

Activation of protic, hydridic and apolar E-H bonds by a boryl-substituted Ge(II) cation

Robert J. Mangan,^[a] Arnab Rit,^[a] Christian P. Sindlinger,^[a] Rémi Tirfoin,^[a] Jesús Campos,^[a] Jamie Hicks,^[a] Kirsten E. Christensen,^[a] Haoyu Niu,^[a] and Simon Aldridge^{*[a]}

Abstract: The synthesis of a boryl-substituted germanium(II) cation, $[\text{Ge}\{\text{B}(\text{NDippCH}_2)_2\}(\text{IPrMe})]^+$, featuring a supporting N-heterocyclic carbene (NHC) donor, has been explored via chloride abstraction from the corresponding (boryl)(NHC)GeCl precursor. Crystallographic studies in the solid state and UV-vis spectra in fluoro-benzene solution show that this species dimerizes under such conditions to give $[(\text{IPrMe})\{\text{HCNDipp}_2\text{B}\}\text{Ge}=\text{Ge}\{\text{B}(\text{NDippCH}_2)_2\}(\text{IPrMe})]^{2+}$, which can be viewed as an imidazolium-functionalized digermene. The dimer is cleaved in the presence of donor solvents such as thf-d₈ or pyridine-d₅, to give monomeric adducts of the type $[\text{Ge}\{\text{B}(\text{NDippCH}_2)_2\}(\text{IPrMe})(\text{L})]^+$. In the case of the thf adduct, the additional donor is shown to be sufficiently labile that it can act as a convenient *in situ* source of the monomeric complex $[\text{Ge}\{\text{B}(\text{NDippCH}_2)_2\}(\text{IPrMe})]^+$ for oxidative bond activation chemistry. Thus, $[\text{Ge}\{\text{B}(\text{NDippCH}_2)_2\}(\text{IPrMe})(\text{thf})]^+$ reacts with silanes and dihydrogen, leading to the formation of Ge^{IV} products, while the cleavage of the N-H bond in ammonia ultimately yields products containing C-H and B-N bonds. The facile reactivity observed in E-H bond activation is in line with the very small calculated HOMO-LUMO gap (132 kJ mol⁻¹).

Introduction

E-H bond activation represents a fundamental step that is critical to many catalytic processes. Such reactivity has traditionally been the preserve of transition metal reagents, particularly those for which ready inter-conversion between *n* and *n*+2 oxidation states can be achieved.^[1] While highly reactive transient systems have been investigated for many years,^[2,3] recent work has seen the emergence of isolable main group compounds capable of the activation of key E-H bonds (E = H, B, C, N, O, Si etc).^[1] One approach that has received significant attention involves the use of carbenes (:CX₂) or their heavier Group 14 metallylene analogues (:EX₂, where E = Si, Ge, Sn) to oxidatively cleave E-H linkages.^[4-6] From a kinetic perspective, such processes depend crucially on the relative energies of the HOMO and LUMO orbitals, which typically correspond to an E-centred lone pair, and a formally vacant perpendicular orbital of

π symmetry. The factors influencing the HOMO-LUMO gap have therefore been investigated in some depth: the angle between the X substituents, for example, is known to be particularly influential – a wider angle implies greater HOMO p-orbital character, a higher HOMO energy and (all other things being equal) a smaller HOMO-LUMO gap. Sterically bulky and electropositive X substituents also tend to be associated with wide E-X angles and high HOMO energies. The HOMO-LUMO gap can also be tuned via variation of the LUMO energy, with π -donor substituents causing elevation of the LUMO due to greater E-X π^* character.^[4]

We have recently explored E-H bond activation by heavier Group 14 metallylenes featuring strongly σ -donating (electropositive) X substituents. Acyclic silylenes featuring α -boryl or silyl groups, for example, have narrow HOMO-LUMO gaps and are capable of the activation of a range of E-H bonds.^[7-9] In similar fashion, the reactivity of germlylenes of the form $\text{Ge}(\text{Ar}^{\text{Mes}})_2\text{X}$ ($\text{Ar}^{\text{Mes}} = \text{C}_6\text{H}_3\text{Mes}_2\text{-2,6}$, where Mes = C₆H₂Me₃-2,4,6) is strongly influenced by the nature of X. Thus, $\text{Ge}(\text{Ar}^{\text{Mes}})\{\text{B}(\text{NDippCH}_2)_2\}$ (where Dipp = C₆H₃Pr₂-2,6) features a HOMO-LUMO separation of 119 kJ mol⁻¹ and undergoes facile intramolecular C-H activation, while the slightly less labile $\text{Ge}(\text{Ar}^{\text{Mes}})\{\text{Si}(\text{SiMe}_3)_3\}$ ($\Delta E_{\text{HOMO-LUMO}} = 134 \text{ kJ mol}^{-1}$) reacts cleanly under ambient conditions with H₂ and NH₃.^[10,11] Amido-substituted $\text{Ge}(\text{Ar}^{\text{Mes}})(\text{NHDipp})$ ($\Delta E_{\text{HOMO-LUMO}} = 275 \text{ kJ mol}^{-1}$), by contrast, is inert to oxidative E-H bond activation.^[10] While the hydrido-Si^{IV} and -Ge^{IV} products of these reactions are stable to reductive elimination, it is interesting to note that a related stannylene system $\text{Sn}\{\text{B}(\text{NDippCH}_2)_2\}_2$ is capable not only of oxidative E-H bond activation, but also (in the cases where E = N or O) of subsequent reductive elimination, reflecting the more reducing Sn^{II/IV} redox couple.^[12]

Until recently the analogous reactivity of cationic analogues of these divalent metallylenes was relatively underexplored.^[13] Early strategies to stabilise germlylium-ylidenes, $[\text{Ge}(\text{X})\text{L}]^+$, involved incorporation into heterocycles,^[14,15] or the use of additional neutral donors,^[16-21] thereby disfavoring further reactivity on electronic and/or steric grounds. Recent examples

[a] Mr R. Mangan, Dr A. Rit, Dr C. Sindlinger, Dr R. Tirfoin, Dr J. Campos, Dr J. Hicks, Dr K.E. Christensen, Dr H. Niu, Prof S. Aldridge
Department of Chemistry, University of Oxford
Inorganic Chemistry Laboratory, South Parks Road,
Oxford, OX1 3QR, UK
E-mail: simon.aldridge@chem.ox.ac.uk

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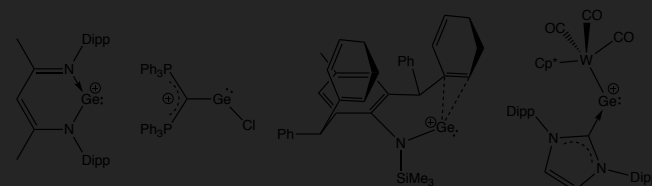
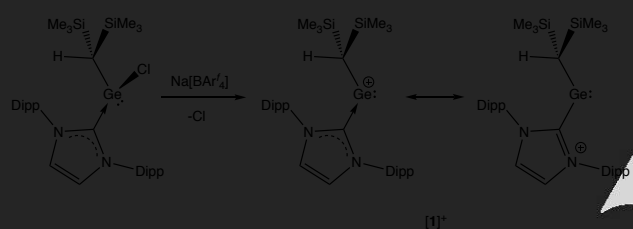


Figure 1. Selected examples of recently reported (and structurally characterized) low-coordinate Ge^{II} cations.

of acyclic low-coordinate germanium cations have been reported (Figure 1), but the use of ancillary π -donor substituents such as amides,^[22] or carbodiphosphoranes,^[23] in a number of these would be expected to elevate the energy of the LUMO and thus increase the HOMO-LUMO gap. More recently still, the mixed *d/p* block cation $[\text{Ge}\{\text{W}(\text{CO})_3\text{Cp}^*\}(\text{IDipp})][\text{BAR}^f_4]$ (IDipp = 1,3-bis(2,6-diisopropyl-phenyl)-imidazol-2-ylidene, $\text{Ar}^f = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) has been reported by Tobita to be capable of the oxidative addition of H_2 at germanium, and (even more remarkably) the reversible activation of silanes and boranes.^[23,24]

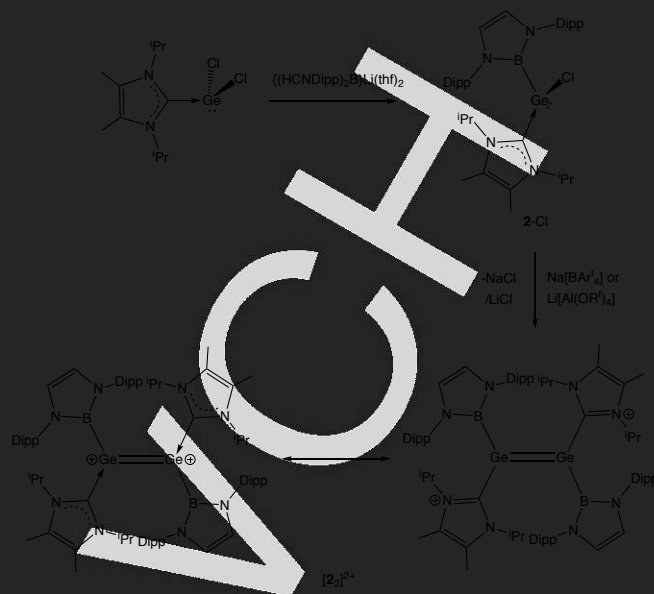
Recently we reported an acyclic, transition metal-free system, $[\text{Ge}\{\text{CH}(\text{SiMe}_3)_2\}(\text{IDipp})]^+$ ($[1]^+$, as the $[\text{BAR}^f_4]$ salt; Scheme 1) which also possesses a small HOMO-LUMO gap (ca. 187 kJ mol⁻¹), and is capable of oxidative bond activation processes.^[23] However, given previous observations with *neutral* Ge^{II} systems that boryl substituents, in particular, promote enhanced reactivity, we were motivated to examine the chemistry of systems of the type $[\text{Ge}(\text{boryl})(\text{NHC})]^+$. The resulting synthetic, structural and reactivity studies are reported here.



