

## E-H bond activation by Main Group compounds

## A systematic study of structure and E-H bond activation chemistry by sterically encumbered germylene complexes

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**Abstract:** A series of new germylene compounds has been synthesized offering systematic variation in the  $\sigma$ - and  $\pi$ -capabilities of the  $\alpha$ -substituent, and differing levels of reactivity towards E-H bond activation (E = H, B, C, N, Si, Ge). Chloride metathesis utilizing (terphenyl)GeCl proves to be an effective synthetic route to complexes of the type (terphenyl)Ge(ER<sub>n</sub>) [**1-6**: ER<sub>n</sub> = NHDipp, CH(SiMe<sub>3</sub>)<sub>2</sub>, P(SiMe<sub>3</sub>)<sub>2</sub>, Si(SiMe<sub>3</sub>)<sub>3</sub> or B(NDippCH)<sub>2</sub>; terphenyl = C<sub>6</sub>H<sub>3</sub>Mes<sub>2-2,6</sub> = Ar<sup>Mes</sup> or C<sub>6</sub>H<sub>3</sub>Dipp<sub>2-2,6</sub> = Ar<sup>Dipp</sup>], while the related complex {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>} (**8**) can be accessed via an amide/boryl exchange route. Metrical parameters have been probed by X-ray crystallography, and are consistent with widening angles at the metal centre as more bulky and/or more electropositive substituents are employed. Thus, the widest germylene units ( $\theta > 110^\circ$ ) are found to be associated with strongly  $\sigma$ -donating boryl or silyl ancillary donors.

HOMO-LUMO gaps for the new germylene complexes have been appraised by DFT calculations. The aryl(boryl)

-germylene system Ar<sup>Mes</sup>Ge{B(NDippCH)<sub>2</sub>} (**6-Mes**), which features a wide C-Ge-B angle [110.4(1)°] and (albeit relatively weak) ancillary  $\pi$ -acceptor capabilities, has the smallest HOMO-LUMO gap (119 kJ mol<sup>-1</sup>). These features result in **6-Mes** being remarkably reactive, undergoing facile intramolecular C-H activation involving one of the mesityl *ortho*-methyl groups. The related aryl(silyl)-germylene system, Ar<sup>Mes</sup>Ge{Si(SiMe<sub>3</sub>)<sub>3</sub>} (**5-Mes**) has a marginally wider HOMO-LUMO gap (134 kJ mol<sup>-1</sup>), rendering it less labile towards decomposition, yet reactive enough to oxidatively cleave H<sub>2</sub> and NH<sub>3</sub> to give the corresponding dihydride and (amido)hydride. Mixed aryl/alkyl, aryl/amido and aryl/phosphido complexes are unreactive, but amido/boryl complex **8** is competent for the activation of E-H bonds (E = H, B, Si) to give hydrido, boryl and silyl products. The results of these reactivity studies imply that the use of the very strongly  $\sigma$ -donating boryl or silyl substituents is an effective strategy for rendering metallylene complexes competent for E-H bond activation.

Dedication ((optional))

## Introduction

The activation of small molecules by metal complexes – traditionally an area strongly linked with transition metal systems – has become a topic of intense recent interest among main group chemists.<sup>[1]</sup> Thus, for example, the activation of E-H bonds

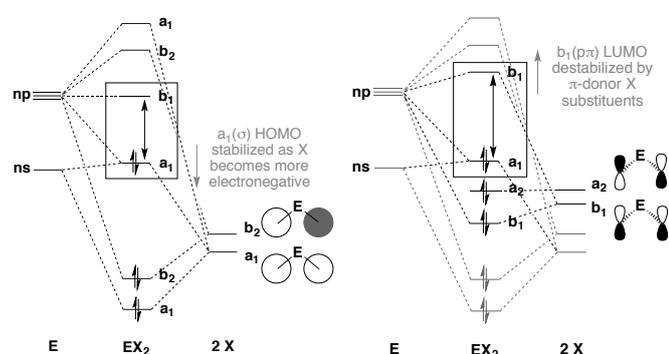
by heavier alkyne analogues,<sup>[2]</sup> by frustrated Lewis pairs (FLPs),<sup>[3]</sup> or by carbenes (and their heavier Group 14 metallylene analogues),<sup>[4-6]</sup> has attracted significant attention, not only from a fundamental perspective, but also with a view to incorporation into novel catalytic cycles.<sup>[1]</sup>

The reactivity of carbenes (X<sub>2</sub>C:) for example, towards E-H bond activation is known to be highly dependent on the nature of the X substituents, reflecting the influence they have on the magnitude of the HOMO-LUMO gap (Figure 1).<sup>[4-6]</sup> Thus, acyclic (amino)alkyl carbenes – which possess a relatively small HOMO-LUMO separation – are capable of the activation of types of chemical bond (e.g. H-H, N-H) which are more resistant to diamino carbene systems.<sup>[7]</sup> Manipulation of the energies of the HOMO and LUMO orbitals in these and related compounds is therefore clearly critical to achieving activity in small molecule activation. A key factor in this respect is the angle defined at the Group 14 centre by the bonds to the X substituents, with a narrower angle being associated with greater HOMO s-orbital character, a lower HOMO energy, and consequently a wider

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HOMO-LUMO gap.<sup>[4]</sup> Such characteristics tend to be found in association with a cyclic backbone (especially for 4- and 5-membered rings) and/or with highly electronegative  $\alpha$ -substituents. The latter finding has been rationalized by Bertrand *et al.* on the basis of the inductive lowering of the contributing orbitals from the X-substituents to the  $\sigma$  ( $a_1$ ) orbital (Figure 1),<sup>[4]</sup> and at a broader level is in accordance with Bent's rule that greater p-character (and hence an angle closer to  $90^\circ$ ) is found in bonds to more electronegative substituents.<sup>[8,9]</sup> Steric factors can also be important, with bulkier X groups causing elevation of the HOMO on the basis of a widened  $CX_2$  angle.<sup>[10]</sup> The influence of the LUMO energy on the HOMO-LUMO gap can also be tuned, with  $\pi$ -donor substituents typically causing the LUMO to take on C-X  $\pi^*$  character and hence to be elevated.<sup>[4]</sup>

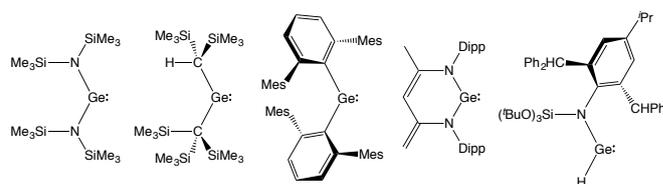


**Figure 1.** Variation in the energies of the HOMO and LUMO of a metallylene system,  $EX_2$ , as a function of the electronegativity (left) and  $\pi$ -donor capabilities (right) of X. Adapted from *Chem. Rev.* **2000**, *100*, 39-92 with permission.<sup>[4]</sup>

We have recently been interested in probing the potential for E-H activation by the heavier Group 14 analogues of carbenes, and have shown that acyclic silylenes possessing strongly  $\sigma$ -donating (i.e. relatively electropositive)  $\alpha$ -substituents possess narrow HOMO-LUMO gaps and are capable of the activation of a range of E-H bonds (E = H, C, N).<sup>[11]</sup> While these processes are uniformly irreversible, related stannylenes also offer the possibility for oxidative E-H activation (for E = H, B, N, O, Si). In some cases (those where E = N or O) the  $Sn^{IV}$  products can undergo a subsequent reductive elimination step - owing to the more favorable  $Sn^{II}/Sn^{IV}$  redox couple.<sup>[11]</sup> With this in mind, we were keen to investigate E-H activation by acyclic germylene compounds, and in particular to probe the potential for tuning the reactivity of such complexes by systematic variation in the nature of the X substituents.

The first reports of isolated germylene complexes go back to the pioneering work of Lappert,<sup>[12-19]</sup> but the application of such systems in E-H bond activation chemistry owes much to the work of Power on bulky terphenyl-substituted systems (Figure 2).<sup>[18]</sup> Thus, for example,  $Ar^{Dipp}_2Ge$  and  $Ar^{Mes}_2Ge$  [ $Ar^{Dipp}$  =  $C_6H_3Dipp_{2,2,6}$ ,  $Ar^{Mes}$  =  $C_6H_3Mes_{2,2,6}$ ; where Dipp =  $C_6H_3Pr_{2,2,6}$  and Mes =  $C_6H_2Me_{3,2,4,6}$ ] have been shown to react with a wide variety of small molecules,<sup>[18f,18i,18j,18o,18p,18r-18t]</sup> including  $H_2$  and  $NH_3$ , leading to the formation of  $Ge^{IV}$  products.<sup>[15b,15c,15e,18]</sup> Reactions with other substrates of the type  $HX$  (e.g. X = CN,  $N_3$ , F,  $SO_3CF_3$ ,  $PH_2$ ,  $NHNRR'$ ) have also been shown to proceed via formal oxidative addition.<sup>[18o,18p,18r]</sup>

The availability of the terphenyl germanium(II) chlorides ( $Ar^{Mes}GeCl$ )<sub>2</sub> (**1-Mes**) and  $Ar^{Dipp}GeCl$  (**1-Dipp**) affords the opportunity for the synthesis of related unsymmetrical germylene and digermene systems via chloride metathesis.<sup>[20]</sup> With this in mind, these precursors were seen as potential starting points for a systematic study of substituent effects on the structural and reaction chemistry of germylene compounds of the types  $ArGeX$  (Ar =  $Ar^{Dipp}$  and  $Ar^{Mes}$ ). In particular, given that boryl- and silyl-substituted silylenes are known to be uniquely capable (among such  $Si^{II}$  systems) of the oxidative activation of  $H_2$ , we sought to target related germylene complexes containing similar substituents at X.

