, when the Ge^{II} chloroamide IPr•Ge(Cl)NHDipp (2) was reacted with $Li[BH_4]$, the formation of a new product, IPr·GeH(BH₃)NHDipp (5), was observed as a component of the product mixture that also contained IPr•BH₂NHDipp (6), IPr•BH₃, and IPrH₂ (as identified by ¹H, ¹³C{¹H}, and ¹¹B NMR spectroscopy). The boranecapped Ge^{II} hydride adduct IPr•GeH(BH₃)NHDipp (5) was isolated as an analytically pure solid by following a procedure similar to that used to obtain the silicon congener 4. The GeH unit in 5 appears as a broad singlet at $\delta =$ 5.66 ppm in the ¹H NMR spectrum, and the amide proton of the -NHDipp group shows a doublet resonance at $\delta =$ 1.97 ppm as a result of discernable coupling to a proximal GeH residue (${}^{3}J_{HH} = 6.5 \text{ Hz}$). As in IPr·SiH(BH₃)NHDipp (4), the BH₃ unit in 5 can be located by using 11 B NMR spectroscopy ($\delta = -39.1$ ppm). Similarly, the IR spectrum of **5** displays a characteristic N–H stretching vibration at $\tilde{\nu}$ = 3346 cm⁻¹, with expected ^{10/11}B-H and Ge-H stretching vibrations at $\tilde{\nu} = 2371 - 2253$ and 1997 cm⁻¹, respectively. The $\tilde{\nu}$ -(Ge-H) band in 5 is in the range expected for Ge^{II} compounds with terminal Ge-H bonds.^[5,20] Additional evidence for the formation of the silvlene and germylene borane adducts (4 and 5) was obtained by X-ray crystallography, and the molecular structures of these adducts are shown in Figure 2.



Figure 2. Molecular structures of IPr-SiH(BH₃)NHDipp (**4**) and IPr-GeH-(BH₃)NHDipp (**5**) with thermal ellipsoids presented at the 30% probability level. All carbon-bound hydrogen atoms and solvate molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Compound **4**: Si–C(1) 1.9431(15), Si–B 1.9760(19), Si–H 1.400(16), Si–N(3) 1.7680(14), N(3)–C(51) 1.422(2); N(3)-Si-C(1) 103.00(7), N(3)-Si-B 119.27(8), C(1)-Si-B 110.04(8), Si-N(3)-C(51) 120.63(13). Compound **5**: Ge–C(1) 2.020(2), Ge–B 2.032(3), Ge–H 1.53(2), Ge–N(3) 1.883(2), N(3)–C(51) 1.416(3); N(3)-Ge-C(1) 100.90(10), N(3)-Ge-B 119.36(12), C(1)-Ge-B 110.57(11), Ge-N(3)-C(51) 117.27(18).

IPr·SiH(BH₃)NHDipp (4) and IPr·GeH(BH₃)NHDipp (5) each represent formal donor–acceptor complexes of encapsulated, heavy group 14 amidohydride units, E(H)NHDipp, with the four-coordinated Si and Ge centers in 4 and 5 locat-

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ed within slightly canted transoid $C_{\mbox{\scriptsize IPr}}\mbox{-}E\mbox{-}N\mbox{-}C_{\mbox{\scriptsize Dipp}}$ bonding arrangements (torsion angles=177.58(13) and 177.98(19)°, respectively). The dative C_{IPr}-Si bond length in 4 is 1.9431(15) Å, which is considerably longer than the C_{IPr} -Si separation reported in the donor-acceptor adduct IPr•SiH₂•BH₃ (1.9284(15) Å).^[5e] Similar C_{IPr}–Si bond lengths to those of ${\bf 4}$ are found in the formal SiH_2 adduct IPr•SiH₂•BH₂-SiH(B₃H₇)•IPr (1.934(4) and 1.944(4) Å).^[19b] The adjacent Si-B bond length in 4 is 1.9760(19) Å and is in the range previously reported for silicon(II)-borane adducts that involve pseudotetrahedral geometries at silicon (1.965(2) to 1.996(4) Å).^[19,21] IPr·GeH(BH₃)NHDipp (5) adopts an analogous geometry to its Si^{II} congener, 4. The constituent C_{IPr}-Ge and Ge-B bond lengths in 5 are 2.020(2) and 2.032(3) Å, respectively, and are comparable to the C_{IPr}-Ge (2.0148(13) Å) and Ge-B (2.0567(18) Å) interactions in IPr•GeH₂•BH₃,^[5a] which suggests the presence of similar dative bonding interactions in 5.

Motivated by the above chemistry, we treated the tin(II) amide IPr·Sn(Cl)NHDipp (3) with one equivalent of Li-[BH₄] in Et₂O, and observed the rapid evolution of gas accompanied by the precipitation of metallic Sn. Analysis of the soluble fraction of the product mixture by ¹H NMR spectroscopy revealed the formation of IPr·BH₂NHDipp (6, 50% yield; see below), IPr·BH₃^[17] (37% yield), and IPrH₂^[5b] (13% yield), with no sign of the target hydridostannylene adduct IPr·SnH(BH₃)NHDipp (Scheme 2). Despite



Scheme 2. The formation of $IPr \cdot BH_2NHDipp$ (6) from the reaction of $IPr \cdot Sn(Cl)NHDipp$ (3) with $Li[BH_4]$.

the absence of a stable tin hydride product, the remaining species that were generated from the reaction were also formed during the synthesis of IPr•EH(BH₃)NHDipp (E=Si or Ge; **4** and **5**). The formation of similar products from the reaction of **3** with Li[BH₄] can be rationalized by the decomposition of a putative IPr•SnH(BH₃)NHDipp intermediate; although thus far, our attempts to identify this intermediate at low temperatures (e.g., -78 to 0° C) by NMR spectroscopy have been unsuccessful.

The soluble products formed from the reaction of IPr·Sn(Cl)NHDipp (3) with Li[BH₄] were identified by NMR spectroscopy, and the new amino-borane adduct IPr·BH₂NHDipp (6) was isolated as a pure, colorless solid by fractional crystallization from Et_2O (55% yield). The

¹H NMR spectrum of **6** shows a broad singlet at $\delta = 2.55$ ppm that is due to the boron-bound hydrogen atoms within the -BH₂NHDipp unit, and the -N*H* proton appears at $\delta = 1.64$ ppm. The -*B*H₂NHDipp residue in **6** gives a broad signal at $\delta = -16$ ppm in the proton-coupled ¹¹B NMR spectrum, with no resolvable coupling to hydrogen. The remaining IPr donor in **6** has ¹H and ¹³C{¹H} NMR spectroscopic features that are in line with a coordinated N-heterocyclic carbene. An N–H stretching band centered at 3402 cm⁻¹ is present in the IR spectrum of **6**, and lower frequency $\tilde{\nu}$ (B–H) stretching modes are found between 2310 and 2393 cm⁻¹. Cooling a solution of **6** in Et₂O/hexanes to -35 °C yielded crystals of suitable quality for single-crystal X-ray analysis, and the refined structure is presented in Figure 3. It is worth noting that our attempts to directly pre-

Figure 3. Molecular structure of IPr-BH₂NHDipp (6) with thermal ellipsoids presented at the 30 % probability level. All carbon-bound hydrogen atoms and solvate (Et₂O) molecules have been omitted for clarity. Only one molecule in the asymmetric unit is presented (molecule B), and parameters for a disordered BH₂NHDipp unit in molecule A are listed in square brackets. Selected bond lengths [Å] and angles [°]: molecule A: C(1)-B(1) 1.627(4) [1.627(4)], N(3)-B(1) 1.542(8) [1.541(8)], N(3)-C(51) 1.427(4) [1.427(4)]; N(3)-B(1)-C(1) 109.2(3) [108.7(5)], B(1)-N(3)-C(51) 118.1(6) [132.6(7)]. molecule B: C(1)-B(1) 1.626(3), N(3)-B(1) 1.534(3), N(3)-C(51) 1.426(3); N(3)-B(1)-C(1) 112.07(17), B(1)-N(3)-C(51) 116.70(17).

pare compound 6 in higher yields from the reaction of the haloborane adducts $IPr \cdot BH_2X$ (X = Cl or I)^[22] with Li-[NHDipp] were unsuccessful, and led only to the recovery of the starting materials.