Scheme 1. Synthesis of $[\text{Ge}\{\text{CH}(\text{SiMe}_3)_2\}(\text{IDipp})][\text{BAR}^f_4]$, $[1][\text{BAR}^f_4]$ via chloride abstraction ($[\text{BAR}^f_4]$ counter-ions omitted for clarity).

Results and Discussion

(i) Synthetic and structural studies of borylgermanium(II) cations. The synthesis of a boryl-substituted analogue of $[1][\text{BAR}^f_4]$, was envisaged via chloride abstraction from $(\text{IDipp})\{(\text{HCNDipp})_2\text{B}\}\text{GeCl}$. However, the attempted synthesis of this intermediate from $\{(\text{HCNDipp})_2\text{B}\}\text{Li}(\text{thf})_2$ and $(\text{IDipp})\text{GeCl}_2$,^[27] generates instead the chloroborane $(\text{HCNDipp})_2\text{BCl}$ as the only boron-containing product. Reasoning that this combination of NHC and bulky boryl group results in excessive steric crowding, the less bulky carbene IPrMe ($\text{IPrMe} = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$) was employed instead. In this case, the reaction of $(\text{IPrMe})\text{GeCl}_2$ with $\{(\text{HCNDipp})_2\text{B}\}\text{Li}(\text{thf})_2$ yields the target compound $(\text{IPrMe})\{(\text{HCNDipp})_2\text{B}\}\text{GeCl}$, **2-Cl**, the reduction chemistry of which has been reported previously.^[28] Subsequent combination of **2-Cl** with either $\text{Na}[\text{BAR}^f_4]$ or $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ in fluorobenzene leads to an immediate colour change to deep red, with accompanying formation of a precipitate. In the case of the $[\text{BAR}^f_4]$ anion, filtration and layering of a concentrated fluorobenzene solution with hexane yields deep red crystals suitable for single crystal X-ray diffraction. Rather than a monocationic analogue of $[1]^+$, however, these are shown to feature the dimeric species $[(\text{IPrMe})\{(\text{HCNDipp})_2\text{B}\}\text{Ge}=\text{Ge}\{\text{B}(\text{NDippCH})_2\}(\text{IPrMe})][\text{BAR}^f_4]_2$, $[2_2][\text{BAR}^f_4]_2$ (Scheme 2 and Figure 2).



Scheme 2. Synthesis of $[2_2]^{2+}$ via chloride abstraction; counter-ions omitted for clarity [$\text{Ar}^f = \text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5}$; $\text{R}^f = \text{C}(\text{CF}_3)_3$].

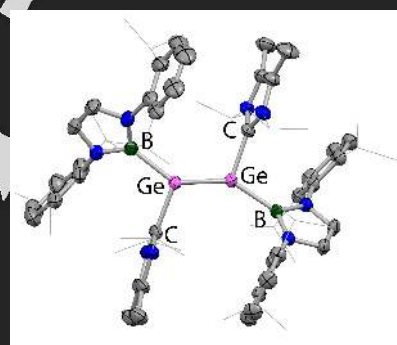


Figure 2. Molecular structure of the dicationic component of $[2_2][\text{BAR}^f_4]_2$ as determined by X-ray crystallography. Hydrogen atoms and counter-ions omitted, and Pr groups shown in wireframe format for clarity. Thermal ellipsoids set at the 50% level. Key bond lengths (Å) and angles ($^\circ$): Ge-B 2.081(3)/2.100(4), Ge-C 2.002(3)/2.016(4), Ge-Ge, 2.300(2), B-Ge-C 105.3(1), 107.4(2), B-Ge-Ge 139.0(1)/136.1(1), C-Ge-Ge 109.3(1)/109.6(1).

The molecular structure of the cationic component, $[2_2]^{2+}$, features pairs of boryl and NHC substituents arranged in *E* fashion about a digermanium core. The Ge-Ge bond length [2.300(2) Å] is consistent with previous reports of Ge=Ge double bonds - as found, for example, in the digermenes R_2GeGeR_2 (2.347(2) and 2.286(1) Å for $\text{R} = \text{CH}(\text{SiMe}_3)_2$ and Mes , respectively),^[29,30] but is markedly shorter than that measured for the tungsten-substituted dication $[(\text{IPrMe})\{\text{Cp}^*\}(\text{CO})_3\text{W}\text{Ge}=\text{Ge}\{\text{W}(\text{CO})_3\text{Cp}^*\}(\text{IPrMe})][\text{BAR}^f_4]_2$, which features the same NHC ligand (2.429(1) Å).^[24] The *trans*-bent geometry about the Ge=Ge bond (sum of angles at $\text{Ge}(1)/\text{Ge}(2) = 353.6, 353.1^\circ$) is also consistent with the heavy-atom skeletons determined for systems of the type R_2GeGeR_2 , and a description of $[2_2]^{2+}$ can be proposed as a digermene featuring pendant (cationic) imidazolium units (Scheme 2). The contrast with the (monomeric) structure determined for $[1]^+$,^[26] presumably reflects

the lower cumulative steric demands of the $-B(NDippCH)_2$ and $IPrMe$ fragments over $-CH(SiMe_3)_2$ and $IDipp$, together with the smaller calculated HOMO-LUMO gap for $[2]^+$ (132 cf. 187 kJ mol $^{-1}$ for $[1]^+$), which promotes dimerization through the formation of a pair of donor/acceptor interactions. The *electrostatic* disincentive to dimerization in the formation of $[2_2]^{2+}$ is presumably also mitigated to some degree by delocalization of the positive charge associated with each metal centre into the carbene heterocycle.

The very low solubility of $[2_2][BAR^f_4]_2$ once crystallized means that attempts to characterize the $[2_2]^{2+}$ dication by NMR spectroscopy in non-donor solvents have proved futile (dissolution in donor solvents leads to fragmentation into monogermanium species – see below). The UV-Vis spectrum of a (very dilute) fluorobenzene solution, however, reveals an intense feature at 462 nm, suggestive of the presence of the dimeric form in solution. This absorption is absent in the spectrum measured for thf solutions, but is similar to those measured for other species containing Ge=Ge double bonds (e.g. 455 nm for $[Ge(IDipp)]_2$; 434 nm for $(IPrMe)\{(HCDippN)_2B\}Ge=Ge\{B(NDippCH)_2\}$).^[28,30] In the case of the digermavinylidene $\{(HCDippN)_2B\}_2Ge=Ge$, a similar band at 460 nm has been assigned with the help of TD-DFT calculations to the Ge=Ge π -to- π^* transition.^[25]

In donor solvents such as thf- d_8 or pyridine- d_5 , $[2_2][BAR^f_4]_2$ dissolves rapidly, leading to cleavage of the germanium-germanium bond and to the formation of monomeric mono-cationic 1:1 adducts of the type $[2-L][BAR^f_4]$. In each case, conclusive structural characterization could be obtained by single crystal X-ray crystallography (Scheme 3 and Figure 3). $[2-(thf-d_8)][BAR^f_4]$ and $[2-(py-d_5)][BAR^f_4]$ each features a three-coordinate germanium centre, a pyramidal geometry at the metal, and Ge-B and Ge-C_{NHC} distances which become progressively longer as the donor strength increases (2.091 (mean)/2.009 (mean), 2.127(5)/2.074(5) and 2.144(4)/2.083(4) Å for $[2_2][BAR^f_4]_2$, $[2-(thf-d_8)][BAR^f_4]$ and $[2-(py-d_5)][BAR^f_4]$, respectively). In both mono-cations, the angle subtended at germanium by the bonds to the neutral donors is close to 90° (87.5(2) and 90.2(1)° for $[2-(thf-d_8)][BAR^f_4]$ and $[2-(py-d_5)][BAR^f_4]$) while those involving the boryl substituent are markedly wider [100.9(2)-105.5(1)°]. These observations presumably reflect not