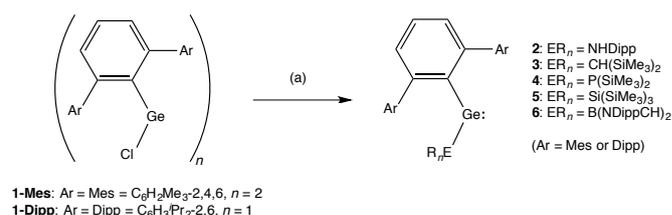


**Figure 2.** Landmark structurally characterized two-coordinate germylenes.

## Results and Discussion

### Synthesis of germylene 'library'

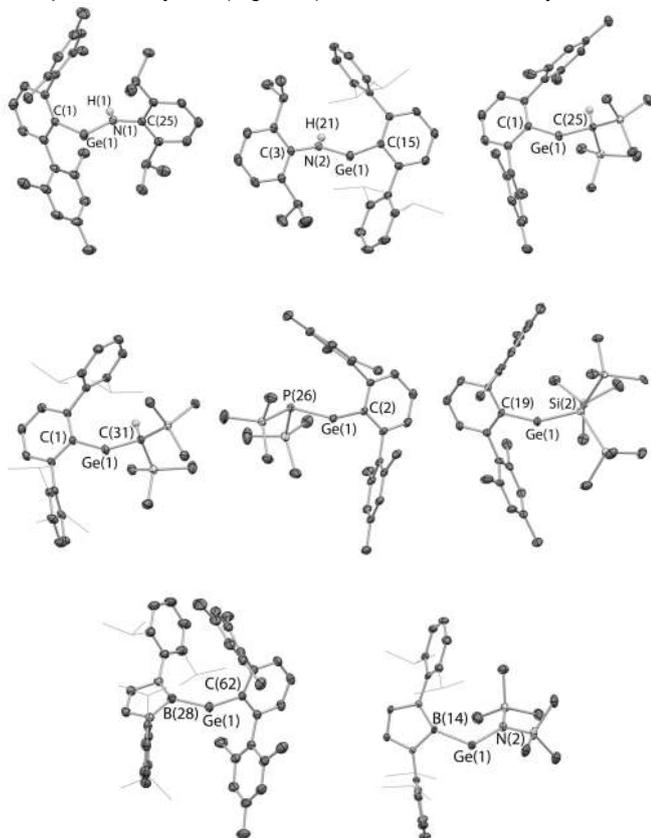
A series of germylene complexes offering systematic variation in the nature of the supporting ancillary framework was targeted using metathesis chemistry from the terphenyl-germanium(II) chlorides **1-Mes** and **1-Dipp** originally reported by Power and co-workers (Scheme 1).<sup>[18b,18d]</sup> The different aryl substituents were employed in tandem with a view to probing peripheral steric effects on reactivity patterns, and at a more pragmatic level in an attempt to manipulate solubility to obtain tractable crystalline products. In the event, a wide range of such systems proves to be accessible, offering variation in both the  $\sigma$ - and  $\pi$  properties of the ancillary substituent  $ER_n$ . Thus, relatively electropositive (and hence strongly  $\sigma$ -donating) substituents such as boryl and silyl groups can be incorporated, in addition to more conventional amido, phosphido and alkyl groups.<sup>[20]</sup> From the perspective of  $\pi$ -bonding, systems displaying characteristics ranging from  $\pi$ -acceptors (boryl) though  $\pi$ -neutral (alkyl) to  $\pi$ -donor (amido) can therefore be selected. As noted above, variation of the substituent  $\sigma/\pi$  characteristics offers a basis for controlling the HOMO-LUMO separation: as such, we viewed these systems as offering the potential for tuneable lability, for example towards E-H oxidative addition chemistry.



**Scheme 1.** Synthesis of a library of unsymmetrical germylene complexes **2-6** by metathesis chemistry. Key reagents and conditions: a) 1 equiv.  $Li[ER_n]$  (for **2, 3, 4, 6**) or  $K[Si(SiMe_3)_3]$  (for **5**),  $Et_2O$ , 22-74%.

The reaction between Li[NH(Dipp)] and **1-Mes** in diethyl ether immediately generates a yellow solution, and the germanium-containing product,  $\text{Ar}^{\text{Mes}}\text{Ge}\{\text{NH}(\text{Dipp})\}$  (**2-Mes**), can be characterized by multinuclear NMR, X-ray crystallography and elemental microanalysis (Scheme 1, Figure 3 and Table 1). *In situ*  $^1\text{H}$  NMR studies show that the reaction converts **1-Mes** into **2-Mes** in essentially quantitative fashion, with the isolated yield of 74% reflecting losses during work-up. Spectroscopically, it is noteworthy that the NH resonance for **2-Mes** is found at significantly lower field ( $\delta_{\text{H}} = 7.19$  ppm) than the signals measured for related donor/acceptor NHC-germylene complexes [e.g.  $\delta_{\text{H}} = 4.11$  ppm for  $\text{IPrGe}(\text{Cl})\text{NHDipp}$ ].<sup>[29]</sup> In the latter complex, coordination of the carbene at germanium effectively eliminates  $\pi$ -bonding with the amido substituent. In **2-Mes**, which features a formally vacant  $p\pi$  orbital, it is hypothesised that the unusually high NH chemical shift is due to the much greater extent of  $\text{N}\rightarrow\text{Ge}$   $\pi$ -donation: significant deshielding of the NH proton can therefore be rationalized on the basis of a resonance structure featuring a formal  $\text{Ge}=\text{N}$  double bond (Scheme 2). That the NH chemical shift measured for **2-Mes** is at a markedly lower field even than that of  $(\text{Ar}^{\text{Mes}}\text{NH})_2\text{Ge}$  ( $\delta_{\text{H}} = 5.46$  ppm) presumably reflects the presence of competing  $\pi$ -donors in the homoleptic amide complex.<sup>[13c]</sup>

**2-Mes** has been characterised by X-ray crystallography and represents a very rare example of a primary amido functionalized Group 14 metallylene (Figure 3).<sup>[13c,16p]</sup> Insofar as X-ray diffraction

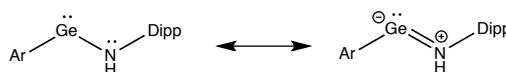


**Figure 3.** Molecular structures of **2-Mes**, **2-Dipp**, **3-Mes**, **3-Dipp**, **4-Mes**, **5-Mes**, **6-Mes** and **8** as determined by X-ray crystallography. Most hydrogen atoms omitted and Dipp 'Pr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 50% probability level. Key bond lengths and angles are given in Table 1.

**Table 1.** Key bond length and angles for germylene complexes **2-Mes**, **2-Dipp**, **3-Mes**, **3-Dipp**, **4-Mes**, **5-Mes**, **6-Mes** and **8**, together with comparative data for related literature germylenes.<sup>[13c,18b,18n,20]</sup>

Compound	X-Ge-X angle (°)	Ge-X distance (Å)
$\text{Ar}^{\text{Mes}}_2\text{Ge}$ [18b]	114.4(2)	aryl: 2.033(4)
$\text{Ar}^{\text{Dipp}}_2\text{Ge}$ [18h]	112.8(1)	aryl: 2.033(2)
<b>2-Mes</b>	96.0(1)	aryl: 2.011(2) amido: 1.808(2)
<b>2-Dipp</b>	102.5(1)	aryl: 2.008(2) amido: 1.815(2)
$(\text{Ar}^{\text{Mes}}\text{NH})_2\text{Ge}$ [13c]	88.6(2)	amido: 1.896(2)
<b>3-Mes</b>	105.4(1)	aryl: 2.020(2) alkyl: 1.999(2)
<b>3-Dipp</b>	104.0(1)	aryl: 2.019(2) alkyl: 1.997(2)
<b>4-Mes</b>	106.6(1)	aryl: 2.011(2) phosphido: 2.329(1)
<b>5-Mes</b> <sup>a</sup>	112.5(1), 112.7(1)	aryl: 1.996(3), 1.997(3) silyl: 2.439(1), 2.440(1)
$\text{Ar}^{\text{Mes}}\text{Ge}(\text{Ge}^{\text{tBu}})_3$ [20]	114.9(1)	aryl: 2.011(5) germyl: 2.544(1)
<b>6-Mes</b>	110.4(1)	aryl: 1.991(2) boryl: 2.127(3)
<b>8</b>	111.7(2)	amido: 1.852(5) boryl: 2.129(6)

<sup>a</sup> Two independent molecules in the asymmetric unit



**Scheme 2.** Contributing resonance forms for amido germylenes **2-Mes/2-Dipp**.

can yield reliable H-atom positions, N(1) appears to be planar, with the sum of angles ( $360.0^\circ$ ) being consistent with significant  $\pi$ -back donation to Ge(1). The Ge(1)-N(1) bond length [1.808(2) Å] is significantly shorter than those found in previously reported acyclic amido(germylenes) [1.897(2)-1.903(3) Å].<sup>[13]</sup> In addition, the C(1)-Ge(1)-N(1) angle is narrow [ $96.0(1)^\circ$ ], suggesting the involvement of germanium orbitals of mostly p-character in the Ge-C/N bonds, and high s-character for the germanium-centred lone pair, as would be predicted on the basis of Bent's Rule (given the relatively high electronegativity of nitrogen).<sup>[8,13c]</sup> These considerations, together with the smaller steric bulk of the NHDipp substituent compared to  $\text{Ar}^{\text{Mes}}$ , are presumably implicated in the closing up of the angle at Ge compared to that reported for  $\text{Ar}^{\text{Mes}}_2\text{Ge}$  [ $114.4(2)^\circ$ ].<sup>[18b]</sup> The corresponding  $\text{Ar}^{\text{Dipp}}$  substituted primary amido complex **2-Dipp** could also be synthesized in analogous fashion; increased solubility, however, results in a lower isolated yield (42 vs. 74%). Characterization by X-ray crystallography could also be achieved, with the structure obtained reflecting the differing steric bulk of the Mes and Dipp substituted terphenyl ligands: the C(3)-Ge(1)-C(15) angle in **2-Dipp** [ $102.5(1)^\circ$ ] is ca.  $6.5^\circ$  wider than that found in **2-Mes**.