IPr•BH₂NHDipp (6) adopts a transoid C_{IPr}-B-N-C_{Dipp} core in the solid state with an average C_{IPr}-B bond length of 1.627(5) Å between two crystallographically independent molecules. These interactions are longer than that in the diborane bisadduct IPr•H₂B-BH₂•IPr (1.577(2) Å),^[18] suggesting that a weaker C_{IPr}-B donor-acceptor interaction is present in 6. However, a similar C_{IPr}-B bond length exists in the structurally related four-coordinate azido-borane adduct IPr•BH₂N₃ (1.614(2) Å).^[22] The central B-N bond length in 6 is 1.538(8) Å (average), which is also comparable to the B-N separation found in IPr•BH₂N₃ (1.573(2) Å).^[22]

Occasionally, during the synthesis of $IPr\cdot BH_2NHDipp$ (6) from the reaction of the stannyl chloride adduct $IPr\cdot Sn(Cl)NHDipp$ (3) with $Li[BH_4]$, we noted the forma-

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tion of trace quantities (< 2% by ¹H NMR spectroscopy) of a new carbene-containing product. Given the existence of a lone pair on the nitrogen center in 6, and the likely presence of free borane in the reaction mixture, we posited that the amine-borane adduct IPr•BH₂NHDipp(BH₃) might be the unknown species that was formed. Therefore, we subsequently treated IPr•BH₂NHDipp (6) with a stoichiometric quantity of H₃B•THF to give the new complex $IPr \cdot BH_2 NHDipp(BH_3)$ (7) as a moisture-sensitive, colorless solid in 81% isolated yield. Importantly, the ¹H NMR spectrum of 7 matched that of the minor product that was produced from the reaction of 3 with Li[BH₄], thus confirming our original postulate. In addition to resonances belonging to the IPr and NHDipp groups in 7, two broad resonances due to the -BH₂ and -BH₃ groups were observed at $\delta = 3.14$ and 2.34 ppm in the ¹H NMR spectrum, and the corresponding ¹¹B NMR resonances for these units were located as broad resonances at $\delta = -14.4$ and -16.5 ppm, respectively. The molecular structure of 7 was determined by single-crystal X-ray crystallography (Figure 4), and the observed C_{IPr}-

Figure 4. Molecular structure of $IPr\cdot BH_2NHDipp(BH_3)$ (7) with thermal ellipsoids presented at the 30% probability level. All carbon-bound hydrogen atoms and solvate (hexane) molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)-B(1) 1.607(3), N(3)-B(1) 1.585(3), N(3)-B(2) 1.604(3), N(3)-C(51) 1.477(2); N(3)-B(1)-C(1) 113.73(15), N(3)-B(2)-B(1) 124.76(16), C(51)-N(3)-B(1) 109.05(14), C(51)-N(3)-B(2) 115.64(16).

B bond length in this complex (1.607(3) Å) was determined to be slightly shorter than the C_{IPr}-B separation in **6** (1.627(5) Å).

As mentioned previously, it was expected that hydridoamide complexes containing the E(H)NHDipp structural unit (as found within the isolated complexes IPr•EH-(BH₃)NHDipp; E=Si or Ge; **4** and **5**) might undergo the thermally induced elimination of H₂NDipp to form new, group 14 element clusters with potentially unique structural and electronic properties. To investigate this possibility, complexes **4** and **5** were each heated at 70 °C in toluene. However, rather than the formation of products with cluster motifs, the formation of a colorless solution and a brightorange precipitate was observed in both instances.^[23] The soluble products from the thermal decomposition of **4** and **5** were identified as a mixture of IPr•BH₂NHDipp (**6**), IPr•BH₃, and IPrH₂ (by using ¹H and ¹¹B NMR spectroscopy), with no sign of soluble carbene-encapsulated clusters. Notably, a similar product mixture arose from the reaction of IPr·Sn(Cl)NHDipp with Li[BH₄], thus lending support to the proposal that IPr•SnH(BH₃)NHDipp is a plausible intermediate in this reaction. In line with these results, carbenebound Sn^{II}-hydride complexes are generally much less thermally stable than their Si and Ge counterparts.^[5] Although both 4 and 5 are stable at ambient temperature in the solid state, they both decompose slowly in THF (ca. 20% decomposition in 10 days at room temperature). The exact mechanism by which IPr•EH(BH₃)NHDipp (E=Si or Ge; 4 and 5) decomposes to give IPr•BH₂NHDipp (6) is unclear; however, the related isotopologue $IPr \cdot BD_2 NHDipp$ ([D₂]-6) can be isolated as a spectroscopically pure product from the reaction of **3** with $Li[BD_4]$, revealing that the BH₂ and BD₂ units are generated directly from Li[BH₄] and Li[BD₄], respectively. One possible pathway for the formation of 6 (and $[D_2]$ -6) involves transmetallation between a BH₃ unit and the Si- or Ge-bound amide group -NHDipp, to yield the transient amino-borane H₂B-NHDipp, which is later intercepted by free IPr to form 6 (or $[D_2]$ -6). Although we do not have direct evidence at this time, the decomposition of $[IPr \cdot SnH_2 \cdot W(CO)_5]$ yields both the free carbene IPr and IPrH₂ as soluble products,^[5b] implying that any IPr·SnH₂ formed by transmetallation could undergo a similar decomposition process to yield free IPr and the IPrH₂ byproduct observed during the formation of 6. It should be mentioned that related transmetallation chemistry was used by Power and co-workers to generate the aryltin(II) hydride dimer $[Ar'Sn(\mu-H)]_2$ from the reaction of $(Ar'Sn-NMe_2)_2$ with H₃B•THF, yielding volatile $(Me_2NBH_2)_x$ as a coproduct.^[11b]

Due to the presence of both acidic $(N-H^{\delta+})$ and hydridic $(B-H^{\delta-})$ functional groups in IPr•BH₂NHDipp (6), we investigated whether the liberation of H_2 from 6 could transpire to yield a carbene-stabilized iminoborane, IPr·HB= NDipp.^[24] To explore this possibility, 6 was combined with the known dehydrogenation catalyst [{Rh(cod)Cl}₂] (cod= 1,5-cyclooctadiene);^[24a] however, no sign of hydrogen loss was observed at ambient temperature when a 5 mol% catalyst loading was used. When the reaction mixture was heated to 100°C in toluene in the presence of [{Rh-(cod)Cl₂], the quantitative formation of a new product was observed. A similar product with a new ¹¹B NMR resonance at $\delta = 28.6$ ppm was also observed when **6** was heated to 100 °C in the absence of the Rh complex. This new product was isolated as a colorless, crystalline solid and was identified by X-ray crystallography (Figure 5) as the new, ring-expanded product [(HCNDipp)₂CH₂BNHDipp] [8; Equation (2)].