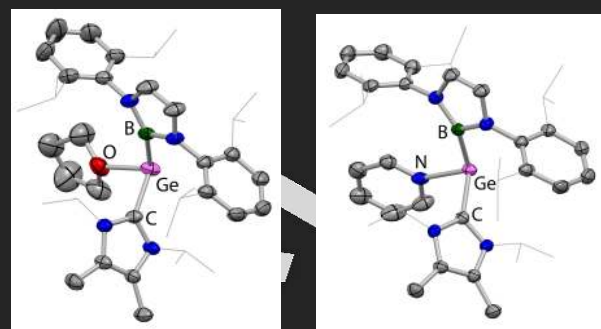
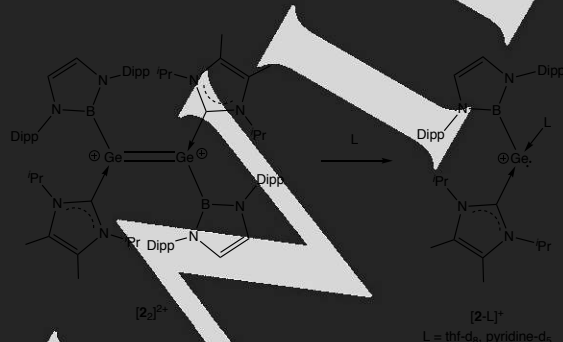


Figure 3. Molecular structures of the cationic components of $[2-(thf-d_8)][BAR^f_4]$ (left) and $[2-(py-d_5)][BAR^f_4]$ (right) as determined by X-ray crystallography. Hydrogen atoms, solvate molecules and counter-ions omitted, and Pr groups shown in wireframe format for clarity. Thermal ellipsoids set at the 50% level. Key bond lengths (Å) and angles (°): (for $[2-(thf-d_8)][BAR^f_4]/[2-(py-d_5)][BAR^f_4]$) Ge-B 2.127(5)/2.114(4), Ge-C 2.074(5)/2.083(4), Ge-O/N 2.120(4)/2.095(3), B-Ge-C 100.9(2)/102.9(1), B-Ge-O/N 105.2(2)/105.5(1), C-Ge-O/N 87.5(2)/90.2(1).

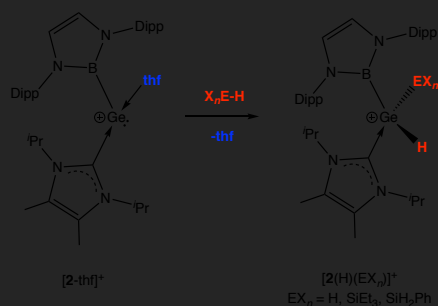
only the greater steric demands of the boryl substituent, but also the tenets of Bent's rule (i.e. concentration of p-orbital character in the bonds to the more electronegative atoms).^[32]

(ii) Reactivity studies. Quantum chemical studies (see Experimental Section and ESI) imply that the HOMO-LUMO gap for $[2]^+$ is significantly narrower than that for $[1]^+$ (132 vs. 187 kJ mol $^{-1}$),^[22] in line with previous reports describing the elevation of the HOMO in metallylene compounds by the strongly donating boryl substituent. Dimerization and the limited solubility of the resulting dication $[2_2][BAR^f_4]_2$, however, caused us to investigate the use of the base-stabilized adducts $[2-L][BAR^f_4]$ (L = thf or py) as potential *in situ* sources of the 'naked' $[2]^+$ fragment, with the more strongly bound pyridine adduct being significantly less labile. As such, most reactivity studies were undertaken by employing solid samples of $[2_2][BAR^f_4]_2$ re-dissolved in thf or thf- d_8 . In the case of $(CH(SiMe_3)_2)$ -substituted $[1][BAR^f_4]$, E-H bond activation chemistry is typically followed by the elimination of $[(IDipp)H]^+$. We hypothesized that the incorporation of the more strongly donating boryl ancillary ligand in $[2]^+$ (cf. $CH(SiMe_3)_2$) would stabilize the Ge^{IV} hydride products to potential reductive elimination processes. Thus, we examined the reactivity of $[2-thf][BAR^f_4]$ towards a range of E-H bonds (possessing apolar, protic and hydric character) to probe the potential scope of such chemistry.

Addition of an equimolar amount of Et_3SiH or $PhSiH_3$ to $[2-thf][BAR^f_4]$ in thf, leads to a rapid colour change from orange to pale yellow, with the 1H NMR spectrum in each case revealing complete conversion to a single new product. These new species can be shown by a combination of spectroscopic, analytical and crystallographic techniques to be the cationic silyl hydrides $[2(H)(SiEt_3)][BAR^f_4]$ and $[2(H)(SiH_2Ph)][BAR^f_4]$, respectively (Scheme 4). The 1H NMR spectrum of the former compound reveals new signals corresponding to the Et_3Si



Scheme 3. Cleavage of dimeric $[2_2]^{2+}$ in the presence of Lewis base donors ($[BAR^f_4]$ counter-ions omitted for clarity).



Scheme 4. Oxidative activation of H_2 and silanes by $[2\text{-thf}]^+$ ($[\text{BAR}'_4]$ counter-ions omitted for clarity).

moiety, and a singlet at 4.17 ppm in the region characteristic of germanium-bound hydrogens. $[2(\text{H})(\text{SiH}_2\text{Ph})][\text{BAR}'_4]$ also gives rise to a signal in this region, in this case a doublet of doublets at $\delta_{\text{H}} = 4.02$ ppm, due to coupling to the diastereotopic protons of the SiH_2Ph moiety. New signals are also observed in the ^{29}Si NMR spectrum at $\delta_{\text{Si}} = 4.0$ ppm and -54.9 ppm, respectively (cf. 0 and -60 ppm for Et_3SiH and PhSiH_3), and single crystals suitable for X-ray diffraction could be obtained for both products by layering a concentrated fluorobenzene solution with hexane. The structures determined (Figure 4) confirm the formation of the respective Ge^{IV} silyl hydrides. In the case of $[2(\text{H})(\text{SiH}_2\text{Ph})][\text{BAR}'_4]$, for example, the formal oxidation from Ge^{II} to Ge^{IV} brings

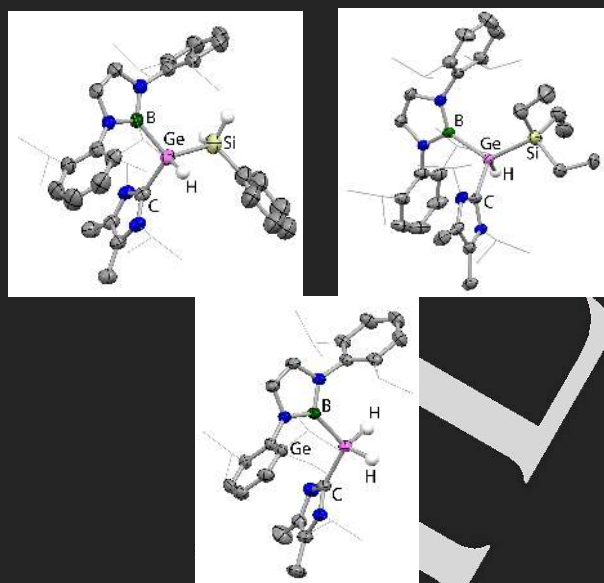


Figure 4. Molecular structures of the cationic components of $[2(\text{H})(\text{SiH}_2\text{Ph})][\text{BAR}'_4]$ (upper left), $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$ (upper right) and $[2(\text{H})_2][\text{BAR}'_4]$ (lower) as determined by X-ray crystallography. Most hydrogen atoms, solvate molecules and counter-ions omitted, and Pr groups shown in wireframe format for clarity. Thermal ellipsoids set at the 50% level. Key bond lengths (Å) and angles ($^\circ$): (for $[2(\text{H})(\text{SiH}_2\text{Ph})][\text{BAR}'_4]$) Ge-B 2.042(3), Ge-C 2.000(3), Ge-Si 2.383(1), Ge-H 1.54, B-Ge-C 110.4(1); (for $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$) Ge-B 2.064(5), Ge-C 2.030(5), Ge-Si 2.444(6), Ge-H 1.45, B-Ge-C 109.3(2); (for $[2(\text{H})_2][\text{BAR}'_4]$) Ge-B 2.048(2), Ge-C 1.991(2), Ge-H 1.51(3), 1.75(2), B-Ge-C 114.4(1).

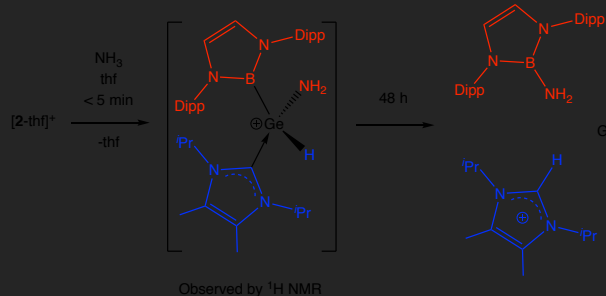
with it a marked shortening in the Ge-B and Ge-C distances (2.042(3)/2.000(3) cf. 2.127(5)/2.074(5) Å for $[2\text{-thf}][\text{BAR}'_4]$, and with it a widening in the B-Ge-C angle [110.4(1) vs. 100.9(2) $^\circ$] in order to minimize the increase in steric repulsion between the relatively bulky boryl/NHC substituents. Similar structural observations can be made for $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$, with the B-Ge-C angle in this case widening to 109.3(2) $^\circ$.