Metathesis chemistry can also be applied to the synthesis of mixed aryl/alkyl germylene species: combination of **1-Mes** and  $\text{Li}[\text{CH}(\text{SiMe}_3)_2]$  in diethyl ether immediately gives rise to a deep red solution, from which  $\text{Ar}^{\text{Mes}}\text{Ge}\{\text{CH}(\text{SiMe}_3)_2\}$  (**3-Mes**) can be obtained as dark red crystals in 69% yield (Scheme 1). The Dipp derivative (**3-Dipp**) could be synthesized in similar manner, although the isolated yield was again lower (38%). As with the

amido complexes **2-Mes/2-Dipp**, *in situ* NMR studies imply near quantitative conversion of the starting materials to **3-Mes/3-Dipp** with the lower isolated yields (particularly for the Dipp substituted system) presumably reflecting high solubility in hydrocarbon solvents. The crystal structures of **3-Mes** and **3-Dipp** are more uniform than their amido counterparts, and possess wider C-Ge-C angles [105.4(1)° and 104.0(1)°, respectively; Figure 3], presumably reflecting both the greater steric demands and the less electronegative nature of the CH(SiMe<sub>3</sub>)<sub>2</sub>  $\alpha$ -substituent (vs. NHDipp). Previous reports of alkyl germynes go back some years: Lappert employed the -CH(SiMe<sub>3</sub>)<sub>2</sub> substituent, for example, to synthesize the first stable alkyl germylene, {(Me<sub>3</sub>Si)<sub>2</sub>HC}<sub>2</sub>Ge, in 1976.<sup>[22]</sup> Subsequently, the related, but slightly more encumbered system {(Me<sub>3</sub>Si)<sub>3</sub>C}{(Me<sub>3</sub>Si)<sub>2</sub>HC}Ge was synthesized, and shown to exist as a monomer in the solid state as well as in solution.<sup>[30]</sup>

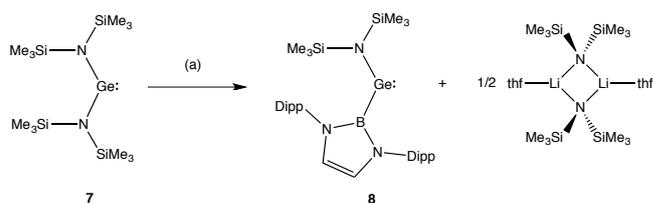
While the syntheses of amido and alkyl derivatives of types **2** and **3** proceed cleanly at room temperature, attempts to synthesize the corresponding phosphido-germylenes under analogous conditions yield intractable mixtures of products. Carrying out the reaction of **1-Mes** with (dme)LiP(SiMe<sub>3</sub>)<sub>2</sub> (dme = 1,2-dimethoxyethane) at -30 °C, however, affords a dark brown/red solution from which deep purple crystals could be obtained and characterized by X-ray crystallography as the -P(SiMe<sub>3</sub>)<sub>2</sub> derivatized germylene complex **4-Mes** (Figure 3). While there is literature precedent for phosphido germynes, the majority are dimeric, with existing examples of two-coordinate systems typically employing very sterically bulky P-substituents.<sup>[17]</sup> In common with most literature examples,<sup>[17d]</sup> **4-Mes** features a pyramidal phosphorus centre [sum of angles at P(26) = 314.6°] and a relatively wide angle at germanium [106.6(1) cf. 106.9(1)° for a closely related ArGe{P(SiMe<sub>3</sub>)<sub>2</sub>} system reported by Scheer and co-workers].<sup>[17b]</sup>

In similar fashion, the silylgermylene Ar<sup>Mes</sup>Ge{Si(SiMe<sub>3</sub>)<sub>3</sub>} (**5-Mes**) could also be synthesized at -30 °C, although the yield of **22%** is significantly lower than that achieved for any of compounds **2-4** (34-79%), potentially reflecting not only solubility issues but also the greater lability of this silyl-substituted system to onward reactivity (*vide infra*). With this in mind, it might be noted that the attempted synthesis of the related homoleptic bis(silyl)germylene {(Me<sub>3</sub>Si)<sub>3</sub>Si}<sub>2</sub>Ge by Stalke resulted instead in the formation of a disilagermirane, an observation which was attributed to the high reactivity of the putative germylene.<sup>[31]</sup> Consistent with his notion, the crystal structure of **5-Mes** (Figure 3) features the widest angle at germanium [112.6(1)° (mean)], among all the new compounds isolated, reflecting the combination of steric bulk and electropositive donor atom in the silyl group employed. A similar angle [114.9(1)°] has been reported for a related germylene featuring the bulky germyl substituent, -Ge<sup>t</sup>Bu<sub>3</sub>.<sup>[20]</sup> The steric bulk of the silyl complex also influences the spectroscopic properties of **5-Mes**; splitting of the Mes *meta*-H and *ortho*-CH<sub>3</sub> signals in the <sup>1</sup>H NMR spectrum is observed at temperatures below 25 °C consistent with restricted rotation around the C-C bonds linking the flanking mesityl groups to the central phenyl ring of the Ar<sup>Mes</sup> ligand.

Attempts to synthesize the boryl-germylenes Ar<sup>Mes</sup>Ge{B(NDippCH)<sub>2</sub>} and Ar<sup>Dipp</sup>Ge{B(NDippCH)<sub>2</sub>} (**6-Mes** and **6-Dipp**) at -30 °C using analogous procedures to those used for **4-Mes/5-Mes**, but employing boryllithium reagent (thf)<sub>2</sub>Li[B(NDippCH)<sub>2</sub>], lead to the formation of mixtures of products including the

borane HB(NDippCH)<sub>2</sub>.<sup>[25]</sup> Ar<sup>Dipp</sup>Ge{B(NDippCH)<sub>2</sub>} (**6-Dipp**) could be isolated, however, as a green compositionally pure solid by ensuring the reaction mixture never warmed up above -10 °C during work-up.<sup>[19]</sup> The use of the very weakly polar solvent Me<sub>3</sub>SiOSiMe<sub>3</sub> was additionally found to be necessary to promote crystallization. The related but less sterically protected **6-Mes** system was found to be extremely labile, undergoing facile onward C-H activation (*vide infra*), and as a result could only be obtained in very low yield. Its lower solubility however, did allow it to be obtained as single crystals suitable for X-ray crystallography, albeit in very small quantities (Figure 3). The B(28)-Ge(1)-C(62) bond angle for **6-Mes** [110.4(9)°] is marginally narrower than that of silyl complex **5-Mes**, consistent with observations made for related boryl- and silylsilylenes.<sup>[11a,11b]</sup> Interestingly the B-Ge bond does not lie coplanar with the diazaboryl heterocycle, as would be expected for an sp<sup>2</sup> hybridised B atom, being projected out-of-plane at an angle of 14.5°. This effect has precedent in related main group boryl complexes such as {(HCDippN)<sub>2</sub>B}<sub>2</sub>Sn, and is thought to be predominantly steric in origin.<sup>[11]</sup> Only one other example of a boryl germylene is available in the current literature,<sup>[11a,19]</sup> and compounds **6-Mes** and **6-Dipp** represent to our knowledge the first such systems to be synthesized without stabilisation by a  $\pi$ -donor  $\alpha$ -substituent.

Understandably then, **6-Mes** in particular is extremely labile towards intramolecular C-H insertion (*vide infra*) and alternative boryl-germylene systems were sought which would be easier to manipulate at ambient temperature for reactivity studies. With this in mind, the reaction of Lappert's diamido-germylene {(Me<sub>3</sub>Si)<sub>2</sub>N}<sub>2</sub>Ge (**7**)<sup>[12]</sup> with equimolar (thf)<sub>2</sub>Li[B(NDippCH)<sub>2</sub>] was shown to give access to {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>} (**8**) through displacement of one equivalent of lithium amide (Scheme 3).<sup>[19]</sup> **8** co-crystallizes from hexane with two molecules of dimeric [(thf)Li{ $\mu$ -N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (Figure 3), allowing the structural metrics of **8** to be assessed. However, attempts to remove the lithium amide co-product at this stage (for example using a weak acid such as [Et<sub>3</sub>NH]Cl) were unsuccessful, with the expected formation of HN(SiMe<sub>3</sub>)<sub>2</sub> being accompanied by the transformation of **8** into a germanium-containing product tentatively assigned as Ge{B(NDippCH)<sub>2</sub>}N(SiMe<sub>3</sub>)<sub>2</sub>(H)Cl (by comparison with the data obtained for the crystallographically characterized iodide analogue obtained from the reaction with [Me<sub>3</sub>NH]I). As such, samples of **8** generated using the approach outlined in Scheme 3 were used *in situ* for studies of onward E-H insertion chemistry, and the amide co-product then removed from the less reactive Ge<sup>IV</sup> final products by the use of [Et<sub>3</sub>NH]Cl. Structurally, the core of **8** is remarkably similar to that of **6-Mes**, (Figure 3), with the two boryl-substituted compounds displaying identical Ge-B distances [2.129(6) and 2.127(3) Å, respectively] and very similar B-Ge-X angles [111.7(2) and 110.4(1)°].



**Scheme 3.** Synthesis of (amido)boryl germylene complex **8** via boryl/amide metathesis. Key reagents and conditions: (a) 1 equiv. (thf)<sub>2</sub>Li[B(NDippCH)<sub>2</sub>], benzene, 95% by <sup>1</sup>H NMR (as **8**·2[(thf)Li{ $\mu$ -N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>).