The ¹H NMR spectrum of **8** is consistent with the X-ray crystallographic data; a singlet resonance at δ =3.17 ppm

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Figure 5. Molecular structure of $[(HCNDipp)_2CH_2BNHDipp]$ (8) with thermal ellipsoids presented at the 30% probability level. All carbonbound hydrogen atoms except those bonded to C(1) have been omitted for clarity. Only one of the two crystallographically independent molecules is shown; parameters for the second molecule are listed in square brackets. Selected bond lengths [Å] and angles [°]: N(1A)–B(1A) 1.4213(18) [1.4183(19)], B(1A)–C(1A) 1.5889(19) [1.583(2)], N(2A)– C(1A) 1.4601(18) [1.4591(18)], N(3A)–B(1A) 1.4148(19) [1.4103(19)]; N(2A)-C(1A)-B(1A) 111.60(11) [111.07(11)], N(1A)-B(1A)-N(3A) 121.62(12) [121.77(13)], N(1A)-B(1A)-C(1A) 117.30(12) [117.51(12)], N(3A)-B(1A)-C(1A) 121.08(12) [120.72(12)].

that corresponds to a CH_2 moiety is present, and the backbone CH groups of the newly formed boracycle appear as two distinct doublet resonances at δ =4.95 and 5.31 ppm (${}^{3}J_{\rm HH}$ =6.0 Hz). The intraring methylene group is found at δ =40.2 ppm in the ${}^{13}C{}^{1}H$ NMR spectrum, and the resonance due to the carbenic carbon in **6**, which is initially present, is absent in the spectrum of **8**. As mentioned, the ${}^{11}B$ NMR spectrum of **8** shows a signal at δ =28.6 ppm, which is in the typical range for three-coordinate boron compounds, commensurate with the assigned structure of **8**.^[25]

As shown in Figure 5, compound 8 consists of a six-membered boron-containing heterocycle in which the intraring CH_2 group is buckled above the BN_2C_2 plane to give a pseudoenvelope conformation. The C(1)-B(1) interatomic separation in 8 was determined to be 1.586(3) Å (an average of two crystallographically independent molecules) and is typical for B-C bonds in three-coordinate boranes (e.g., 1.589(5) Å in Ph₃B and 1.574(4) Å [2,6in $(MeO)_{2}C_{6}H_{3}]_{3}B).^{[26]}$ The average endocyclic B-N(1)(1.420(3) Å), and exocyclic B-N(3) (1.413(3) Å) bond lengths in 8 are the same within experimental error, and are slightly shorter than the B-N bond lengths in N-triphenylborazine ([PhNBH]₃; 1.429(2) to 1.431(2) Å),^[27] suggesting the presence of partial B=N bond character between the boron atom and nitrogen centers in 8.

To gain some mechanistic insight into the thermal conversion of IPr•BH₂NHDipp (6) into the carbene-activated product 8, the ring-expansion reaction was repeated with the use of the deuterium isotopologue IPr•BD₂NHDipp ([D₂]-6). Heating a sample of [D₂]-6 to 100 °C for 12 h generated a product with NMR and IR spectroscopic data that were consistent with the formation of the isotopically labeled species [(HCNDipp)₂CD₂BNHDipp] ([D₂]-8). For example, ²H{¹H} NMR spectroscopy revealed the presence of deuterium at the intraring methylene carbon (CD₂) at $\delta = 3.17$ ppm, whereas the corresponding proton resonance was absent in the ¹H NMR spectrum. The clean formation of [(HCNDipp)₂CD₂BNHDipp] ([D₂]-8) indicates that the direct transfer of two boron-bound deuterium atoms from the BD₂ unit in [D₂]-6 to the carbene-carbon center of the IPr group occurred. As no H/D exchange was observed for the pendant -NHDipp group, it can be concluded that the N-H bond is not directly involved in the deuterium migration process [see Equation (2)].

The observation of C-N bond insertion chemistry involv-N-heterocyclic ing the carbene-borane adduct IPr•BH₂NHDipp (6) is significant given the role NHCborane adducts have recently had in advancing catalytic transformations.^[4] In general, the C-H bond activation of a ring-backbone-positioned hydrogen atom is a more commonly observed reaction pathway amongst N-heterocyclic carbenes, such as IPr.^[28] Notably, Hill and co-workers uncovered a Be-H-mediated C-N bond-activation/ring-expansion reaction that is mechanistically related to the formation of 8. Moreover, these authors provided compelling evidence for the migration of hydrides directly from the main-group element, beryllium, to the carbenic carbon of IPr.^[29] Therefore, our combined research efforts indicate that maingroup-element hydrides have the potential to undergo C-N bond-activation/ring-expansion reactions with typically inert NHCs, thus leading to possible catalyst deactivation pathways when NHC-based catalysts (or precatalysts) are exposed to elevated temperatures. We are currently exploring the generality of this ring-expansion reaction in our laboratory.

Conclusion

A series of low oxidation state group 14 element chloroamines, $IPr \cdot E(Cl)NHDipp$ (1-3; E = Si, Ge, or Sn), that are stabilized by N-heterocyclic carbenes have been prepared. Compounds 1 and 2 react with Li[BH₄] to give the new, lowvalent hydrido-amide adducts IPr•EH(BH₃)NHDipp (4 and 5; E = Si or Ge). The tin congener IPr·Sn(Cl)NHDipp (3) interacts with Li[BH₄] to give the amino-borane adduct IPr•BH₂NHDipp (6) as the major product, with no evidence for the formation of IPr•SnH(BH₃)NHDipp as a stable species. Thermolysis of 4 and 5 was also investigated as a potential route to Si- and Ge-based clusters; however, in each case the formation of IPr•BH₂NHDipp (6) occurred. Upon further heating, IPr•BH₂NHDipp (6) participated in a rare ring-expansion reaction involving C-N bond activation of the coordinated N-heterocyclic carbene IPr, and which was mediated by BH-hydride transfer chemistry. This ring-expansion reaction shows that N-heterocyclic carbenes are prone to ring-activation processes in the presence of maingroup hydrides at elevated temperatures, and thus highlights a potential deactivation pathway in NHC-based catalysis.

FULL PAPER

Experimental Section

General methods: All of the reactions were performed by using standard Schlenk-line techniques under an atmosphere of nitrogen or in an inertatmosphere glovebox (Innovative Technology, Inc.). Solvents were dried by using a Grubbs-type solvent-purification system^[30] (Innovative Technology, Inc.), degassed (freeze-pump-thaw method), and stored under an atmosphere of nitrogen prior to use. Li[BH4] and Li[BD4] were purchased from Aldrich and used as received. 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),^[31] IPr•SiCl₂,^[15] IPr•GeCl₂,^[5a] IPr•SnCl₂,^[5a] and $Li[NHDipp]^{[32]}$ (Dipp=2,6-*i*Pr₂C₆H₃) were synthesized by following literature procedures. ¹H, ¹³C{¹H}, ²⁹Si, ¹¹B, and ¹¹⁹Sn NMR spectra were recorded on Varian iNova-400 or iNova-500 spectrometers and were referenced externally to SiMe₄ (¹H, ¹³C[¹H] and ²⁹Si), Et₂O·BF₃ (¹¹B), and SnMe4 (119Sn). The Analytical and Instrumentation Laboratory at the University of Alberta performed elemental analyses. Infrared spectra were recorded on a Nicolet IR100 FTIR spectrometer as Nujol mull samples between NaCl plates. Melting points were measured in sealed glass capillaries by using a MelTemp melting-point apparatus under a nitrogen atmosphere and are uncorrected.