Interestingly, Et_3SiH also reacts with $[2]_2[\text{BAR}'_4]_2$ in fluorobenzene and with $[2\text{-py}][\text{BAR}'_4]$ in pyridine- d_5 to generate the same product, $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$, although the reaction in each case proceeds significantly more slowly than with $[2\text{-thf}][\text{BAR}'_4]$, consistent with less facile access to the putative base-free monomeric cation $[2]^+$ in solution. The reaction of $[2\text{-py}][\text{BAR}'_4]$ with Et_3SiH , for example, takes 10 h to proceed to completion at 333 K, while the corresponding reaction with $[2\text{-thf}][\text{BAR}'_4]$ is complete in the time taken to acquire an NMR spectrum.

$[2\text{-thf}][\text{BAR}'_4]$ also reacts with dihydrogen under relatively mild conditions, albeit significantly more slowly than with silanes. Thus, storage under one atmosphere pressure in $\text{thf-}d_6$, leads to complete conversion over 7 d at room temperature. The product is characterized by a signal at $\delta_{\text{H}} = 4.17$ ppm which integrates as two germanium-bound hydrogens, and the formation of the dihydride species $[2(\text{H})_2][\text{BAR}'_4]$ is also consistent with the results obtained from X-ray crystallography (Figure 4). Although the positions of the hydrogen atoms must be viewed with the usual caveats relating to the location of metal-bound hydrides by X-ray techniques, the shortened Ge-B and Ge-C distances [2.048(2) and 1.991(2) Å, respectively] and widened B-Ge-C angle [114.4(1) $^\circ$] are consistent with those found for other Ge^{IV} species, including the (silyl)hydrides $[2(\text{H})(\text{SiH}_2\text{Ph})][\text{BAR}'_4]$ and $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$.

The reactivity of the $[2]^+$ fragment towards protic E-H bonds has also been examined. Exposure of $[2\text{-thf}][\text{BAR}'_4]$ to NH_3 (at 1 atmosphere pressure), leads to complete conversion to a new product over a period of < 5 min. Monitoring of the reaction by *in situ* NMR measurements shows that the new compound is characterized by a broad GeH singlet at $\delta_{\text{H}} = 5.66$ ppm (integrating to 1H) together with resonances associated with the NHC and boryl substituents. In addition, a high-field signal (at $\delta_{\text{H}} = 0.32$ ppm) integrating to 2H can be assigned to a GeNH_2 unit. The similarity in the chemical shifts of both signals to the GeH and GeNH_2 signals measured for structurally characterized species of the type $\text{Ar}_2\text{Ge}(\text{H})(\text{NH}_2)$ (e.g. GeH : $\delta_{\text{H}} = 5.47, 5.84$ ppm for $\text{Ar} = \text{C}_6\text{H}_3\text{Mes}_2\text{-}2,6$ and $\text{C}_6\text{H}_3\text{Dipp}_2\text{-}2,6$ in benzene- d_6 and toluene- d_8 , respectively; GeNH_2 : $\delta_{\text{H}} = -0.37, -0.37$ ppm),^[11a] suggests that this species is the N-H activation product $[2(\text{H})(\text{NH}_2)][\text{BAR}'_4]$ (Scheme 5). Even at short reaction times, however, the characteristic imidazolium CH resonance of the $[(\text{IPrMe})\text{H}]^+$ cation ($\delta_{\text{H}} = 8.76$ ppm) is observed to grow in, together with a new set of resonances corresponding to the (known) boryl amine, $\text{H}_2\text{NB}(\text{NDippCH})_2$.^[12a,32] After 2 days, the initially formed intermediate is completely converted into $[(\text{IPrMe})\text{H}]^+$ and $\text{H}_2\text{NB}(\text{NDippCH})_2$ (Scheme 5). Presumably, the very strong B-N bond, and its facile formation through the coupling of electrophilic and nucleophilic fragments, provides

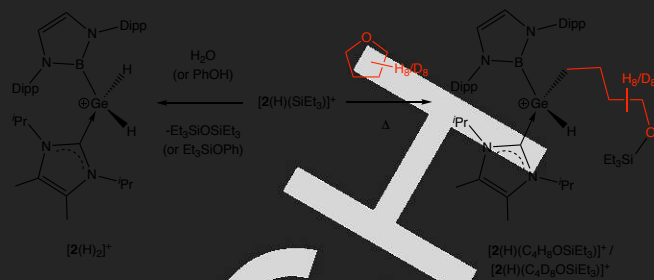
both thermodynamic and kinetic driving forces for this chemistry. Such a hypothesis is consistent with the observation that (unlike the chemistry seen for $[1]^+$), this is the only example encountered of reductive elimination from Ge^{IV} products derived from $[2]^+$. Moreover, the B-N reductive elimination process has direct parallels with the chemistry observed for the bis(boryl)tin system $(\{\text{HCDippN}\}_2\text{B})_2\text{Sn}(\text{H})\text{NH}_2$.^[12a]



Scheme 5. Generation of $[(\text{IPrMe})\text{H}]^+$ and $\text{H}_2\text{NB}(\text{NDippCH})_2$ in the reaction of $[2\text{-thf}]^+$ with NH_3 , via the postulated intermediate $[2(\text{H})(\text{NH}_2)][\text{BAR}'_4]$ ($[\text{BAR}'_4]$ counter-ions omitted for clarity).

Tobita and co-workers have reported that the addition of B-H/Si-H bonds across the Ge^{II} centre in $[\text{Ge}\{\text{W}(\text{CO})_3\text{Cp}^*\}(\text{IDipp})]^+$ is reversible.^[25] With this in mind, we were interested to probe whether similar behaviour could be observed in the case of $[2]^+$, and specifically whether reductive release of silane could be promoted from $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$ at elevated temperatures. Solutions in thf-d_8 were heated to 333 K and their behaviour monitored by *in situ* NMR measurements. Over a period of several days, clean formation of a new product is observed, although this process does not appear to involve the evolution of Et_3SiH , or the formation of $[2\text{-thf}][\text{BAR}'_4]$. Analysis by ESI-MS (envelope centred on $m/z = 837.6$) suggests the formation of a cationic species from $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$ via the uptake of one equivalent of thf-d_8 , and the ^{29}Si NMR spectrum features a resonance at $\delta_{\text{Si}} = 17.4$ ppm consistent with a compound of the type ROSiEt_3 (cf. 17.9 ppm for $^{29}\text{C}_5\text{H}_{11}\text{OSiEt}_3$).^[34] When the reaction is carried out in protio thf , the corresponding peak in the mass spectrum comes at $m/z = 829.5$ and additional ^1H NMR signals are seen in the region associated with ring-opened thf (e.g. an OCH_2 multiplet at $\delta_{\text{H}} = 3.34$ ppm integrating to 2H). The identity of the product is also suggested by the results of a single crystal X-ray diffraction study (Scheme 6 and Figure 5), with the cationic component being formed via formal insertion of thf-d_8 into the Ge-Si bond. Ring opening proceeds via the formation of Ge-C and Si-O bonds, with the implication being that the silyl ligand in $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$ possesses electrophilic character at silicon. This hypothesis is consistent with simple electronegativity arguments (Pauling electronegativities: Si, 1.90; Ge, 2.01),^[32] and also with the finding that $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$ reacts with water or phenol, leading to the formation of $[2(\text{H})_2][\text{BAR}'_4]$ together with products containing Si-O bonds (Scheme 6).

In the case of $[2(\text{H})(\text{C}_4\text{D}_8\text{OSiEt}_3)][\text{BAR}'_4]/[2(\text{H})(\text{C}_4\text{H}_8\text{OSiEt}_3)][\text{BAR}'_4]$, we propose a mechanism involving initial nucleophilic



Scheme 6. Reactivity of $[2(\text{H})(\text{SiEt}_3)]^+$ towards thf and protic reagents ($[\text{BAR}'_4]$ counter-ions omitted for clarity).