### Bond activation chemistry

The five  $\text{Ar}^{\text{Mes}}$  derivatives **2-Mes** – **6-Mes** and amido(boryl) system **8** have been studied using Density Functional Theory (DFT) calculations at the BP86/TZP level, with a view to assaying the nature and relative energies of the HOMO and LUMO for each (Table 2). These orbitals for the aryl(boryl) germylene **6-Mes** are illustrated in Figure 4, and show that the LUMO is constituted primarily of the vacant  $p\pi$  orbital at Ge (47%), with the HOMO being a Ge-centred lone pair (with 13% 4s and 33% 4p character). In the case of the aryl(amido) system **2-Mes**, the composition of the LUMO is perturbed by the incorporation of a contribution from the  $p\pi$  orbital at nitrogen (4.5%), leading to a pronounced elevation in its energy ( $-253 \text{ kJ mol}^{-1}$  cf.  $-294$  and  $-305 \text{ kJ mol}^{-1}$  for **3-Mes** and **6-Mes**, respectively), consistent with the well-known effects of  $\alpha$ -amido groups in group 14 metallylene systems.

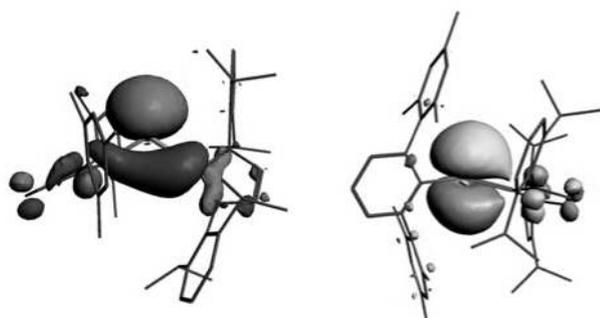


Figure 4. DFT calculated HOMO (left) and LUMO (right) of **6-Mes**.

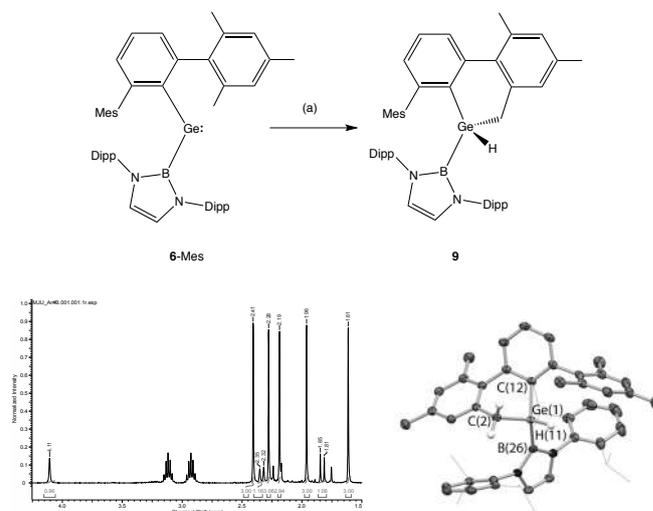
Table 2. DFT calculated HOMO and LUMO energies (in $\text{kJ mol}^{-1}$ ) for compounds <b>2-Mes</b> – <b>6-Mes</b> and <b>8</b> .					
Compound	Substituents	Angle at Ge ( $^\circ$ ) <sup>a</sup>	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$
<b>2-Mes</b>	$\text{Ar}^{\text{Mes}}/\text{NHDipp}$	96.0(1)	-528	-253	275
<b>3-Mes</b>	$\text{Ar}^{\text{Mes}}/\text{CH}(\text{SiMe}_3)_2$	105.4(1)	-471	-294	177
<b>4-Mes</b>	$\text{Ar}^{\text{Mes}}/\text{P}(\text{SiMe}_3)_2$	106.6(1)	-466	-263	203
<b>5-Mes</b>	$\text{Ar}^{\text{Mes}}/\text{Si}(\text{SiMe}_3)_3$	112.6(1) <sup>b</sup>	-446	-312	134
<b>6-Mes</b>	$\text{Ar}^{\text{Mes}}/\text{B}(\text{NDippCH})_2$	110.4(1)	-424	-305	119
<b>8</b>	$\text{N}(\text{SiMe}_3)_2/$ $\text{B}(\text{NDippCH})_2$	111.7(2)	-429	-249	180

<sup>a</sup> As determined by X-ray crystallography. <sup>b</sup> Mean of two crystallographically independent molecules in the asymmetric unit.

The HOMO-LUMO gaps calculated for all six systems are tabulated in Table 2;  $\pi$ -donor substituents in general lead to elevation of the LUMO, while more electropositive (stronger  $\sigma$ -donor) groups elevate the HOMO, in line with general principles summarized by Bertrand *et al.*, for related carbene systems.<sup>[4]</sup> As such, the smallest HOMO-LUMO gaps (and hence greatest kinetic lability with respect to oxidative bond activation) are predicted for silyl- and boryl-substituted systems **5-Mes** and **6-Mes**. In a wider context, these numbers can be put into perspective by comparison with those calculated for diarylgermylenes (HOMO-LUMO gaps of  $278 \text{ kJ mol}^{-1}$  and  $266 \text{ kJ mol}^{-1}$  for the  $\text{Ar}^{\text{Mes}}$  and  $\text{Ar}^{\text{Dipp}}$  complexes respectively).<sup>[18j]</sup>

Consistent with the above quantum chemical data is the finding that solutions of **6-Mes** undergo intramolecular C-H

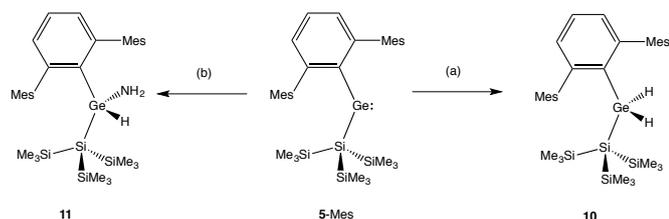
activation at room temperature to form a  $\text{Ge}^{\text{IV}}$  hydride **9** (Scheme 4). Multinuclear NMR data provide compelling evidence for the identity of the product: the upfield shift in the  $^{11}\text{B}$  resonance from  $\delta_{\text{B}} = 50.5 \text{ ppm}$  for **6-Mes** to  $26.5 \text{ ppm}$  for **9** is consistent with the conversion of  $\text{M}^{\text{II}}$  to  $\text{M}^{\text{IV}}$  (cf.  $\delta_{\text{B}} = 96 \text{ ppm}$  for  $\text{Sn}\{\text{B}(\text{NDippCH})_2\}_2$ , and  $28.3, 27.9 \text{ ppm}$  for  $\text{Sn}\{\text{B}(\text{NDippCH})_2\}_2\text{H}_2$  and  $\text{Sn}\{\text{B}(\text{NDippCH})_2\}_2(\text{H})\text{SiH}_3$ , respectively).<sup>[11c]</sup> Consistently, the  $^1\text{H}$  NMR spectrum shows a Ge-H resonance at  $\delta_{\text{H}} = 4.11 \text{ ppm}$ , and five signals for the remaining  $\text{CH}_3$  mesityl groups, together with mutually coupled doublets for the  $\text{GeCH}_2$  unit ( $^2J_{\text{HH}} = 13.1 \text{ Hz}$ ). The structure of **9** was ultimately determined by X-ray crystallography, which confirms the activation of one of the mesityl *ortho*-methyl C-H bonds at germanium (Scheme 4).



**Scheme 4.** (upper) Intramolecular C-H activation by **6-Mes**. Key reagents and conditions: (a) benzene- $d_6$ , room temperature, 12 h. (lower) *in situ*  $^1\text{H}$  NMR spectrum (aliphatic region) and molecular structure of **9** as determined by X-ray crystallography. Most hydrogen atoms omitted and Dipp  $^i\text{Pr}$  groups shown in wireframe format for clarity; thermal ellipsoids shown at the 50% probability level. Key bond lengths (Å) and angles ( $^\circ$ ): Ge(1)-C(2) 1.974(1), Ge(1)-C(12) 1.973(1), Ge(1)-B(26) 2.074(1), C(12)-Ge(1)-B(26) 126.9(1).

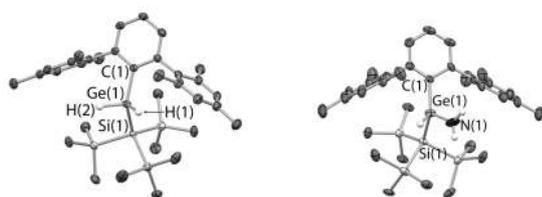
Intramolecular C-H bond activation is not unheard of for metallylene systems: the acyclic silylene  $\{(\text{Me}_3\text{Si})\text{DippN}\}\text{Si}\{\text{B}(\text{NDippCH})_2\}$ , for example, undergoes insertion of  $\text{Si}^{\text{II}}$  into the methine CH bond of one of the boryl Dipp groups, although this chemistry requires more forcing conditions (heating at  $50 \text{ }^\circ\text{C}$  for 48 h).<sup>[11a]</sup> C-H activation occurs at much lower temperatures for systems with more readily accessible triplet states [notably  $(\text{Bu}_2\text{Si})_2\text{Si}$ ],<sup>[32]</sup> but ambient temperature C-H activation by two-coordinate germanium systems is rare.<sup>[18m]</sup>

With **6-Mes** undergoing ready onward reaction by intramolecular C-H activation, it was decided instead to probe the use of the less labile silyl-substituted system **5-Mes** and (amido)boryl complex **8** for *intermolecular* E-H bond activation. Initial studies were carried out with dihydrogen at room temperature and 4 atm. pressure (conditions under which amido, alkyl and phosphido compounds **2-Mes**, **3-Mes** and **4-Mes** showed no reaction after 1 week). A solution of **5-Mes** in toluene, on the other hand, changed colour from green to colourless overnight, and the dihydride product  $\text{Ar}^{\text{Mes}}\text{Ge}\{\text{Si}(\text{SiMe}_3)_3\}(\text{H})_2$  (**10**) could be characterized by standard spectroscopic and crystallographic techniques (Scheme 5).



**Scheme 5.** Activation of E-H bonds (E = H, N) by silylgermylene **5-Mes**. Key reagents and conditions (a) H<sub>2</sub> (ca. 4 atm), toluene, room temperature, 3 h, 70%; (b) NH<sub>3</sub> (ca. 1 atm), toluene, room temperature, < 5 min, 74%.