X-ray Crystallography: Crystals of suitable quality for X-ray diffraction studies were removed from a vial (in a glovebox) and immediately covered with thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was selected, mounted on a glass fiber, and quickly placed in a low-temperature stream of nitrogen on an X-ray diffractometer.^[33] All data were collected by using $Mo_{K\alpha}$ or $Cu_{K\alpha}$ radiation (Bruker APEX II CCD detector/D8 diffractometer), with the crystals cooled to -100 °C. The data were corrected for absorption by Gaussian integration from the indexing of the crystal faces.^[34] Structures were solved by using the direct-methods programs SHELX-97^[35] (compound 5) and SIR97^[36] (compounds 2 and 6), or by using the Patterson search/structure expansion facilities within the DIRDIF-2008 $^{\left[37\right] }$ (compounds 1 and 3) and SHELXD $^{\left[38\right] }$ program suites (compounds 4 and 7); structure refinement was accomplished by using SHELXL-97.^[35] Hydrogen atoms were assigned positions based on the sp² or sp³ hybridization geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms. See Tables 1 and 2 for a list of crystallographic data.

Tabl

CCDC-881533 (1), CCDC-881534 (2·Et₂O), CCDC-881535 (3·THF), CCDC-881536 (4), CCDC-881537 (5), CCDC-881538 (6.0.4Et₂O), CCDC-881539 (7-hexane), and CCDC-881540 (8) 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

Special refinement conditions:

Compound 2: The following distance restraints were applied to the disordered solvent (diethyl ether) molecules: C-C 1.530(2) Å, C-O 1.430(2) Å, C-C 2.340(4) Å, C-O 2.420(4) Å.

Compound 3: Attempts to refine peaks of residual electron density located about the inversion center (1/2, 1/2, 0) as disordered, half-occupancy tetrahydrofuran-solvent oxygen or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure^[38] as implemented in PLATON.^[39] A total solventaccessible void volume of 790.6 Å³ with a total electron count of 177 (consistent with 4 molecules of solvent (tetrahydrofuran), or 0.5 molecules per formula unit of the tin complex) was found in the unit cell in addition to the inversion-disordered solvent tetrahydrofuran molecule located near the inversion center (1/4, 1/4, 0) that had been successfully modeled.

Compound 4: Attempts to refine peaks of residual electron density as disordered or partial-occupancy n-hexane-solvent carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure^[39] as implemented in PLATON.^[40] A total solvent-accessible void volume of 2346.5 Å³ with a total electron count of 439 (consistent with 8 molecules of solvent (nhexane), or 1 molecule per formula unit of the {1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene}SiH(BH₃)NH(2,6-diisopropylphenyl) molecule) was found in the unit cell.

Compound 5: Attempts to refine peaks of residual electron density as disordered or partial-occupancy n-hexane-solvent carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure^[39] as implemented in PLATON.^[40] A total solvent-accessible void volume of 2392.7 Å³ with a total electron count of 511 (consistent with 8 molecules of solvent (hexane), or 1 molecule per formula unit of 5) was found in the unit cell. Compound 6: Pairs of distances for atoms C1-B1, B1-N3, and N3-C51

the

tropic

and O1S/O2S.

within the disordered BH₂NH-(C₆H₃*i*Pr₂) fragment of molecule A

were restrained to have the same bond lengths by use of the SHELXL SAME instruction. Additionally, the phenyl

rings within this disordered fragment

were constrained to be idealized hexa-

gons. The minor (20%) orientation of

group in molecule B was restrained to

have the same geometry as that of the

major orientation by use of the

SHELXL SAME instruction. The dis-

ordered solvent (diethyl ether) mole-

cule had the following restraints ap-

plied: C-C 1.53(1) Å; C-O 1.43(1) Å;

C-O 2.42(1) Å; C-C 2.34(1) Å. Final-

ly, the following pairs of atoms were

restrained to have equivalent aniso-

C51A/C, C52A/C, C53A/C, C54A/C,

C55A/C, C56A/C, C62A/C, B1A/C,

Compound 7: Attempts to refine

peaks of residual electron density as

disordered or partial-occupancy n-

hexane-solvent carbon atoms were un-

successful. The data were corrected

for disordered electron density

through use of the SQUEEZE proce-

displacement parameters:

disordered diisopropylphenyl

Table 1. Summary of crystallographic data for 1, 2·Et ₂ O, 3·THF, and 4.							
	1	$2 \cdot Et_2O$	3.THF	4			
empirical formula	C ₃₉ H ₅₄ ClN ₃ Si	C43H64ClGeN3O	C43H62ClN3OSn	C45H72BN3Si			
M _r	628.39	747.01	791.10	693.96			
crystal size [mm ³]	$0.36 \times 0.18 \times 0.08$	$0.41 \times 0.36 \times 0.18$	$0.56 \times 0.50 \times 0.46$	$0.40 \times 0.37 \times 0.15$			
crystal system	monoclinic	monoclinic	monoclinic	monoclinic			
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	C2/c (No. 15)	I2/a (No. 15)			
a [Å]	19.8052 (17)	19.4351 (11)	43.642 (3)	23.8535 (4)			
b [Å]	12.3167 (11)	23.3885 (14)	12.0988 (8)	14.3021 (2)			
c [Å]	15.8436 (14)	20.1177 (12)	16.7555 (11)	27.0924 (4)			
α [°]	90	90	90	90			
β[°]	98.8045 (12)	104.8410 (10)	104.3880 (8)	95.4166 (9)			
γ [°]	90	90	90	90			
V [Å ³]	3819.3 (6)	8839.6 (9)	8569.8 (10)	9201.4 (2)			
Ζ	4	8	8	8			
$\rho \left[\text{g cm}^{-3} \right]$	1.093	1.123	1.226	1.002			
$\mu [{\rm mm}^{-1}]$	0.160	0.786	0.692	0.663			
T [K]	173(1)	173(1)	173(1)	173(1)			
2θ _{max} [°]	51.40	50.50	54.98	139.82			
total data	27859	17242	37306	30372			
unique data (R_{int})	7257 (0.0946)	17242 (0.0428)	9835 (0.0143)	8496 (0.0204)			
obs data $[I > 2\sigma(I)]$	4223	14046	9255	7276			
params	401	857	444	417			
$R_1 \left[I > 2\sigma(I)\right]^{[a]}$	0.0527	0.0483	0.0309	0.0530			
wR_2 [all data] ^[a]	0.1378	0.1527	0.0786	0.1669			
max/min $\Delta \rho \left[e^{-} \text{\AA}^{-3} \right]$	0.256/-0.304	0.843/-0.598	0.677/-0.627	0.280/-0.263			

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$; w $R_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^4)]^{1/2}$.

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CHEMISTRY

Table 2.	Summary	of crystal	lographic	data fo	or 5, 6	6 •0.4Et ₂ O,	7.Hexane	and 8.