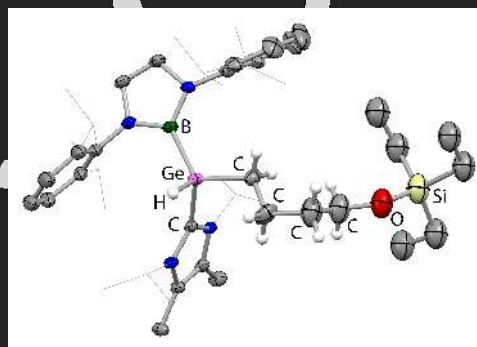
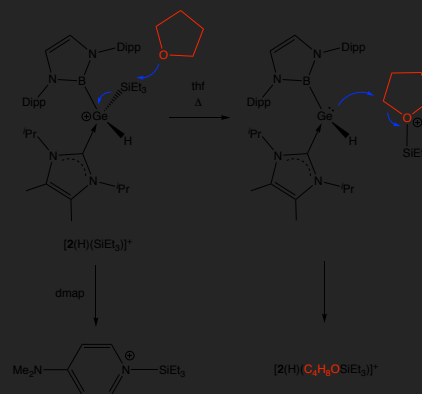


Figure 5. Molecular structure of the cationic component of $[2(\text{H})(\text{C}_4\text{D}_8\text{OSiEt}_3)]^+$ as determined by X-ray crystallography. Most hydrogen atoms, solvent molecules and counter-ions omitted, and Pr groups shown in wireframe format for clarity. Thermal ellipsoids set at the 35% level. Key bond lengths (Å) and angles ($^\circ$): Ge-B 2.047(4), Ge-C(27) 2.005(3), Ge-C(38) 1.969(4), B-Ge-C 110.8(1).

attack by thf on the silicon centre in $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$ to give a thf -stabilized silylium cation and a three-coordinate NHC-stabilized hydrido gerylene (Scheme 7).^[36] The formation of the former is supported by examination of the corresponding reaction of $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]$ with 4-(*N,N*-dimethylamino)-pyridine (dmap), which yields the related (but less labile) $[(\text{dmap})\text{SiEt}_3]^+$ cation. The very similar trimethylsilylium adduct $[(\text{dmap})\text{SiMe}_3]^+$ has been reported previously by Burford and co-workers,^[37] and the spectroscopic data for $[(\text{dmap})\text{SiEt}_3]^+$ obtain-



Scheme 7. Proposed mechanism for the activation of thf by $[2(\text{H})(\text{SiEt}_3)]^+$. ($[\text{BAR}'_4]$ counter-ions omitted for clarity)

ed from $[2(\text{H})(\text{SiEt}_3)][\text{BAR}'_4]/\text{dmap}$ are identical to those obtained from the reaction of $\text{Et}_3\text{SiCl}/\text{dmap}$ in the presence of $\text{Ag}(\text{OTf})$. In the formation of $[2(\text{H})(\text{C}_4\text{H}_8\text{OSiEt}_3)]^+$, subsequent nucleophilic attack by the (neutral) hydrido germylene at the α -carbon of the activated thf moiety then brings about ring opening in a manner similar to numerous other thf activation processes reported in the literature.^[38] The overall process amounts to cleavage of thf by the combined action of a silicon-centred Lewis acid and a germanium-centred Lewis base.

Conclusions

Attempts to synthesize an NHC-ligated (boryl)germanium(II) cation, $[\text{Ge}\{\text{B}(\text{NDippCH}_2)\}(\text{IPrMe})]^+$, analogous to recently reported alkyl and $[\text{Cp}^*\text{W}(\text{CO})_3]$ -stabilized systems, lead instead to the formation of the corresponding dimer $[(\text{IPrMe})\{\text{HCN-Dipp}_2\text{B}\}\text{Ge}=\text{Ge}\{\text{B}(\text{NDippCH}_2)\}(\text{IPrMe})]^{2+}$, $[2_2]^{2+}$. The reduced steric demands of the carbene ligand employed and the strong σ -donating capabilities of the boryl substituent (with consequent narrowing of the HOMO-LUMO gap) presumably contribute to these structural differences. Nonetheless, $[2_2]^{2+}$ is readily cleaved in the presence of donors such as thf or pyridine to give monomeric adducts, and in the case of $[\text{Ge}\{\text{B}(\text{NDippCH}_2)\}(\text{IPrMe})(\text{thf})]^+$, the additional donor is sufficiently labile that it can act as a convenient source of the $[\text{Ge}\{\text{B}(\text{NDippCH}_2)\}(\text{IPrMe})]^+$ fragment. This lability, together with the very small HOMO-LUMO gap calculated for the putative two-coordinate germylium-ylidene (132 kJ mol^{-1}) contribute to the facile oxidative bond activation chemistry observed. Thus, $[\text{Ge}\{\text{B}(\text{NDippCH}_2)\}(\text{IPrMe})(\text{thf})]^+$ reacts with silanes and hydrogen, leading to the formation of Ge^{IV} products, while the cleavage of the N-H bond in ammonia proceeds via similar initial steps, but ultimately yields products containing C-H and B-N bonds.

Experimental Section

General details

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. Hexane was degassed by sparging with argon and dried using a commercially available Braun SPS; fluorobenzene was dried by refluxing over CaH_2 . Thf-d_8 was dried over LiAlH_4 ; pyridine- d_5 was dried over CaCl_2 . NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. NMR spectra were measured on Varian Mercury-VX, Bruker Avance III HD Nanobay or Bruker AVII spectrometers operating at 300, 400 or 500 MHz, respectively (for ^1H measurements); ^1H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0 \text{ ppm}$). ^{11}B , ^{19}F and ^{27}Al NMR spectra were referenced with respect to $\text{BF}_3\cdot\text{OEt}_2$, CFCl_3 and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out at London Metropolitan University. The synthesis of 2-Cl was carried out as per the literature method.^[28]

Crystallography

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N or Fomblin Y oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.^[39a] Data were collected at 150 K using mirror monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$; Oxford Diffraction Supernova). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).^[39b] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.^[39b] Structures were solved ab initio from the integrated intensities using SHELXT^[39c] or Superflip^[39d] and refined on F^2 using SHELXL^[39e] with the graphical interface Olex2^[39f] or X-Seed,^[39g] or using full-matrix least-squares refinement with CRYSTALS.^[39h-i] CCDC deposition numbers 1952685–1952691.

DFT calculations

DFT calculations, including geometry optimizations were performed using the Amsterdam Density Functional (ADF) 2014 software package. Calculations were performed using the Vosko-Wilk-Nusair local density approximation with exchange from Becke,^[40a] and correlation correction from Perdew,^[40b] and three dimension dispersion effect.^[40c] Slater-type orbitals (STOs) were used for the triple zeta basis set with an additional set of polarization functions (TZP).^[40d] The large core basis set approximation was applied with no molecular symmetry. General numerical quality was good. Geometric details and molecular orbital energies were obtained after unrestricted geometry optimization.

Syntheses of Novel Compounds

$[2_2][\text{BAR}'_4]_2$: 2-Cl (750 mg, 1.11 mmol) and $\text{Na}[\text{BAR}'_4]$ (984 mg, 1.11 mmol) were combined in fluorobenzene. The solution immediately turned a deep red, and was stirred for a further 1 h. After filtration, the solution was concentrated and layered with hexane. Storage at 248 K for 3 d yielded deep red crystals, which were isolated, washed with a small amount of cold fluorobenzene, and dried in vacuo. Yield: 812 mg, 49%. The very low solubility of $[2_2][\text{BAR}'_4]_2$ precluded attempts to characterize it by NMR spectroscopy in non-donor solvents. Dissolution in donor solvents (such as thf) leads to fragmentation into mono-germanium species which were amenable to NMR study (see below). UV-vis (fluorobenzene): $\lambda_{\text{max}} = 462 \text{ nm}$ ($\epsilon = 9840 \text{ M}^{-1} \text{ cm}^{-1}$). Elemental microanalysis: found (calc. for $\text{C}_{69}\text{H}_{68}\text{B}_2\text{F}_{24}\text{GeN}_4$): C 54.98 (55.12)%, H 4.62 (4.56)%, N 3.71 (3.73)%. Crystallographic data: $\text{C}_{138}\text{H}_{136}\text{B}_4\text{F}_{48}\text{Ge}_2\text{N}_8$, $M_r = 3006.99$, triclinic, P-1, $a = 17.0530(2)$, $b = 17.6136(2)$, $c = 28.6924(4) \text{ \AA}$, $\alpha = 94.938(1)$, $\beta = 103.799(1)$, $\gamma = 106.493(1)^\circ$, $V = 7914.9(2) \text{ \AA}^3$, $Z = 2$, $R_1 = 0.0775$ (28091, $I > 2\sigma(I)$), $wR_2 = 0.2186$ (all 32903 unique reflections).