Previous reports of the formation of a dihydride by oxidative addition of H<sub>2</sub> to a germylene complex come from the work of Power on homoleptic bis(terphenyl) systems, although there is also precedent for arene elimination to take place (depending on ligand steric demands), ultimately yielding a metal trihydride after assimilation of a second molecule of H<sub>2</sub>.<sup>[18]</sup> Confirmation that **10** results from straightforward H<sub>2</sub> oxidative addition could be obtained from NMR spectroscopy and X-ray crystallography (Figure 5). Although the germanium-bound hydrogen atoms could not be unambiguously located in the difference Fourier map, their presence is consistent (i) with a new resonance at  $\delta_{\text{H}} = 3.80$  ppm in the <sup>1</sup>H NMR spectrum of crystals redissolved in benzene-d<sub>6</sub>, and (ii) with the marked widening of the Si-Ge-C angle [125.4(2)° cf. 112.6(1)° (mean) for **5-Mes**] – a phenomenon previously observed to accompany oxidative formation of E<sup>IV</sup> dihydride species (E = Si, Ge, Sn). Thus, similar widening of the angle at the Group 14 centre accompanies the oxidative addition of H<sub>2</sub> at silylene, germylene, and stannylenes complexes [e.g. from 114.4(2)° to 127.9(2)° for Ar<sup>Mes</sup><sub>2</sub>Ge].<sup>[18b,18]</sup> <sup>11</sup> and presumably results from the reduced size of E<sup>IV</sup>, and the consequent need to open up the angle between bulky peripheral substituents. Consistently, the Ge-Si bond length is shortened in **10** [2.407(3) Å] compared to that measured in **5-Mes** [2.437(2) Å].



**Figure 5.** Molecular structures of **10** and **11** as determined by X-ray crystallography. Most hydrogen atoms omitted and mesityl groups shown in wireframe format for clarity; thermal ellipsoids shown at the 50% probability level. Key bond lengths (Å) and angles (°): (for **10**) Ge(1)-Si(1) 2.405(1), Ge(1)-C(1) 1.973(6), C(1)-Ge(1)-Si(1) 125.2(2); (for **11**) Ge(1)-Si(1) 2.400(1), Ge(1)-C(1) 1.984(3), Ge(1)-N(1) 1.76(1), C(1)-Ge(1)-Si(1) 125.8(2).

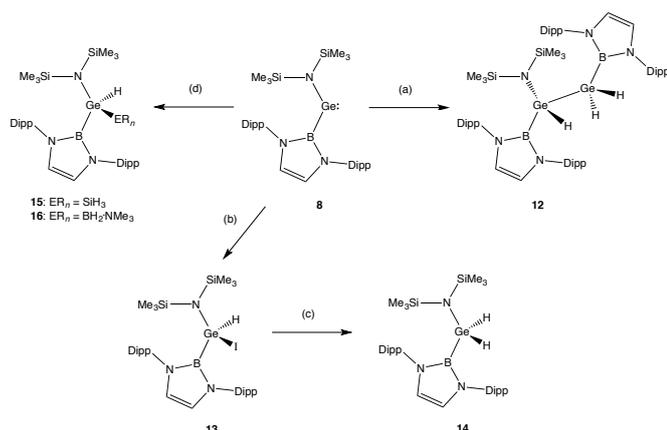
The reactivity of **5-Mes** towards ammonia was also probed (with compounds of types **2-4** again showing no hint of reactivity). Clean reaction was observed between **5-Mes** and NH<sub>3</sub> at room temperature and 1 atm. pressure, leading immediately to the formation of a colourless solution, from which X-ray quality crystals of the (amido)hydride **11** could be isolated (Scheme 5 and Figure 5). There is some recent precedent for the reaction of germylenes with NH<sub>3</sub>: Power's bis(terphenyl)germylene systems

undergo NH oxidative addition on reaction with liquid NH<sub>3</sub> at -78 °C,<sup>[18]</sup> and Nacnac' germanium systems activate NH<sub>3</sub> at ambient temperature, albeit in 1,4 fashion.<sup>[15b,15e]</sup> **11** gives rise to characteristic GeNH<sub>2</sub> and GeH resonances in the <sup>1</sup>H NMR spectrum (mutually coupled doublet and triplet signals at  $\delta_{\text{H}} = -0.06$  and 5.10 ppm, respectively), these being similar to those reported by Power and co-workers for the related bis(terphenyl)germanium (amido)hydride, Ar<sup>Mes</sup><sub>2</sub>Ge(NH<sub>2</sub>)H (-0.37 and 5.47 ppm, respectively).<sup>[18]</sup> As with dihydride complex **10**, the Si-Ge-C bond angle determined crystallographically for **11** is widened significantly [to 125.8(2)°] from that found in the germylene precursor, and the Ge-Si bond is contracted [to 2.401(1) Å], consistent with the formation of a Ge<sup>IV</sup> complex. Although modelled extensively in computational studies, the pathway for NH bond activation in ammonia remains little investigated in experimental work; recent work on boryl-stannylenes, however, suggests that mechanistic steps involving initial coordination of NH<sub>3</sub> via the metallylene p $\pi$  orbital, followed by N-to-M proton shuttling (mediated by a second molecule of NH<sub>3</sub>) are feasible.<sup>[11c,18j,33]</sup>

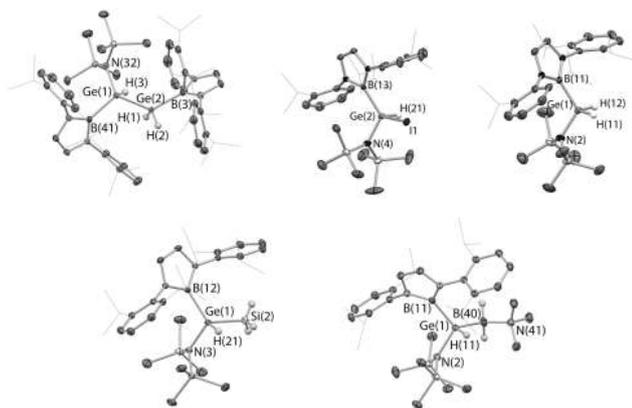
While (aryl)boryl germylene complex **6-Mes** proves to be too reactive with respect to intramolecular C-H activation to use in any productive chemistry towards external substrates, the related (amido)boryl system, **8**, has a wider HOMO-LUMO gap (180 vs. 119 kJ mol<sup>-1</sup>) and is stable in hydrocarbon solution at ambient temperature. Accordingly, the reactivity of **8** towards compounds containing E-H bonds (E = H, B, Si) was probed.<sup>[34]</sup> However, unlike the corresponding reaction of **5-Mes** with H<sub>2</sub>, which proceeds via simple oxidative H-H bond cleavage, the product of the reaction of **8** with dihydrogen appears from *in situ* <sup>1</sup>H NMR spectroscopy to be more complex. Thus, three GeH signals are observed (at  $\delta_{\text{H}} = 1.73$ , 2.53 and 4.92 ppm) together with signals for two distinct boryl ligands and one N(SiMe<sub>3</sub>)<sub>2</sub> group. In addition, <sup>1</sup>H resonances are observed corresponding to one equivalent each of the borane HB(NDippCH)<sub>2</sub> and the diamido-germylene **7**. The identity of the germanium hydride product was definitively established by single crystal X-ray diffraction studies as the unsymmetrical digermene **12** (Scheme 6 and Figure 6), featuring two germanium centres linked by a single bond [ $d(\text{Ge-Ge}) = 2.431(1)$  Å]; Ge(1) is additionally bound to boryl, N(SiMe<sub>3</sub>)<sub>2</sub> and hydride ligands, while Ge(2) is linked to a single boryl substituent and two hydrides.

While the mechanism for the formation of **12** has not been definitively established, it seems unlikely that it proceeds via the Ge<sup>IV</sup> dihydride {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>}H<sub>2</sub> (**14**) i.e. the product of simple oxidative addition of H<sub>2</sub> to **8**. This compound can be synthesized independently via the sequential reactions of **8** with [Me<sub>3</sub>NH]I to give {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>}H(I) (**13**), followed by hydride/iodide metathesis with K[Et<sub>3</sub>BH] (Scheme 6). The identities of both **13** and **14** have been established by spectroscopic and crystallographic means (Figure 6). In terms of reactivity, **14** proves to be thermally stable both as an isolated compound and in the presence of germylene **8**, and thus seems unlikely to be a competent intermediate in the formation of **12**.

An alternative pathway for the formation of **12** involves initial reaction of **8** with H<sub>2</sub> generating [(HCDippN)<sub>2</sub>B]Ge(H)]<sub>n</sub> [and one equivalent of HN(SiMe<sub>3</sub>)<sub>2</sub>] in a concerted fashion, with the former then taking up a second equivalent of H<sub>2</sub> to give [(HCDippN)<sub>2</sub>B]GeH<sub>3</sub>. Such steps would closely mimic the synthesis of Ar<sup>Dipp</sup>GeH<sub>3</sub> via the hydrogenation of Ar<sup>Dipp</sup><sub>2</sub>Ge, as



**Scheme 6.** E-H bond activation (E = H, B, Si) by (amido)boryl germylene complex **8**. Key reagents and conditions: (a) H<sub>2</sub> (ca. 1 atm), hexane, room temperature, 6 h, 23% isolated yield; (b) [Me<sub>3</sub>NH], benzene, room temperature, 5 min, 78% isolated yield; (c) K[Et<sub>3</sub>BH], benzene-d<sub>6</sub>, 70° C, 3 d, 86% isolated yield; (d) (for **15**) SiH<sub>4</sub> (1 atm), benzene-d<sub>6</sub>, room temperature, 1 min, 24% isolated yield; (e) (for **16**) Me<sub>3</sub>NBH<sub>3</sub> (1 equiv.), benzene-d<sub>6</sub>, room temperature, 10 min, 32% isolated yield.