	5	6- 0.4Et ₂ O	7-Hexane	8
empirical formula	C45H72BGeN3	C40.6H60BN3O0.4	$C_{45}H_{73}B_2N_3$	C39H56BN3
M _r	738.46	607.33	677.68	577.68
crystal size [mm ³] crystal system	$0.45 \times 0.42 \times 0.05$ monoclinic	$0.45 \times 0.36 \times 0.18$ monoclinic	$0.41 \times 0.33 \times 0.21$ monoclinic	$0.34 \times 0.25 \times 0.17$ monoclinic
space group	I2/a (No. 15)	C2/c (No. 15)	C2/c (No. 15)	$P2_1/n$ (No. 14)
a [Å]	23.8622 (12)	47.114 (3)	22.5387 (11)	10.5312 (1)
b Å	14.3819 (7)	12.1840 (7)	14.7074 (7)	18.7236 (3)
c [Å]	27.3526 (14)	29.0791 (17)	25.9542 (13)	36.5391 (5)
α [°]	90	90	90	90
β[°]	95.6700 (10)	110.5450 (7)	90.5331 (8)	90.1432 (6)
γ [°]	90	90	90	90
V [Å ³]	9341.0 (8)	15630.6 (16)	8603.1 (7)	7204.83 (17)
Z	8	16	8	8
$\rho \left[\text{g cm}^{-3} \right]$	1.050	1.032	1.065	1.065
$\mu [{\rm mm}^{-1}]$	0.686	0.060	0.059	0.456
<i>T</i> [K]	173(1)	173(1)	173(1)	173(1)
2θ _{max} [°]	50.50	50.50	50.80	141.48
total data	32964	52431	30770	48851
unique data (R_{int})	8477 (0.0699)	14167 (0.0460)	7934 (0.0422)	13784 (0.0197)
obs data $[I > 2\sigma(I)]$	5797	9171	4747	12394
params	408	856	421	775
$R_1 [I > 2\sigma(I)]^{[a]}$	0.0439	0.0666	0.0574	0.0532
wR_2 [all data] ^[a]	0.0998	0.2212	0.1751	0.1463
max/min $\Delta \rho \left[e^{-} \text{ Å}^{-3} \right]$	0.397/-0.313	0.246/-0.243	0.246/-0.243	0.775/-0.450

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{\frac{1}{2}}$.

dure^[39] as implemented in *PLATON*.^[40] A total solvent-accessible void volume of 1670.0 Å³ with a total electron count of 370 (consistent with 8 molecules of solvent (*n*-hexane), or one molecule per formula unit of the {1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene]BH₂NH(BH₃)(2,6-diisopropylphenyl) molecule) was found in the unit cell.

Synthetic procedures:

IPr·Si(Cl)NHDipp (1): A solution of Li[NHDipp] (0.031 g, 0.17 mmol) in of cold Et₂O (10 mL, -35 °C) was added dropwise to a cold (-35 °C) slurry of IPr-SiCl₂ (0.081 g, 0.17 mmol) in Et₂O (3 mL). The resulting mixture was warmed slowly to room temperature and stirred for 20 min to give an orange solution over a white precipitate (LiCl). The reaction mixture was filtered through Celite and the volatiles were removed in vacuo to yield 1 as a yellow powder. Crystals of 1 suitable for X-ray crystallography were grown by cooling a solution of 1 in THF/hexanes to -35°C for 7 days (0.047 g, 45% yield). M.p. 179-181°C; ¹H NMR (500 MHz, C₆D₆): $\delta = 0.96$ (d, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.02 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.14 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.27 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.34 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH- $(CH_{3})_{2}$), 1.48 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH $(CH_{3})_{2}$), 2.96 (septet, ${}^{3}J_{HH} =$ 7.0 Hz, 4H; CH(CH₃)₂), 3.20 (septet, ${}^{3}J_{HH} = 7.0$ Hz, 2H; CH(CH₃)₂), 4.14 (s, 1H; -NH), 6.36 (s, 2H; NCH-), 6.94 (t, ³J_{HH}=7.5 Hz, 1H; ArH), 6.99-7.19 ppm (m, 8H; ArH); ${}^{13}C{}^{1}H$ NMR (125 MHz, C₆D₆): $\delta = 22.9$ (CH-(CH₃)₂), 23.1 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 25.8 (CH-(CH₃)₂), 25.9 (CH(CH₃)₂), 27.8 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 29.5 (CH-(CH₃)₂), 121.3 (ArC), 123.7 (ArC), 123.9 (ArC), 124.3 (ArC), 124.5 (-NCH-), 131.4 (ArC), 133.7 (ArC), 140.5 (ArC), 141.9 (ArC), 145.8 (ArC), 146.3 (ArC), 171.7 ppm (NCN); ²⁹Si NMR (80 MHz, C₆D₆): $\delta =$ -6.0 ppm; IR (Nujol): $\tilde{\nu} = 3360 \text{ cm}^{-1}$ (s, N-H); elemental analysis calcd (%) for C39H54ClN3Si: C 74.54, H 8.66, N 6.69; found: C 74.54, H 8.49, N 6.58.

IPr·Ge(Cl)*NHDipp* (2): A solution of Li[NHDipp] (0.18 g, 0.98 mmol) in cold Et₂O (12 mL, -35 °C) was added dropwise to a cold (-35 °C) slurry of IPr·GeCl₂ (0.51 g, 0.96 mmol) in Et₂O (5 mL). The resulting mixture was warmed slowly to room temperature and stirred overnight to form a pale-yellow solution over a white precipitate (LiCl). The reaction mixture was then filtered through Celite and the volatiles were removed in vacuo to yield **2** as a pale-yellow powder (0.63 g, 98% yield). Crystals of **2** suitable for X-ray crystallography were grown by cooling a saturated solution

of 2 in Et₂O layered with hexanes to -35 °C. M.p. 152-154 °C; ¹H NMR (500 MHz, C_6D_6): $\delta = 0.96$ (d, ${}^3J_{\rm HH} =$ 7.0 Hz, 6H; CH(CH₃)₂), 1.02 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.08 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.28 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.36 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.47 (d, ${}^{3}J_{\rm HH} = 7.0 \text{ Hz}, 6 \text{ H}; CH(CH_{3})_{2}), 2.96$ (septet, ${}^{3}J_{HH} = 7.0 \text{ Hz}, 4 \text{ H}; CH(CH_{3})_{2}),$ 3.20 (septet, ${}^{3}J_{\rm HH} = 7.0$ Hz, 2H; CH-(CH₃)₂), 4.11 (s, 1H; -NH), 6.43 (s, 2H; NCH-), 6.88 (t, ${}^{3}J_{HH}$ =7.5 Hz, 1H; ArH), 7.01–7.20 ppm (m, 8H; ArH); ¹³C{¹H} NMR (125 MHz, C₆D₆): $\delta =$ 23.1 (CH(CH₃)₂), 23.2 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 25.86 (CH(CH₃)₂), 25.91 (CH(CH₃)₂), 27.6 (CH(CH₃)₂), 29.3 (CH(CH₃)₂), 29.4 (CH(CH₃)₂), 119.8 (ArC), 123.8 (ArC), 124.43 (ArC), 124.46 (ArC), 124.51 (-NCH-), 131.4 (ArC), 133.6 (ArC), 139.1 (ArC), 144.3 (ArC), 145.9 (ArC), 146.7 (ArC), 177.1 ppm (NCN); IR (Nujol): $\tilde{\nu} = 3371 \text{ cm}^{-1}$ (br, N-H); elemental analysis calcd (%) for C₃₉H₅₄ClN₃Ge: C 69.50, H 8.23, N 6.23; found: C 69.20, H 8.22, N 5.73.