$[2-(\text{thf-d}_8)][\text{BAR}'_4]$ and $[2-(\text{py-d}_5)][\text{BAR}'_4]$ were obtained in essentially quantitative yields by dissolving $[2_2][\text{BAR}'_4]_2$ in thf- d_8 or pyridine- d_5 , respectively. Single crystals suitable for X-ray crystallography were obtained by layering a concentrated solution with hexane and storage at room temperature. Data for $[2-(\text{py-d}_5)][\text{BAR}'_4]$: ^1H NMR (400 MHz, pyridine- d_5 , 298 K): 1.10 (br overlapping m, 12H, $\text{CH}(\text{CH}_3)_2$, boryl), 1.10 (br overlapping m, 12H, $\text{CH}(\text{CH}_3)_2$, NHC), 1.23 (d, $^3J_{\text{HH}} = 6.5 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$, boryl), 2.14 (s, 6H, backbone CH_3 , NHC), 3.37 (br m, 4H, $\text{CH}(\text{CH}_3)_2$, boryl), 5.06 (sept, $^3J_{\text{HH}} = 7.0 \text{ Hz}$, 2H, $\text{CH}(\text{CH}_3)_2$, NHC), 6.66 (s, 2H, backbone CH, boryl), 7.34 (br m, 4H, *m*-CH, boryl), 7.51 (t, $^3J_{\text{HH}} = 7.8 \text{ Hz}$, 2H, *p*-CH, boryl), 7.84 (s, 4H, *p*-CH, $[\text{BAR}'_4]$), 8.43 (s, 8H, *o*-CH, $[\text{BAR}'_4]$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, pyridine- d_5 , 298 K): -6 ($[\text{BAR}'_4]$), 33 (boryl). Crystallographic data: (contains 1.5 pyridine solvate molecules) $\text{C}_{81.5}\text{H}_{80.5}\text{B}_2\text{F}_{24}\text{GeN}_{6.5}$, $M_r = 1701.23$, orthorhombic, $\text{Pba}2$, $a = 22.8649(3)$

A, b = 26.8024(3) Å, c = 13.2326(1) Å, V = 8109.4(2) Å³, Z = 4, R₁ = 0.0441 (15211, I>2σ(I)), wR₂ = 0.1178 (all 16849 unique reflections). Data for [2-(thf-d₈)]([BAR'₄]): ¹H NMR (400 MHz, thf-d₈, 298 K): δ_H 1.18 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂, boryl), 1.24 (br m, 12H, CH(CH₃)₂, boryl), 1.29 (br m, 12H, CH(CH₃)₂, NHC), 2.29 (s, 6H, backbone CH₃, NHC), 3.24 (sept, ³J_{HH} = 6.4 Hz, 4H, CH(CH₃)₂, boryl), 4.83 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂, NHC), 6.43 (s, 2H, backbone CH, boryl), 7.26 (d, ³J_{HH} = 7.5 Hz, 4H, *m*-CH, boryl), 7.33 (t, ³J_{HH} = 7.5 Hz, 2H, *p*-CH, boryl), 7.59 (s, 4H, *p*-CH, [BAR'₄]), 7.80 (s, 8H, *o*-CH, [BAR'₄]). ¹¹B{¹H} NMR (128 MHz, thf-d₈, 298 K): δ_B -6 ([BAR'₄]), 34 (boryl). ¹³C{¹H} NMR (101 MHz, thf-d₈, 298 K): δ_C 10.6 (backbone CH₃, NHC), 21.8 (CH(CH₃)₂, NHC), 24.0, 26.6 (CH(CH₃)₂, boryl), 29.5 (CH(CH₃)₂, boryl), 55.0 (CH(CH₃)₂, NHC), 118.4 (br m, *p*-CH, [BAR'₄]), 124.2 (backbone CH, boryl), 125.2 (*m*-CH, boryl), 125.7 (q, ¹J_{C-F} = 271.8 Hz, CF₃, [BAR'₄]), 129.5 (*p*-CH, boryl), 130.0 (backbone C, NHC), 130.2 (qq, ³J_{C-B} = 2.4 Hz, ²J_{C-F} = 32.2 Hz, *m*-C, [BAR'₄]), 135.8 (*o*-CH, [BAR'₄]), 140.4 (*i*-C, boryl), 147.4 (*o*-C, boryl), 163.0 (q, ¹J_{C-B} = 50.1 Hz, *i*-C, [BAR'₄]), 167.0 (imidazolylidene C, NHC). ¹⁹F NMR (377 MHz, thf-d₈, 298 K): δ_F -63.4 ([BAR'₄]). Elemental microanalysis: found (calc. for C₇₅H₇₆B₂F₂₄GeN₄O): C 55.12 (55.65)%, H 4.73 (4.86)%, N 3.66 (3.56)%. Crystallographic data: (contains 1 thf solvate molecule) C₇₇H₈₄B₂F₂₄GeN₄O₂, M_r = 1647.69, monoclinic, P2₁/c, a = 13.1361(2), b = 23.9448(4), c = 26.3106(4) Å, β = 89.683(2)°, V = 8275.6(2) Å³, Z = 4, R₁ = 0.0847 (12843, I>2σ(I)), wR₂ = 0.2472 (all 14624 unique reflections).

[2(H)(SiEt₃)]([BAR'₄]): Et₃SiH (5.3 μL, 0.03 mmol) was added to a solution of [2-(thf-d₈)]([BAR'₄]) (50 mg, 0.03 mmol) in thf-d₈ (0.5 mL) in a J. Young's NMR tube. The solution immediately changed colour from yellow to colourless, and ¹H NMR spectroscopy revealed complete conversion to the product within 5 min. Alternatively, the reaction can be performed by mixing Et₃SiH and [2]₂[BAR'₄]₂ in fluorobenzene or d₅-pyridine, in which case the reaction mixture was respectively stirred for 3 h at room temperature or heated at 333 K for 10 h. Single crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution with hexane and storage at 248 K. Yield: 0.020 g, 57%. ¹H NMR (400 MHz, thf-d₈, 298 K): δ_H 0.20 (m, 3H, SiCH(H)CH₃, SiEt₃), 0.49 (m, 3H, SiCH(H)CH₃, SiEt₃), 0.70 (d, ³J_{HH} = 6.7 Hz, 3H, CH(CH₃)₂, NHC), 0.77 (t, ³J_{HH} = 7.9 Hz, 9H, SiCH₂CH₃, SiEt₃), 1.14 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.17 (br m, 12H, CH(CH₃)₂, boryl), 1.38 (d, ³J_{HH} = 6.6 Hz, 3H, CH(CH₃)₂, NHC), 1.43 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂, boryl), 1.57 (d, ³J_{HH} = 7.0 Hz, 3H, CH(CH₃)₂, NHC), 1.61 (d, ³J_{HH} = 7.0 Hz, 3H, CH(CH₃)₂, NHC), 2.23 (s, 3H, backbone CH₃, NHC), 2.35 (s, 3H, backbone CH₃, NHC), 2.74 (br m, 2H, CH(CH₃)₂, boryl), 3.13 (br m, 2H, CH(CH₃)₂, boryl), 4.17 (s, 1H, GeH), 4.36 (sept, ³J_{HH} = 7.3 Hz, 1H, CH(CH₃)₂, NHC), 4.48 (sept, ³J_{HH} = 6.9 Hz, 1H, CH(CH₃)₂, NHC), 6.61 (s, 2H, backbone CH, boryl), 7.10-7.40 (m, 6H, *m*- and *p*-CH, boryl), 7.58 (s, 4H, *p*-CH, [BAR'₄]), 7.80 (s, 8H, *o*-CH, [BAR'₄]). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ_H 0.12 (m, 3H, SiCH(H)CH₃, SiEt₃), 0.41 (m, 3H, SiCH(H)CH₃, SiEt₃), 0.64 (d, ³J_{HH} = 6.5 Hz, 3H, CH(CH₃)₂, NHC), 0.73 (t, ³J_{HH} = 7.6 Hz, 9H, SiCH₂CH₃, SiEt₃), 1.12 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.15 (br m, 12H, CH(CH₃)₂, boryl), 1.27 (d, ³J_{HH} = 6.5 Hz, 3H, CH(CH₃)₂, NHC), 1.38 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.48 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂, NHC), 1.53 (d, ³J_{HH} = 7.0 Hz, 3H, CH(CH₃)₂, NHC), 2.14 (s, 3H, backbone CH₃, NHC), 2.25 (s, 3H, backbone CH₃, NHC), 2.66 (br m, 2H, CH(CH₃)₂, boryl), 3.05 (br m, 2H, CH(CH₃)₂, boryl), 4.09 (s, 1H, GeH), 4.30 (sept, ³J_{HH} = 7.3 Hz, 1H, CH(CH₃)₂, NHC), 4.41 (sept, ³J_{HH} = 7.1 Hz, 1H, CH(CH₃)₂, NHC), 6.45 (s, 2H, backbone CH, boryl), 7.13-7.39 (m, 6H, *m*- and *p*-CH, boryl), 7.56 (s, 4H, *p*-CH, [BAR'₄]), 7.72 (s, 8H, *o*-CH, [BAR'₄]). ¹¹B{¹H} NMR (128 MHz, thf-d₈, 298 K): δ_B -6 ([BAR'₄]), 25 (boryl). ¹³C{¹H} NMR (101 MHz, thf-d₈, 298 K): δ_C 5.9 (SiCH₂CH₃), 8.4 (SiCH₂CH₃), 10.8, 10.9 (backbone CH₃, NHC), 21.2, 21.4 (2 overlapping signals), 21.6, (CH(CH₃)₂, NHC), 22.8, 23.1, 26.3, 27.0 (CH(CH₃)₂, boryl), 29.5, 29.9 (CH(CH₃)₂, boryl), 55.2, 56.2 (CH(CH₃)₂, NHC), 118.4 (br m, *p*-CH, [BAR'₄]), 125.1, 125.3