**Figure 6.** Molecular structures of **12-16** as determined by X-ray crystallography. Most hydrogen atoms omitted and Dipp 'Pr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 50% probability level. Key bond lengths (Å) and angles (°): (for **12**) Ge(1)-Ge(2) 2.431(1), Ge(1)-N(32) 1.908(2), Ge(1)-B(41) 2.070(3), Ge(2)-B(3) 2.051(3), N(32)-Ge(1)-B(41) 113.1(1); (for **13**) Ge(2)-I(1) 2.577(1), Ge(2)-N(4) 1.844(2), Ge(2)-B(13) 2.058(2), N(4)-Ge(2)-B(13) 121.8(1); (for **14**) Ge(1)-N(2) 1.877(1), Ge(1)-B(11) 2.045(2), N(2)-Ge(1)-B(11) 116.5(1); (for **15**) Ge(1)-Si(2) 2.390(1), Ge(1)-N(3) 1.885(2), Ge(1)-B(12) 2.057(3), N(3)-Ge(1)-B(12) 114.8(1); (for **16**) Ge(1)-B(40) 2.104(2), B(40)-N(41) 1.827(3), Ge(1)-N(2) 1.920(2), Ge(1)-B(11) 2.094(2), N(2)-Ge(1)-B(11) 111.3(1).

reported by Power and co-workers.<sup>[18]</sup> In the presence of a second molecule of the starting material **8**, oxidative addition of one of the three Ge-H bonds would then generate the observed product **12**. The last step does not seem unreasonable given that **8** is also shown to be capable of the oxidative addition of stronger Si-H bonds (vide infra). The amine HN(SiMe<sub>3</sub>)<sub>2</sub> generated in the first step then reacts with a third equivalent of **8** to generate the observed co-products Ge{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (**7**) and HB(NDippCH)<sub>2</sub>. More generally, it is noteworthy that the silylene, germylene and stannylene complexes of the type (amido)(boryl)E, show three different modes of interaction with H<sub>2</sub>, with the silicon system undergoing simple oxidative addition to the Si<sup>IV</sup> dihydride, and the tin system being inert. The tetrel containing product in the three cases therefore contains Si<sup>IV</sup>, Ge<sup>III</sup> and Sn<sup>II</sup>, respectively.

Given the complex onward chemistry revealed in the reaction of **8** with dihydrogen, its reactivity towards other E-H bonds was investigated – notably towards systems containing hydric Si-H and B-H bonds. In contrast, however, the reactions of **8** with SiH<sub>4</sub> and Me<sub>3</sub>NBH<sub>3</sub> can be shown to proceed cleanly via simple E-H oxidative addition, leading to the formation of the respective silyl- and (boryl)hydrides {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>}H(SiH<sub>3</sub>) (**15**) and {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>}H(BH<sub>2</sub>NMe<sub>3</sub>) (**16**; Scheme 6 and Figure 6). The formation of a straightforward E-H insertion product is consistent with the observation in each case of a single Ge-H resonance in the respective <sup>1</sup>H NMR spectra (at δ<sub>H</sub> = 4.88 and 4.53 ppm), and in the case of **15** by mutual coupling (<sup>3</sup>J<sub>HH</sub> = 3.4 Hz) between the quartet GeH and doublet SiH<sub>3</sub> resonances. The structures of both compounds could also be determined crystallographically (Figure 6), and thus offer rare structurally authenticated examples of B-H and Si-H oxidative addition at a germylene complex.<sup>[35]</sup>

Of interest from a structural viewpoint for compounds **12-16** are the relatively small changes in the N-Ge-B angle brought about by oxidation of the parent germylene compound. Thus, the angle measured for **8** is 111.7(2)°, while those determined for the corresponding Ge-H, H-H, Si-H and B-H insertion products are 113.1(1) [for Ge(1)], 116.5(1), 114.8(1) and 111.3(1)°, respectively. This relatively limited widening contrasts with the much more marked effects observed for the addition of dihydrogen or ammonia to **5-Mes**, for example [112.6(1) to 125.4(2)/125.8(2)°]. Conceivably, this reflects the fact that the essentially planar GeN(SiMe<sub>3</sub>)<sub>2</sub> unit can vary its orientation so as to minimize unfavourable steric interactions with the other substituents. Thus, in **8** the NSi<sub>2</sub> plane is inclined at an angle of 16.1° that of the N-Ge-B unit, consistent with the expected π-stabilization of the germylene centre by the α-amido substituent. In each of **12** and **14-16** the corresponding angle is much closer to orthogonal (60.3, 71.8, 66.5 and 86.1°, respectively). In addition, while the widening of the angle at germanium for **5-Mes** on E-H insertion can be attributed to the shortening of the bonds to the bulky ancillary ligands associated with the change from Ge<sup>II</sup> to Ge<sup>IV</sup>, the Ge-N distances in **12** and **14-16** are actually longer than that found in germylene **8** [1.908(2), 1.877(2), 1.885(2) and 1.920(2) vs. 1.852(5) Å] reflecting the loss of the π-bonding component.

## Conclusions

A series of seven new germylene compounds of the type (terphenyl)Ge(ER<sub>n</sub>) has been synthesized by chloride metathesis, with systematic variation in the σ- and π-capabilities of the ER<sub>n</sub> substituent being readily accomplished. The related system {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>} (**8**) can also be accessed, utilizing an alternative amide/boryl exchange route. In each case, the metrical parameters associated with the two-coordinate germanium centre are accessible via X-ray crystallography, and are consistent with widening angles as more bulky and/or more electropositive substituents are employed. Thus, the widest germylene units (θ > 110°) are found to be associated with boryl or silyl ancillary donors.

In terms of electronic structure, the HOMO-LUMO gaps for the new germylene complexes – appraised by DFT calculations – are found to be a function both of the angle at the germanium centre,

and the  $\pi$ -characteristics of the  $\alpha$ -substituents. In common with related systems, a larger HOMO-LUMO separation is associated with a narrow angle at germanium (greater HOMO  $\sigma$ -character) and  $\pi$ -donor substituents (LUMO destabilization). Conversely, aryl(boryl)germylene system **6-Mes** which features a wide C-Ge-B angle and (if anything) ancillary  $\pi$ -acceptor capabilities has the smallest HOMO-LUMO gap – a feature which results in it being unworkably reactive on the basis of intramolecular C-H activation. The related aryl(silyl)germylene system **5-Mes** has a marginally wider HOMO-LUMO gap, rendering it less labile towards decomposition, yet reactive enough to oxidatively cleave  $H_2$  and  $NH_3$  to give the corresponding dihydride and (amido)hydride, respectively. In a similar fashion, formal replacement of the aryl substituent by an  $N(SiMe_3)_2$  group yields (amido)boryl complex **8** which is also competent for the activation of a range of E-H bonds (E = H, B, Si). In the case of  $H_2$  activation, the formation of an unsymmetrical digermene product implies a subsequent step involving Ge-H insertion chemistry. The results of these reactivity studies imply that the use of the very strongly  $\sigma$ -donating boryl or silyl substituents is an effective strategy for rendering metallocene complexes active in E-H activation processes. The narrow HOMO-LUMO gaps for these systems imply low activation barriers and hence kinetically facile oxidation processes. Moreover, the strong  $\sigma$ -donor capabilities of these substituents imply that – for germanium at least – the  $E^{IV}$  products are thermodynamically stable, with little hint of the possibility for subsequent reductive elimination that has been seen for related tin compounds.<sup>[11c]</sup>

## Experimental Section

### General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. THF was refluxed over potassium-sodium alloy and distilled prior to use; hexamethyldisiloxane was vacuum distilled prior to use. NMR spectra were measured in benzene- $d_6$  which was dried over potassium, or  $thf-d_6$  (over  $LiAlH_4$ ) with the solvent then being distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra were recorded on Varian Mercury-VX 300 MHz, Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer at ambient temperature unless stated otherwise and referenced internally to residual protio-solvent ( $^1H$ ) or solvent ( $^{13}C$ ) resonances and are reported relative to tetramethylsilane ( $\delta = 0$  ppm).  $^{11}B\{^1H\}$  NMR spectra were referenced to external  $Et_2O \cdot BF_3$ . Assignments were confirmed using two dimensional  $^1H$ - $^1H$  and  $^{13}C$ - $^1H$  NMR correlation experiments. Chemical shifts are quoted in  $\delta$  (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. Starting materials **1-Mes**,<sup>[16b]</sup> **1-Dipp**,<sup>[18d]</sup> **7**,<sup>[12a]</sup>  $Li[NH(Dipp)]$ ,<sup>[21]</sup>  $Li[CH(SiMe_3)_2]$ ,<sup>[22]</sup>  $Li(dme)[P(SiMe_3)_2]$ ,<sup>[23]</sup>  $KS(SiMe_3)_3$ ,<sup>[24]</sup> and  $(thf)_2Li[B(N(Dipp)CH_2)_2]$ ,<sup>[25]</sup> were synthesized according to published procedures. Silane was prepared in a similar manner to that described in ref 26 from  $SiCl_4$  (2.78 g, 16.3 mmol) and  $LiAlH_4$  (0.63 g, 16.6 mmol) in  $Et_2O$  (20 mL) in a degassed 400 mL ampoule and used without fractionation (**CAUTION:  $SiH_4$  reacts violently with air!**).  $[Me_3NH]$  was prepared from equimolar amounts of  $[Me_3NH]Cl$  and NaI in EtOH and recrystallized from hot ethanol. Ammonia was dried by condensing onto a Na mirror and distilling the required amount into a Young's tap ampoule of such volume so that one atmosphere pressure of  $NH_3$  was achieved at RT.  $BH_3 \cdot NMe_3$  (Aldrich) was carefully degassed and stored under a protective atmosphere.

### Crystallography

Diffraction data were collected using a Nonius Kappa CCD or Oxford Diffraction (Agilent) SuperNova diffractometer at 150 K; data were reduced using either DENZO, SCALEPACK or CrysAlisPro, and the structures were solved with either SIR92, SuperFlip or SHELXT and refined with full-matrix least squares within CRYSTALS or SHELXL-2014, as described in the CIF.<sup>[27]</sup> Complete details of the X-ray analyses reported herein have been deposited at The Cambridge Crystallographic Data Centre (CCDC 1474309-1474324).