Synthesis of IPr·Sn(Cl)NHDipp (3): A cold (-35°C) solution of Li[NHDipp]

(0.23 g, 1.2 mmol) in Et₂O (12 mL) was added dropwise to a cold (-35°C) slurry of IPr·SnCl₂ (0.71 g, 1.2 mmol) in Et₂O (5 mL). The resulting mixture was warmed slowly to room temperature and stirred for 2 h to give a beige solution over a white precipitate (LiCl). The reaction mixture was then filtered through Celite and the volatiles were removed in vacuo to yield 3 as a pale-brown powder (0.83 g, 85% yield). Crystals of 3 suitable for X-ray crystallography were grown by cooling a solution of 3 in THF layered with hexanes to -35 °C. M.p. 180-182 °C; ¹H NMR (500 MHz, C₆D₆): $\delta = 0.96$ (d, ${}^{3}J_{HH} = 7.0$ Hz, 6 H; CH(CH₃)₂), 1.03 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.12 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.30 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.36 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH- $(CH_3)_2$), 1.48 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH $(CH_3)_2$), 2.92 (septet, ${}^{3}J_{HH} =$ 7.0 Hz, 4H; $CH(CH_3)_2$), 3.10 (septet, ${}^{3}J_{HH} = 7.0$ Hz, 2H; $CH(CH_3)_2$), 3.82 (s, 1H, -NH), 6.46 (s, 2H; NCH-), 6.83 (t, ³J_{HH}=7.5 Hz, 1H; ArH), 7.03-7.22 ppm (m, 8H; ArH); ${}^{13}C{}^{1}H$ NMR (125 MHz, C₆D₆): $\delta = 23.1$ (CH-(CH₃)₂), 23.4 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 25.73 (CH(CH₃)₂), 25.76 (CH(CH₃)₂), 25.81 (CH(CH₃)₂), 27.5 (CH(CH₃)₂), 29.2 (CH(CH₃)₂), 29.4 (CH(CH₃)₂), 117.7 (ArC), 123.4 (ArC), 124.4 (ArC), 124.6 (ArC), 131.3 (-NCH-), 133.9 (ArC), 137.1 (ArC), 146.1 (ArC), 146.2 (ArC), 146.6 (ArC), 147.2 (ArC), 184.8 ppm (NCN); ¹¹⁹Sn{¹H} NMR (149 MHz, C₆D₆): $\delta = -93.2$ ppm; IR (Nujol): $\tilde{\nu} = 3358$ cm⁻¹ (m, N–H); elemental analysis calcd (%) for C₃₉H₅₄ClN₃Sn: C 65.15, H 7.57, N 5.84; found: C 64.67, H 7.93, N 5.82.

Reaction of 1 with Li[BH₄] to form IPr·SiH(BH₃)NHDipp (4): Cold Et₂O (-35°C, 10 mL) was added to a mixture of 1 (77 mg, 0.12 mmol) and Li[BH4] (2.9 mg, 0.13 mmol). The reaction mixture was then warmed to room temperature and stirred overnight to give a yellow solution over a white precipitate (LiCl). The precipitate was allowed to settle and the resulting supernatant was filtered through Celite to obtain a brightyellow solution. Removal of the volatiles from the filtrate yielded a paleyellow solid that was identified by ¹H NMR spectroscopy as a mixture of 4 (ca. 47%), 6 (ca. 3%), IPr•BH₃ (ca. 31%), and IPrH₂ (ca. 10%). Spectroscopically pure 4 was isolated by fractional crystallization (cooling a saturated solution of the crude material in Et₂O layered with hexanes to -35°C). Crystals of 4 suitable for X-ray crystallography were grown by cooling a solution of 4 in Et₂O layered with hexanes to -35 °C for 3 days (25 mg, 34 %). M.p. 182–184 °C; ¹H NMR (300 MHz, C_6D_6): $\delta = 0.01-0.62$ $(brq, {}^{1}J_{BH} = 89.5 Hz, 3H; BH_3), 0.93 (d, {}^{3}J_{HH} = 6.9 Hz, 6H; CH(CH_3)_2),$ 0.97 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H; CH(CH₃)₂), 0.99 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H; CH-

 $(CH_3)_2$, 1.27 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H; CH $(CH_3)_2$), 1.38 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H; CH(CH₃)₂), 1.47 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6H; CH(CH₃)₂), 1.94 (d, ${}^{3}J_{HH} =$ 5.5 Hz, 1H; -NH), 2.88 (septet, ${}^{3}J_{HH} = 6.9$ Hz, 4H; CH(CH₃)₂), 3.19 (septet, ${}^{3}J_{HH} = 6.9$ Hz, 2H; CH(CH₃)₂), 5.12 (s, 1H; -SiH-; satellites: J_{HSi}=163.0 Hz), 6.39 (s, 2H; NCH-), 7.01–7.19 ppm (m, 9H; ArH); ¹³C{¹H} NMR (125 MHz, C₆D₆): $\delta = 22.7$ (CH(CH₃)₂), 22.9 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 26.1 (CH(CH₃)₂), 27.5 (CH(CH₃)₂), 29.3 (CH(CH₃)₂), 29.4 (CH(CH₃)₂), 123.1 (ArC), 123.6 (ArC), 124.6 (ArC), 125.2 (ArC), 131.7 (-N-CH-), 133.6 (ArC), 139.9 (ArC), 143.4 (ArC), 145.7 (ArC), 146.2 (ArC), 166.4 ppm (NCN); ¹¹B{¹H} NMR (159 MHz, C₆D₆): $\delta = -44.1$ ppm (s); ¹¹B NMR (159 MHz, C₆D₆): $\delta = -44.1$ ppm (q, ¹*J*_{BH} = 89.5 Hz); IR (Nujol): $\tilde{\nu} = 3359$ (m, N–H), 2326 (br, B-H), 2237 (m, B-H), 2096 cm⁻¹ (m, Si-H); elemental analysis calcd (%) for C39H58BN3Si: C 77.07, H 9.62, N 6.91; found: C 77.07, H 9.02, N 6.30.