(backbone CH and *m*-CH, boryl), 125.7 (q, ¹J_{C-F} = 273.6 Hz, CF₃, [BAR'₄]), 129.8 (*p*-CH of boryl), 130.2 (qq, ³J_{C-B} = 3.6 Hz, ²J_{C-F} = 31.0 Hz, *m*-C, [BAR'₄]), 132.2 (backbone C, NHC), 135.8 (*o*-CH, [BAR'₄]), 139.8 (*i*-C, boryl), 146.6 (*o*-C, boryl), 151.1 (imidazolylidene C), 163.0 (q, ¹J_{C-B} = 48.9 Hz, *i*-C, [BAR'₄]). ¹⁹F NMR (377 MHz, thf-d₈, 298 K): δ_F -63.4 ([BAR'₄]). ²⁹Si{¹H} NMR (99 MHz, thf-d₈, 298 K): δ_{Si} 4.0 (GeSiEt₃). Elemental microanalysis: found (calc. for C₇₅H₇₆B₂F₂₄GeN₄Si·0.5(C₆H₆F₆)): C 56.46 (56.14)%, H 4.91 (5.23)%, N 3.58 (3.36)%. Crystallographic data: (contains 0.5 fluorobenzene solvate molecules) C₁₅₆H₁₇₃B₄F₄₉Ge₂N₈Si₂, M_r = 3335.66, monoclinic, P2₁/c, a = 13.1239(2), b = 24.0267(3), c = 26.8459(3) Å, β = 90.023(1)°, V = 8466.0(2) Å³, Z = 2, R₁ = 0.0775 (12989, I>2σ(I)), wR₂ = 0.2277 (all 17260 unique reflections).

[2(H)(SiH₂Ph)]([BAR'₄]): PhSiH₃ (6.1 μL, 0.05 mmol) was added to a solution of [2-(thf-d₈)]([BAR'₄]) (50 mg, 0.03 mmol) in thf-d₈ (0.5 mL) in a J. Young's NMR tube (the reaction also proceeds to completion, albeit more slowly with the use of 1.0 equiv. of silane). The solution immediately changed colour from yellow to colourless, and ¹H NMR spectroscopy revealed complete conversion to the product within 5 min. Single crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution with hexane, followed by storage at room temperature. Yield: 0.030 g, 56%. ¹H NMR (400 MHz, thf-d₈, 298 K): δ_H 0.68 (br m, 3H, CH(CH₃)₂, NHC), 0.93 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.04 (br m, 3H, CH(CH₃)₂, NHC), 1.16 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.21 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂, boryl), 1.34 (br m, 3H, CH(CH₃)₂, NHC), 1.45 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂, boryl), 1.60 (br m, 3H, CH(CH₃)₂, NHC), 2.24 (br s, 6H, backbone CH₃, NHC), 2.77 (sept, ³J_{HH} = 6.7 Hz, 2H, CH(CH₃)₂, boryl), 3.11 (sept, ³J_{HH} = 6.7 Hz, 2H, CH(CH₃)₂, boryl), 3.65 (d, ³J_{HH} = 3.3 Hz, 1H, GeSiH(H)Ph), 4.02 (dd, ³J_{HH} = 3.4, 8.8 Hz, 1H, GeH), 4.38 (d, ³J_{HH} = 8.7 Hz, 1H, GeSiH(H)Ph), 4.58 (br m, 2H, CH(CH₃)₂, NHC), 6.68 (s, 2H, backbone CH, boryl), 7.10-7.43 (11H, overlapping m, *m*- and *p*-CH, boryl + *o*-, *m*- and *p*-CH, Ph), 7.59 (s, 4H, *p*-CH, [BAR'₄]), 7.81 (s, 8H, *o*-CH, [BAR'₄]). ¹¹B{¹H} NMR (128 MHz, thf-d₈, 298 K): δ_B -6 ([BAR'₄]), 24 (boryl). ¹³C{¹H} NMR (101 MHz, thf-d₈, 298 K): δ_C 10.6, 10.7 (backbone CH₃, NHC), 21.2, 22.7, 23.4, 23.9, 24.4, 26.0, 26.8, 27.2 (CH(CH₃)₂, boryl and NHC), 29.5, 29.9 (CH(CH₃)₂, boryl), 51.5, 56.2 (CH(CH₃)₂, NHC), 118.4 (br m, *p*-CH, [BAR'₄]), 125.2, 125.3 (backbone CH and *m*-CH, boryl), 125.7 (q, ¹J_{C-F} = 273.0 Hz, CF₃, [BAR'₄]), 126.8 (*i*-C, PhSi), 129.1 (*m*-CH, PhSi), 129.6 (*p*-CH, boryl), 130.0 (*p*-CH, PhSi), 130.2 (qq, ³J_{C-B} = 2.4 Hz, ²J_{C-F} = 32.2 Hz, *m*-C, [BAR'₄]), 131.6 (backbone C, NHC), 135.8 (*o*-CH, [BAR'₄]), 136.2 (*o*-CH, PhSi), 139.1 (*i*-C, boryl), 146.6 (*o*-C, boryl), 147.1 (imidazolylidene C), 163.0 (q, ¹J_{C-B} = 50.1 Hz, *i*-CH, [BAR'₄]). ¹⁹F{¹H} NMR (377 MHz, thf-d₈, 298 K): -63.4 ([BAR'₄]). ²⁹Si{¹H} NMR (80 MHz, thf-d₈, 298 K): -54.9 (GeSiH₂Ph). Elemental microanalysis: found (calc. for C₇₅H₇₆B₂F₂₄GeN₄Si): C: 56.39 (55.89)%, H: 4.67 (4.75)%, N: 3.39 (3.48)%. Crystallographic data: C₇₅H₇₆B₂F₂₄GeN₄Si, M_r = 1611.73, monoclinic, I2/c, a = 27.8824(9), b = 13.5656(4), c = 43.9247(14) Å, β = 93.686(3)°, V = 16579.8(9) Å³, Z = 8, R₁ = 0.0558 (17251, I>2σ(I)), wR₂ = 0.1107 (all 17323 unique reflections).

Reaction of [2-thf][BAR'₄] with ammonia: A J. Young's NMR tube containing a solution of [2-thf][BAR'₄] (50 mg, 0.03 mmol) in thf-d₈ (0.5 mL) was degassed via three freeze-pump-thaw cycles, and back-filled with NH₃ (ca. 1 atm. pressure). Monitoring via ¹H NMR spectroscopy revealed essentially instantaneous conversion to a single product, which underwent subsequent conversion over 2 d to the known compounds [(iPrMeH)]([BAR'₄]) and [(HCNDipp)₂B]NH₂.^[10a] Data for first-formed species: ¹H NMR (400 MHz, thf-d₈, 298 K): 0.32 (s, 2H, GeNH₂), 1.01 (d, ³J_{HH} = 7.0 Hz, 6H), 1.18 (overlapping m, 12H), 1.23 (overlapping m, 6H), 1.37 (d, ³J_{HH} = 7.0 Hz, 6H), 1.41 (d, ³J_{HH} = 6.8 Hz, 6H) [all CH(CH₃)₂, boryl and NHC], 2.28 (s, 6H, backbone CH₃, NHC), 2.88 (sept, ³J_{HH} = 6.7 Hz, 2H, CH(CH₃)₂, boryl), 3.07 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂, boryl), 4.68 (br m, 2H, CH(CH₃)₂, NHC), 5.66 (s, 1H, GeH), 6.65 (s, 2H, backbone CH, boryl), 7.27-7.48 (m, 6H, *m*- and *p*-CH, boryl),

7.58 (s, 4H, *p*-CH, [BAR₄]), 7.80 (s, 8H, *o*-CH, [BAR₄]). ¹¹B{¹H} NMR (128 MHz, thf-d₈, 298 K): -6 ([BAR₄]), 23 (boryl).