### DFT calculations

DFT calculations were performed using the Amsterdam Density Functional (ADF) Package Software 2013. Calculations were performed using the Vosko-Wilk-Nusair local density approximation with exchange from Becke, and correlation corrections from Perdew (BP).<sup>[28]</sup> Slater-type orbitals (STOs), were used for the triple zeta basis set with an additional set of polarization functions (TZP). The large frozen core basis set approximation was applied with no molecular symmetry.

### Syntheses of Novel Compounds

**Ar<sup>Mes</sup>Ge(NH(Dipp)) (2-Mes) and Ar<sup>Dipp</sup>Ge(NH(Dipp)) (2-Dipp):** 1-Mes (0.200 g, 0.47 mmol) and  $Li[NH(Dipp)]$  (0.087 g, 0.47 mmol) were dissolved in diethyl ether (15 mL) and the reaction mixture stirred at room temperature for 3 h. Volatiles were removed *in vacuo* and the resulting pale yellow solid extracted with pentane (10 mL). The solution was reduced to incipient crystallisation and stored at  $-20$  °C overnight to give yellow crystals which were suitable for X-ray crystallography. Yield: 0.196 g, 74%. Elemental microanalysis: calc. for  $C_{40}H_{53}GeNO$  (2-Mes  $Et_2O$ ): C 75.48, H 8.39, N 2.20%; meas. C 75.86, H 8.59, N 2.42%.  $^1H$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.99 (12H, d,  $^3J_{HH} = 6.8$  Hz,  $CHMe_2$  of Dipp), 2.18 (6H, s, p-Me of Mes), 2.24 (12H, s, o-Me of Mes), 2.70 (2H, sept,  $^3J_{HH} = 6.9$  Hz,  $CHMe_2$  of Dipp), 6.83 (4H, s, m-CH of Mes), 6.96 (2H, d,  $^3J_{HH} = 7.5$  Hz, m-CH of Ar), 7.02 – 7.08 (3H, overlapping m, p/m-CH of Dipp), 7.19 (1H, br s, NH), 7.27 (1H, t,  $^3J_{HH} = 7.5$  Hz, p-CH of Ar).  $^{13}C\{^1H\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_C$  21.6 (p-Me of Mes), 21.9 (o-Me of Mes), 25.1 ( $CHMe_2$  of Dipp), 28.1 ( $CHMe_2$  of Dipp), 123.7 (m-CH of Dipp), 124.9 (p-CH of Dipp), 128.5 (m-CH of Ar), 129.5 (m-CH of Mes), 129.6 (p-CH of Ar), 136.4 (o-C of Mes), 137.5 (p-C of Mes), 138.4 (i-C of Mes), 142.2 (i-C of Dipp), 143.4 (o-C of Dipp), 145.6 (o-C of Ar), 161.3 (i-C of Ar). Crystallographic data:  $C_{36}H_{43}GeN$ ,  $M_r = 562.32$ , triclinic,  $P-1$ ,  $a = 8.251(2)$ ,  $b = 11.678(2)$ ,  $c = 16.310(3)$  Å,  $\alpha = 92.36(3)$ ,  $\beta = 94.26(3)$ ,  $\gamma = 99.09(3)^\circ$ ,  $V = 1545.3(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_c = 1.209$  g cm<sup>-3</sup>,  $T = 150$  K,  $\lambda = 0.71073$  Å. 28157 reflections collected, 7037 independent [ $R(int) = 0.018$ ], which were used in all calculations.  $R_1 = 0.0351$ ,  $wR_2 = 0.0922$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0421$ ,  $wR_2 = 0.0978$  for all unique reflections. Max. and min. residual electron densities 0.44 and -0.58 e Å<sup>-3</sup>. CCDC reference: 1474310. **2-Dipp** was prepared in analogous fashion from **1-Dipp** (0.200 g, 0.39 mmol) and  $Li[NH(Dipp)]$  (0.072 g, 0.39 mmol) and recrystallized from pentane (10 mL) at  $-20$  °C to give yellow crystals which were suitable for X-ray crystallography. Yield: 0.106 g, 42%.  $^1H$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.97 (12H, d,  $^3J_{HH} = 6.8$  Hz,  $CHMe_2$  of NDipp), 1.10 (12H, d,  $^3J_{HH} = 6.7$  Hz,  $CHMe_2$  of Dipp), 1.27 (12H, d,  $^3J_{HH} = 6.8$  Hz,  $CHMe_2$  of Dipp), 2.48 (2H, sept,  $^3J_{HH} = 6.8$  Hz,  $CHMe_2$  of NDipp), 3.16 (4H, sept,  $^3J_{HH} = 6.8$  Hz,  $CHMe_2$  of Dipp), 7.00 – 7.30 (12H, overlapping m, aromatic CH of NDipp, and Ar).  $^{13}C\{^1H\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_C$  23.3 ( $CHMe_2$  of Dipp), 25.8 ( $CHMe_2$  of NDipp), 26.2 ( $CHMe_2$  of Dipp), 27.8 ( $CHMe_2$  of NDipp), 31.6 ( $CHMe_2$  of Dipp), 124.0, 124.1, 125.2, 128.3, 129.5, 129.6 (o/p-C of Dipp and NDipp), 139.0 (o-C of Dipp), 141.4 (i-C of NDipp), 144.1 (i-C of Dipp), 144.6 (o-C of NDipp), 147.2 (o-C of Ar), 162.2 (i-C of Ar). Crystallographic data:  $C_{42}H_{55}GeN$ ,  $M_r = 646.49$ , monoclinic,  $P2_1/c$ ,  $a = 9.5454(1)$ ,  $b = 23.6771(2)$ ,  $c = 17.0230(2)$  Å,  $\beta = 103.152(1)^\circ$ ,  $V = 3746.4(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.146$  g cm<sup>-3</sup>,  $T = 150$  K,  $\lambda = 0.71073$  Å. 16055 reflections collected, 8490 independent [ $R(int) = 0.021$ ], which were used in all calculations.  $R_1 = 0.0381$ ,  $wR_2 = 0.0836$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0484$ ,  $wR_2 = 0.0929$  for all unique reflections. Max. and min. residual electron densities 1.12 and -0.76 e Å<sup>-3</sup>. CCDC reference: 1474309.

**Ar<sup>Mes</sup>Ge(CH(SiMe<sub>3</sub>)<sub>2</sub>) (3-Mes) and Ar<sup>Dipp</sup>Ge(CH(SiMe<sub>3</sub>)<sub>2</sub>) (3-Dipp):** 1-Mes (0.200 g, 0.47 mmol) and  $Li[CH(SiMe_3)_2]$  (0.079 g, 0.47 mmol) were dissolved in diethyl ether (10 mL) and the reaction mixture stirred at room temperature for 3 h. Volatiles were removed *in vacuo* and the resulting dark red/pink solid was extracted with pentane (10 mL). The solution was reduced to incipient crystallisation and stored at  $-20$  °C overnight to give red crystals which were

suitable for X-ray crystallography. Yield: 0.177g, 69%. Elemental microanalysis: calc. for  $C_{31}H_{44}GeSi_2$  (**3-Mes**): C 68.28, H 8.13%; meas. C 68.11, H 7.98%.  $^1H$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.03 (18H, s, SiMe $_3$ ), 1.86 (1H, s, CH(SiMe $_3$ ) $_2$ ), 2.13 (6H, s, p-Me of Mes), 2.29 (12H, s, o-Me of Mes), 6.78 (4H, s, m-H of Mes), 7.01 (2H, d,  $^3J_{HH} = 7.8$  Hz, m-H of Ar), 7.28 (1H, t,  $^3J_{HH} = 7.8$  Hz, p-H of Ar).  $^{13}C\{^1H\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_C$  3.2 (CH $_3$  of SiMe $_3$ ), 21.4 (p-Me of Mes), 22.4 (o-Me of Mes), 56.7 (CH), 129.6 (m-C of Mes), 129.7 (m-C of Ar), 129.8 (p-C of Ar), 136.5 (i-C of Mes), 137.5 (p-C of Mes), 139.0 (o-C of Mes), 144.4 (o-C of Ar), 170.5 (i-C of Ar). Crystallographic data:  $C_{31}H_{44}GeSi_2$ ,  $M_r = 545.45$ , monoclinic,  $P2_1/n$ ,  $a = 9.581(2)$ ,  $b = 18.296(4)$ ,  $c = 17.253$  Å,  $\beta = 92.50(3)^\circ$ ,  $V = 3020.1(10)$  Å $^3$ ,  $Z = 4$ ,  $\rho_c = 1.200$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 0.71073$  Å. 44537 reflections collected, 6887 independent [ $R(int) = 0.027$ ], which were used in calculations.  $R_1 = 0.0360$ ,  $wR_2 = 0.0927$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0501$ ,  $wR_2 = 0.1006$  for all unique reflections. Max. and min. residual electron densities 0.35 and  $-0.51$  e Å $^{-3}$ . CCDC reference: 1474312. **3-Dipp** was prepared in analogous fashion from **1-Dipp** (0.200 g, 0.39 mmol) and Li[CH(SiMe $_3$ ) $_2$ ] (0.065 g, 0.39 mmol), and recrystallized from pentane (10 mL) at  $-20^\circ C$  as red crystals which were suitable for X-ray diffraction. Yield: 0.093 g, 38%.  $^1H$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.04 (18H, s, SiMe $_3$ ), 1.11 (12H, d,  $^3J_{HH} = 6.8$  Hz, CHMe $_2$  of Dipp), 1.32 (12H, d,  $^3J_{HH} = 6.8$  Hz, CHMe $_2$  of Dipp), 3.33 (4H, sept,  $^3J_{HH} = 6.8$  Hz, CHMe $_2$  of Dipp), 7.10 – 7.27 (9H, m, aromatic CH).  $^{13}C\{^1H\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_C$  3.2 (SiMe $_3$ ), 23.5 (CHMe $_2$  of Dipp), 27.2 (CHMe $_2$  of Dipp), 31.6 (CHMe $_2$  of Dipp), 56.4 (CH), 124.1 (m-C of Dipp), 128.0 (m-C of Ar), 128.7 (p-C of Dipp), 129.5 (p-C of Ar), 131.3 (m-C of Ar), 138.9 (i-C of Dipp), 142.8 (o-C of Ar), 147.5 (o-C of Dipp), 171.3 (i-C of Ar). Crystallographic data:  $C_{37}H_{56}GeSi_2$ ,  $M_r = 629.61$ , monoclinic,  $C2/c$ ,  $a = 35.086(7)$ ,  $b = 10.171(2)$ ,  $c = 21.068(4)$  Å,  $\beta = 103.49(3)^\circ$ ,  $V = 7311(3)$  Å $^3$ ,  $Z = 8$ ,  $\rho_c = 1.144$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 0.71073$  Å. 37542 reflections collected, 8320 independent [ $R(int) = 0.033$ ], which were used in all calculations.  $R_1 = 0.0415$ ,  $wR_2 = 0.1157$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0624$ ,  $wR_2 = 0.1333$  for all unique reflections. Max. and min. residual electron densities 0.59 and  $-0.74$  e Å $^{-3}$ . CCDC reference: 1474311.