Reaction of 2 with Li[BH₄] to form IPr·GeH(BH₃)NHDipp (5): Cold Et₂O (-35°C, 10 mL) was added to a mixture of compound 2 (88 mg, 0.13 mmol) and Li[BH₄] (2.8 mg, 0.13 mmol). The reaction mixture was stirred overnight at ambient temperature to give an orange solution with a yellow precipitate. The resulting mixture was then filtered through Celite to give an orange filtrate. Removal of the volatiles from the filtrate yielded an orange solid that was identified by ¹H NMR spectroscopy as a mixture of 5 (ca. 55% yield), 6 (ca. 30% yield), IPr•BH₃ (ca. 5% yield), and IPrH₂ (ca. 7% yield). Spectroscopically pure 5 was isolated by fractional crystallization (cooling a saturated solution of the crude material in Et₂O layered with hexanes to -35 °C). Crystals of 5 suitable for X-ray crystallography were grown by cooling a solution of 5 in Et₂O layered with hexanes to -35°C for 3 days (43 mg, 50%). M.p. 151-153°C (decomposed, turned red), 159-161 °C (melted); ¹H NMR (500 MHz, C_6D_6): $\delta = 0.93$ (d, ${}^{3}J_{HH} = 6.5$ Hz, 6H; CH(CH₃)₂), 0.97 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.01 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.29 (d, ${}^{3}J_{HH} =$ 6.5 Hz, 6H; CH(CH₃)₂), 1.41 (d, ${}^{3}J_{HH} = 7.0$ Hz, 6H; CH(CH₃)₂), 1.48 (d, ${}^{3}J_{\rm HH} = 6.5$ Hz, 6H; CH(CH₃)₂), 1.97 (d, ${}^{3}J_{\rm HH} = 6.5$ Hz, 1H; -NH), 2.84 (septet, ${}^{3}J_{HH} = 7.0$ Hz, 2H; CH(CH₃)₂), 2.85 (septet, ${}^{3}J_{HH} = 6.5$ Hz, 2H; $CH(CH_3)_2$, 3.20 (septet, ${}^{3}J_{HH} = 7.0$ Hz, 2H; $CH(CH_3)_2$), 5.67 (br s, 1H; -GeH), 6.41 (s, 2H; NCH-), 6.95-7.21 ppm (m, 9H; ArH); the -BH₃ unit was not located; ${}^{13}C{}^{1}H$ NMR (125 MHz, C_6D_6): $\delta = 22.7$ (CH(CH₃)₂), 22.9 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 27.3 (CH(CH₃)₂), 29.3 (CH(CH₃)₂), 29.4 (CH(CH₃)₂), 121.9 (ArC), 123.5 (ArC), 124.6 (ArC), 125.2 (ArC), 131.7 (-NCH-), 133.5 (ArC), 141.2 (ArC), 143.2 (ArC), 145.7 (ArC), 146.3 (ArC), 169.7 ppm (NCN); ¹¹B{¹H} NMR (128 MHz, C₆D₆): $\delta = -39.0$ ppm; IR (Nujol): $\tilde{\nu}$ = 3346 (m, N-H), 2371 (br s, B-H), 2253 (sh, B-H), 1997 cm⁻¹ (m, Ge-H); elemental analysis calcd (%) for C₃₉H₅₈BN₃Ge: C 71.80, H 8.96, N 6.44; found: C 71.57, H 9.11, N 5.87.

Reaction of 3 with Li[BH₄] to form IPr·BH₂NHDipp (6): Cold Et₂O (-35°C, 12 mL) was added to a mixture of 3 (366 mg, 0.51 mmol) and Li-[BH₄] (11.1 mg, 0.51 mmol). The reaction mixture was stirred for 2 h at ambient temperature to give a clear solution along with an insoluble black precipitate. The precipitate was then allowed to settle and the mother liquor was filtered through Celite. Removal of the volatiles from the filtrate yielded 6 as a white solid that was identified by ¹H NMR spectroscopy as a mixture of 6 (ca. 58% yield), IPr•BH₃ (ca. 30% yield), and $IPrH_2$ (ca. 12% yield). Spectroscopically pure 6 was isolated by fractional crystallization (cooling a saturated solution of the crude materials in Et₂O to -35°C). Crystals of 6 suitable for X-ray crystallography were grown by cooling a solution of 6 in Et_2O to $-35\,^{\rm o}\!{\rm C}$ for 2 days (163 mg, 55%). M.p. 145–147°C; ¹H NMR (500 MHz, C_6D_6): $\delta = 1.03$ (d, ³ $J_{HH} =$ 7.0 Hz, 12 H; CH(CH₃)₂), 1.09 (d, ${}^{3}J_{HH} = 7.0$ Hz, 12 H; CH(CH₃)₂), 1.36 (d, ${}^{3}J_{HH} = 7.0$ Hz, 12 H; CH(CH₃)₂), 1.64 (t, ${}^{3}J_{HH} = 6.5$ Hz, 1 H; -NH), 2.55 (s, 2H; -BH₂; located in the ¹H{¹¹B} NMR spectrum), 2.74 (septet, ${}^{3}J_{HH} =$ 7.0 Hz, 4H; $CH(CH_3)_2$), 3.01 (septet, ${}^{3}J_{HH} = 7.0$ Hz, 2H; $CH(CH_3)_2$), 6.35 (s, 2H; NCH-), 6.98 (t, ${}^{3}J_{HH} = 7.5$ Hz, 2H; ArH), 7.08 (d, ${}^{3}J_{HH} = 7.5$ Hz, 1 H; Ar*H*), 7.10 (d, ${}^{3}J_{HH}$ = 7.5 Hz, 2 H; Ar*H*), 7.23 ppm (t, ${}^{3}J_{HH}$ = 7.5 Hz, 4H; ArH); ${}^{13}C{}^{1}H$ NMR (125 MHz, C₆D₆): $\delta = 22.9$ (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 27.1 (CH(CH₃)₂), 29.2 (CH(CH₃)₂), 119.5 (ArC), 122.3 (ArC), 123.3 (ArC), 124.2 (ArC), 130.6 (-NCH-), 134.5 (ArC), 140.9 (ArC), 145.9 (ArC), 150.3 ppm (NCN); ${}^{11}B{}^{1}H{}$ NMR (128 MHz, C₆D₆): $\delta = -16.5$ ppm (s); ¹¹B NMR (C₆D₆, 128 MHz): $\delta =$

-16.5 ppm (brt); IR (Nujol): $\tilde{\nu}$ =3373 (br, N-H), 2393 (sh, B-H), 2310 cm $^{-1}$ (br, B–H); elemental analysis calcd (%) for $C_{39}H_{56}BN_3\colon C$ 81.08, H 9.77, N 7.27; found: C 81.05, H 9.92, N 7.36.

Synthesis of $IPr \cdot BD_2 NHDipp$ ([D_2]-6): Et₂O (12 mL) was added to a mixture of 3 (430 mg, 0.51 mmol) and Li[BD₄] (15.5 mg, 0.60 mmol). The reaction mixture was stirred for 2 h at ambient temperature to give a clear solution over a black precipitate. The precipitate was then allowed to settle and the mother liquor was filtered through Celite to give a colorless filtrate. Removal of the volatiles from the filtrate vielded a white solid from which spectroscopically pure [D₂]-6 was isolated (188 mg, 54% yield) by fractional crystallization following the same procedure as 6. ¹H NMR (500 MHz, C₆D₆): essentially the same as 6 except the N-H resonance at $\delta = 1.64 \text{ ppm}$ was observed as a singlet; ¹¹B{¹H} NMR (128 MHz, C_6D_6): same as compound 6; ²H{¹H} NMR (61 MHz, C_6D_6): $\delta = 2.53$ ppm (brs; -BD₂-); IR (Nujol): similar to 6 except for the absence of B-H stretches; the B-D stretching frequencies were observed at $\tilde{\nu}$ = 1724 (sh, B-D) and 1630 cm⁻¹ (br, B-D).