[2(H)(C₄D₈OSiEt₃)] [BAR₄] and **[2(H)(C₄H₈OSiEt₃)] [BAR₄]**: An *in situ*-generated solution of [2(H)(SiEt₃)] [BAR₄] (0.03 mmol) in thf-d₈ (0.5 mL) in a J. Young's NMR tube was heated with a further excess of Et₃SiH (26.6 μL, 0.17 mmol, 5 equiv.) at 333 K for 5 d, after which time complete conversion to [2(H)(C₄D₈OSiEt₃)] [BAR₄] was observed by ¹H NMR spectroscopy. A similar procedure using protio-thf could be exploited to yield [2(H)(C₄H₈OSiEt₃)] [BAR₄]. Single crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution with hexane, followed by storage at 248 K for several days. Yield: 0.020 g, 35%. Data for [2(H)(C₄D₈OSiEt₃)] [BAR₄]: ¹H NMR (500 MHz, thf-d₈, 298 K): δ_H 0.50 (q, ³J_{HH} = 7.9 Hz, 6H, SiCH₂CH₃, SiEt₃), 0.87 (t, ³J_{HH} = 8.1 Hz, 9H, SiCH₂CH₃, SiEt₃), 0.97 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂, boryl), 1.16 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂, boryl), 1.20 (overlapping m, 3H, CH(CH₃)₂, NHC), 1.21 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂, boryl), 1.28 (d, ³J_{HH} = 7.0 Hz, 3H, CH(CH₃)₂, NHC), 1.41 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.54 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂, NHC), 2.31 (br s, 6H, backbone CH₃, NHC), 2.80 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂, boryl), 3.07 (sept, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂, boryl), 4.38 (br m, 2H, CH(CH₃)₂, NHC), 4.52 (br s, 1H, GeH), 6.66 (s, 2H, backbone CH, boryl), 7.25–7.42 (m, 6H, *m*- and *p*-CH, boryl), 7.57 (s, 4H, *p*-CH, [BAR₄]), 7.79 (s, 8H, *o*-CH, [BAR₄]). ¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ_H 0.48 (q, ³J_{HH} = 7.9 Hz, 6H, SiCH₂CH₃, SiEt₃), 0.85 (t, ³J_{HH} = 8.2 Hz, 9H, SiCH₂CH₃, SiEt₃), 0.91 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂, boryl), 1.15 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.18 (overlapping m, 3H, CH(CH₃)₂, NHC), 1.19 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂, boryl), 1.23 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂, NHC), 1.36 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂, boryl), 1.54 (overlapping m, 6H, CH(CH₃)₂, NHC), 2.21 (br s, 6H, backbone CH₃, NHC), 2.72 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂, boryl), 3.00 (sept, ³J_{HH} = 7.0 Hz, 2H, CH(CH₃)₂, boryl), 4.29 (br m, 2H, CH(CH₃)₂, NHC), 4.44 (br s, 1H, GeH), 6.49 (s, 2H, backbone CH, boryl), 7.20 (d, ³J_{HH} = 7.9 Hz, 2H, *m*-CH, boryl), 7.30 (d, ³J_{HH} = 7.6 Hz, *m*-CH, boryl), 7.39 (t, ³J_{HH} = 7.8 Hz, 2H, *p*-CH, boryl), 7.56 (s, 4H, *p*-CH, [BAR₄]), 7.72 (s, 8H, *o*-CH, [BAR₄]). ¹¹B{¹H} NMR (128 MHz, thf-d₈, 298 K): δ_B -6 ([BAR₄]), 24 (boryl). ¹⁹F{¹H} NMR (377 MHz, thf-d₈, 298 K): δ_F -63.4 ([BAR₄]). ²⁹Si{¹H} NMR (99 MHz, thf-d₈, 298 K): δ_{Si} 17.4 (-OSiEt₃). ESI-MS: calc. (M⁺), 837.59; meas., 837.59. Crystallographic data: C₇₉H₈₂B₂F₂₄GeN₄OSi, M_r = 1694.86, monoclinic, P2₁/c, a = 13.2539(2), b = 23.6210(4), c = 26.8839(4) Å, β = 91.4860(10)°, V = 8413.7(2) Å³, Z = 4, R_i = 0.0841 (14156, I>2σ(I)), wR₂ = 0.2567 (all 17437 unique reflections). Data for [2(H)(C₄H₈OSiEt₃)] [BAR₄]: ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ_H 0.48 (q, ³J_{HH} = 8.1 Hz, 6H, SiCH₂CH₃, SiEt₃), 0.85 (t, ³J_{HH} = 8.1 Hz, 9H, SiCH₂CH₃, SiEt₃), 0.91 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂, boryl), 1.09 (t, ³J_{HH} = 5.9 Hz, 2H, CH₂OCH₂(CH₂)₃Ge [other CH₂ peaks obscured due to overlap with CH(CH₃)₂ peaks], 1.15 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.18 (overlapping m, 3H, CH(CH₃)₂, NHC), 1.19 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂, boryl), 1.23 (d, ³J_{HH} = 7.0 Hz, 3H, CH(CH₃)₂, NHC), 1.36 (d, ³J_{HH} = 7.0 Hz, 6H, CH(CH₃)₂, boryl), 1.51 (d, ³J_{HH} = 6.7 Hz, 6H, CH(CH₃)₂, NHC), 2.19 (br s, 6H, backbone CH₃, NHC), 2.78 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂, boryl), 3.01 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂, boryl), 3.34 (m, 2H, OCH₂), 4.31 (br sept, 2H, CH(CH₃)₂, NHC), 4.46 (br s, 1H, GeH), 6.50 (s, 2H, backbone CH, boryl), 7.20 (dd, ⁴J_{HH} = 1.5 Hz, ³J_{HH} = 7.7 Hz, 2H, *m*-CH, boryl), 7.30 (dd, ⁴J_{HH} = 1.5 Hz, ³J_{HH} = 7.7 Hz, 2H, *m*-CH, boryl), 7.39 (t, ³J_{HH} = 7.7 Hz, 2H, *p*-CH, boryl), 7.57 (s, 4H, *p*-CH, [BAR₄]), 7.73 (s, 8H, *o*-CH, [BAR₄]). ¹¹B{¹H} NMR (128 MHz, CD₂Cl₂, 298 K): δ_B -7 ([BAR₄]), 24 (boryl). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): δ_C 4.8 (SiCH₂CH₃), 7.0 (SiCH₂CH₃), 11.1 (backbone CH₃, NHC), 12.9, 13.2 (CH₂, O(CH₂)₄), 23.0, 23.4, 23.6, 24.6, 25.2, 26.0, 26.7, 27.4 (CH(CH₃)₂, boryl and NHC), 29.0, 29.3 (CH(CH₃)₂, boryl), 35.9 (CH₂, O(CH₂)₄), 52.2, 54.9 (CH(CH₃)₂, NHC), 61.7 (OCH₂), 118.0 (br m, *p*-CH, [BAR₄]), 124.3, 124.4 (backbone CH and *m*-CH, boryl), 125.2 (q, ¹J_{C-F} = 272.8 Hz, CF₃, [BAR₄]), 128.3 (*p*-CH, boryl), 129.5 (q, ³J_{C-B} = 2.9 Hz, ²J_{C-F} = 31.5 Hz, *m*-

C, [BAR₄]), 129.5 (backbone C, NHC), 135.4 (*o*-CH, [BAR₄]), 138.1 (*i*-C, boryl), 146.0, 146.3 (*o*-C, boryl), 148.9 (imidazolylidene C), 162.3 (q, ¹J_{C-B} = 48.6 Hz, *i*-C, [BAR₄]). ESI-MS: calc. (for [C₇₉H₈₀BGeN₄OSi]⁺), 829.54; meas., 829.54.

Acknowledgements

We acknowledge funding from Oxford University Clarendon Scholarship Fund (RM) the EU 7th Framework Program, Marie Skłodowska-Curie actions (PIEF-GA-2013-622806 for an IEF Fellowship (AR), the EU 7th Framework Program, Marie Skłodowska-Curie actions (COFUND, Grant Agreement no. 267226) and Junta de Andalucía for a Talentia Postdoc (JC), the Alexander von Humboldt Stiftung (GS), Oxford-SCG Centre of Excellence and the Leverhulme Trust (grant number RP-2018-246, JH).

Keywords: germanium • cation • low valent • bond activation • N-heterocyclic carbene

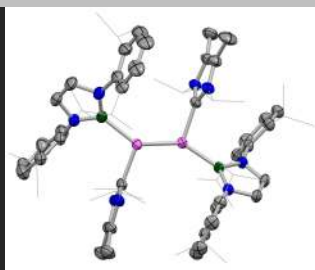
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Entry for the Table of Contents

FULL PAPER

Chloride abstraction from the boryl/NHC stabilized Ge(II) precursor (IPrMe)GeCl{B(NDippCH)₂} yields [(IPrMe){(HCNDipp)₂B}Ge=Ge{B(NDippCH)₂}(IPrMe)]²⁺ which can be viewed as an imidazolium-functionalized digermene, and is cleaved in the presence of donor solvents to give monomeric adducts of the type [Ge{B(NDippCH)₂}(IPrMe)(L)]⁺. The thf adduct is sufficiently labile that it can act as a convenient source of monomeric [Ge{B(NDippCH)₂}(IPrMe)]⁺, which undergoes oxidative bond activation chemistry with silanes, dihydrogen, and ammonia, in line with the very small HOMO-LUMO gap for this system (132 kJ mol⁻¹).



Robert J. Mangan, Arnab R., Christian P., Sindlinger, Rémi Tirfoin, Jesus Campos, Jamie Hicks, Kirsten E. Christensen, Haoyu Niu and Simon Aldridge*

Page No. – Page No.

Activation of protic, hydridic and apolar E-H bonds by a boryl-substituted Ge(II) cation