Reaction of **6** with H_3B ·THF to form IPr·B $H_2NHDipp(BH_3)$ (7): H₃B•THF (0.16 mL, 1.0 M solution in THF) was added dropwise to a solution of 6 (86 mg, 0.15 mmol) in Et₂O (10 mL). The reaction mixture was stirred overnight at room temperature to give a colorless solution and the volatiles were then removed in vacuo to yield a white powder. The powder was washed with hexanes (4 mL) and dried to afford spectroscopically pure 7. Crystals of 7 suitable for X-ray crystallography were grown by cooling a saturated solution of 7 in Et₂O layered with hexanes to -35°C for 4 days (71 mg, 81% yield). M.p. 156-158°C; ¹H NMR (500 MHz, C₆D₆): $\delta = 0.93$ (d, ${}^{3}J_{HH} = 6.5$ Hz, 3H; CH(CH₃)₂), 0.96 (d, ${}^{3}J_{\rm HH} = 6.5$ Hz, 9H; CH(CH₃)₂), 1.01 (d, ${}^{3}J_{\rm HH} = 6.5$ Hz, 3H; CH(CH₃)₂), 1.06 (d, ${}^{3}J_{HH} = 6.5$ Hz, 9H; CH(CH₃)₂), 1.38–1.42 (overlapping broad doublets, ${}^{3}J_{HH} = 6.5 \text{ Hz}$, 9H; CH(CH₃)₂), 1.45 (d, ${}^{3}J_{HH} = 6.5 \text{ Hz}$, 3H; CH- $(CH_3)_2$, 1.68 (septet, ${}^{3}J_{HH} = 6.5 \text{ Hz}$, 1H; $CH(CH_3)_2$), 2.34 (brs, 3H; -B H_3), 2.90 (septet, ${}^{3}J_{HH} = 6.5$ Hz, 2H; C $H(CH_3)_2$), 3.14 (brs, 2H; -B H_2 -), 4.15 (septet, ${}^{3}J_{HH} = 6.5$ Hz, 1H; CH(CH₃)₂), 4.36 (brs, 2H; CH(CH₃)₂), 4.70 (s, 1H; -NH-), 6.55 (s, 2H; NCH-), 6.87-7.25 ppm (m, 9H; ArH); ¹³C[¹H] NMR (125 MHz, C₆D₆): $\delta = 22.5$ (CH(CH₃)₂), 22.9 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 25.6 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 26.2 (CH(CH₃)₂), 26.3 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 28.9 (CH(CH₃)₂), 29.0 (CH(CH₃)₂), 122.4 (ArC), 122.8 (-NCH-), 124.4 (ArC), 124.5 (ArC), 124.7 (ArC), 126.8 (ArC), 130.7 (ArC), 134.1 (ArC), 138.6 (ArC), 144.3 (-NCH-), 145.5 (ArC), 146.5 ppm (NCN); ¹¹B{¹H} NMR (128 MHz, C₆D₆): $\delta = -14.4$ (-*B*H₂-), -16.5 ppm (-BH₃); IR (Nujol): $\tilde{\nu}$ = 3321 (m, N-H), 2484 (m, B-H), 2388 (sh, B-H), 2308 (s, B-H), 2266 cm⁻¹ (s, B-H); elemental analysis calcd (%) for C39H59B2N3: C 79.19, H 10.05, N 7.10; found: C 78.99, H 10.13, N 6.98.

Thermolvsis *IPr*•*BH*₂*NHDipp* of (6) to form [(HCNDipp)₂CH₂BNHDipp] (8): A solution of 6 (142 mg, 0.25 mmol) in toluene (10 mL) was heated at 100 °C for 12 h to form a pale-yellow solution. The reaction mixture was then filtered through Celite and the volatiles were removed in vacuo to yield crude 8 as a bright-yellow oil. Crystals of 8 suitable for X-ray crystallography were grown by cooling a saturated solution of 8 in hexanes layered with (Me₃Si)₂O to -35°C for 4 days (113 mg, 80 % yield). M.p. 124–126 °C; ¹H NMR (500 MHz, C₆D₆): $\delta = 1.14$ (d, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 9H; CH(CH₃)₂), 1.20 (d, ${}^{3}J_{\text{HH}} = 7.0$ Hz, 9H; CH(CH₃)₂), 1.31 (d, ${}^{3}J_{HH} = 7.0$ Hz, 9H; CH(CH₃)₂), 1.34 (d, ${}^{3}J_{HH} = 7.0$ Hz, 9H; CH(CH₃)₂), 3.17 (s, 2H; -CH₂-), 3.45 (septet, ${}^{3}J_{HH} = 7.0$ Hz, 2H; CH- $(CH_3)_2$) 3.58 (septet, ${}^{3}J_{HH} = 7.0 \text{ Hz}$, 2H; $CH(CH_3)_2$), 3.67 (s, 1H; -NH), 3.85 (septet, ${}^{3}J_{HH} = 7.0 \text{ Hz}$, 2H; CH(CH₃)₂), 4.95 (d, ${}^{3}J_{HH} = 6.0 \text{ Hz}$, 1H; NCH-), 5.31 (d, ³*J*_{HH}=6.0 Hz, 1 H; NCH-), 6.95–7.22 ppm (m, 9 H; ArH); ¹³C{¹H} NMR (125 MHz, C₆D₆): $\delta = 23.4$ (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 27.8 (CH(CH₃)₂), 28.1 (CH(CH₃)₂), 29.4 (CH(CH₃)₂), 40.2 (-CH₂-), 109.5 (-NCH-), 118.7 (-NCH-), 122.9 (ArC), 124.1 (ArC), 124.2 (ArC), 126.2 (ArC), 135.9 (ArC), 140.1 (ArC), 145.3 (ArC), 145.7 (ArC), 147.2 (ArC), 147.9 ppm (NCN); ¹¹B{¹H} NMR (128 MHz, C₆D₆): $\delta = 28.6$ ppm; IR (Nujol/cm⁻¹): $\tilde{\nu} = 3391$ cm⁻¹ (br, N-H); elemental analysis calcd (%) for C₃₉H₅₆BN₃: C 81.08, H 9.77, N 7.27; found: C 81.17, H 9.74, N 7.23.

Thermolysis ofIPr•BD₂NHDipp $([D_2]-6)$ to form $[(HCNDipp)_2CD_2BNHDipp]$ ($[D_2]$ -8): A solution of $[D_2]$ -6 (85 mg,

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0.15 mmol) in toluene (10 mL) was heated at 100 °C for 12 h to give a pale-yellow solution. The reaction was then filtered through Celite and the volatiles were removed in vacuo to yield [D₂]-**8** as a bright-yellow oil (57 mg, 79% yield). ¹H NMR (500 MHz, C₆D₆): essentially the same as compound **8** except for the absence of a resonance for the $-CH_{2^-}$ group at $\delta = 3.17$ ppm; ²H{¹H} NMR (61 MHz, C₆H₆): $\delta = 3.16$ ppm (-CD₂-).

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Ring Expansion -

S. M. I. Al-Rafia, R. McDonald, M. J. Ferguson, E. Rivard* .

Preparation of Stable Low Oxidation State Group 14 Element Amidohydrides and Hydride-Mediated Ring-Expansion Chemistry of N-Heterocyclic Carbenes

Breaking the ring that binds: A series of low oxidation state group 14 element hydridoamides, NHC•EH-(BH₃)NHDipp (E=Si or Ge; NHC=N-heterocyclic carbene; Dipp=2,6-*i*Pr₂C₆H₃), is reported. These hydrides underwent transmetallation upon heating to give IPr•H₂BNHDipp; this borane participates in C–N bond-activation reactions involving a carbene donor at 100 °C.