**Ar<sup>Mes</sup>Ge{P(SiMe $_3$ ) $_2$ } (4-Mes)**: **1-Mes** (0.200 g, 0.47 mmol) and LiP(SiMe $_3$ ) $_2$ dme (0.130 g, 0.47 mmol) were dissolved in diethyl ether (10 mL) at  $-30^\circ C$  and stirred for 4 h between  $-20$  and  $-30^\circ C$ . Volatiles were removed *in vacuo* at  $-20^\circ C$  and the resulting brown solid washed with cold pentane (10 mL,  $-50^\circ C$ ) and then extracted with pentane (10 mL) at room temperature. The red/brown solution was reduced and stored at  $-20^\circ C$  to give dark purple/red crystals which were suitable for X-ray diffraction. Yield: 0.123 g, 46%. Elemental microanalysis: calc. for  $C_{30}H_{43}GePSi_2$  (**4-Mes**): C 63.98, H 7.69%; meas. C 63.64, H 7.39%.  $^1H$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.22 (9H, s, SiMe $_3$ ), 0.23 (9H, s, SiMe $_3$ ), 2.10 (6H, s, p-Me of Mes), 2.39 (12H, s, o-Me of Mes), 6.79 (4H, s, m-CH of Mes), 7.02 (2H, d,  $^3J_{HH} = 7.6$  Hz, m-H of Ar), 7.28 (1H, t,  $^3J_{HH} = 7.8$  Hz, p-H of Ar).  $^{13}C\{^1H\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_C$  5.3 (SiMe $_3$ ), 5.4 (SiMe $_3$ ), 21.4 (p-Me of Mes), 22.4 (o-Me of Mes), 128.7 (m-CH of Ar), 129.7 (m-CH of Mes), 135.5 (i-C of Mes), 136.7 (o-C of Mes), 136.9 (p-C of Mes), 144.0 (o-C of Mes), 163.0 (i-C of Mes).  $^{31}P\{^1H\}$  NMR (162 MHz, benzene- $d_6$ , 298 K):  $\delta_P$  -18.2. Crystallographic data:  $C_{30}H_{43}GePSi_2$ ,  $M_r = 563.40$ , triclinic,  $P-1$ ,  $a = 9.9278(3)$ ,  $b = 10.4997(4)$ ,  $c = 16.9814(6)$  Å,  $\alpha = 95.338(3)$ ,  $\beta = 98.815(3)$ ,  $\gamma = 113.527(3)^\circ$ ,  $V = 1548.9(1)$  Å $^3$ ,  $Z = 2$ ,  $\rho_c = 1.208$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 1.54180$  Å. 14642 reflections collected, 6887 independent [ $R(int) = 0.072$ ], which were used in all calculations.  $R_1 = 0.0557$ ,  $wR_2 = 0.1480$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0571$ ,  $wR_2 = 0.1509$  for all unique reflections. Max. and min. residual electron densities 0.86 and  $-1.07$  e Å $^{-3}$ . CCDC reference: 1474313.

**Ar<sup>Mes</sup>Ge{Si(SiMe $_3$ ) $_3$ } (5-Mes)**: **1-Mes** (0.200 g, 0.47 mmol) and K[Si(SiMe $_3$ ) $_3$ ] (0.093 g, 0.47 mmol) were dissolved in diethyl ether (10 mL) and the reaction mixture stirred at  $-20^\circ C$  for 3 h. Volatiles were removed *in vacuo* and the resulting brown/green solid washed with cold pentane (10 mL,  $-78^\circ C$ ) to leave a green solid. The solid was extracted with toluene and was then reduced to incipient crystallisation, storage at  $-20^\circ C$  gave pale green crystals which were suitable for X-ray diffraction. Yield: 0.066 g, 22%.  $^1H$  NMR (400 MHz, thf- $d_8$ , 298 K):  $\delta_H$  -0.01 (27H, s, SiMe $_3$ ), 2.19 (6H, s, p-Me of Mes), 23.1 (br, o-Me of Mes), 2.25 (12H, br s, o-Me of Mes), 6.80 (4H, br s, m-CH of Mes), 6.98 (2H, d,  $^3J_{HH} = 7.6$  Hz, m-CH of Ar), 7.42 (1H, t,  $^3J_{HH} = 7.4$  Hz, p-CH of Ar).  $^{13}C\{^1H\}$  NMR (100 MHz, thf- $d_8$ , 298 K):  $\delta_C$  4.3 (SiMe $_3$ ), 21.4 (p-Me of Mes), 129.4 (p-CH of Ar), 129.6 (m-CH of Ar), 136.4 (i-C of Mes), 138.9 (p-C of Mes), 142.1 (o-C of Ar), 168.4 (i-C of Ar).  $^{29}Si$  NMR (59.6 MHz, thf- $d_8$ , 298 K):  $\delta_{Si}$  -58.3 (Si(SiMe $_3$ ) $_3$ ), -6.5 (SiMe $_3$ ). Crystallographic data:  $C_{33}H_{52}GeSi_4$ ,  $M_r = 633.71$ , triclinic,  $P-1$ ,  $a = 11.2921(2)$ ,  $b = 16.3626(3)$ ,  $c = 19.3991(3)$  Å,  $\alpha = 89.982(1)$ ,  $\beta = 89.961(1)$ ,  $\gamma = 89.964(1)^\circ$ ,  $V = 3584.3(1)$  Å $^3$ ,  $Z = 4$ ,  $\rho_c = 1.174$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 0.71073$  Å. 195350 reflections collected, 16155 independent [ $R(int) = 0.027$ ], which were

used in all calculations.  $R_1 = 0.0430$ ,  $wR_2 = 0.0852$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0572$ ,  $wR_2 = 0.0972$  for all unique reflections. Max. and min. residual electron densities 0.65 and  $-0.49$  e Å $^{-3}$ . CCDC reference: 1474314.

**Ar<sup>Mes</sup>Ge{B(NDippCH) $_2$ } (6-Mes) and Ar<sup>Dipp</sup>Ge{B(NDippCH) $_2$ } (6-Dipp)**: **1-Mes** (0.200 g, 0.47 mmol) and (thf) $_2$ Li[B(N(Dipp)CH) $_2$ ] (0.255 g, 0.47 mmol) were dissolved in diethyl ether (10 mL) at  $-30^\circ C$  and the reaction mixture stirred for 4 h between  $-20$  and  $-30^\circ C$ . Volatiles were removed *in vacuo* at  $-20^\circ C$  and the resulting green solid extracted with pentane (10 mL). The brown solution was reduced in volume and stored at  $-20^\circ C$  to give dark green crystals which were suitable for X-ray diffraction. No NMR data could be collected due to rapid decomposition in solution at temperatures close to ambient. Crystallographic data:  $C_{50}H_{61}BGeN_2$ ,  $M_r = 773.45$ , monoclinic,  $P2_1/a$ ,  $a = 19.8279(2)$ ,  $b = 11.1435(1)$ ,  $c = 22.6952(3)$  Å,  $\beta = 112.496(1)^\circ$ ,  $V = 4633.0(1)$  Å $^3$ ,  $Z = 4$ ,  $\rho_c = 1.109$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 0.71073$  Å. 10570 reflections collected, 10570 independent [ $R(int) = 0.031$ ], which were used in all calculations.  $R_1 = 0.0471$ ,  $wR_2 = 0.1123$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0673$ ,  $wR_2 = 0.1325$  for all unique reflections. Max. and min. residual electron densities 0.57 and  $-0.83$  e Å $^{-3}$ . CCDC reference: 1474315. **6-Dipp** was prepared in analogous fashion from **1-Dipp** (0.200 g, 0.39 mmol) and (thf) $_2$ Li[B(NDipp)CH] $_2$  (0.255 g, 0.39 mmol) in diethyl ether (10 mL), and recrystallized from hexamethylsiloxane (10 mL) at  $-20^\circ C$  as a dark green microcrystalline solid. Yield: 0.124 g, 34%. Elemental microanalysis: calc. for  $C_{116}H_{164}B_2Ge_2N_4OSi_2$  (**6-Dipp**·0.5(Me $_3$ SiOSiMe $_3$ )): C 75.48, H 8.80, N 2.98%; meas. C 75.71, H 8.58, N 3.13%.  $^1H$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.91 (12H, d,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$  of NDipp), 0.96 (12H, d,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$  of Dipp), 1.05 (12H, d,  $^3J_{HH} = 6.7$  Hz, CHMe $_2$  of Dipp), 1.11 (12H, d,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$  of NDipp), 3.31 (4H, sept,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$  of NDipp), 3.32 (4H, sept,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$  of Dipp), 6.20 (2H, s, NCH), 6.91 – 7.18 (15H, m, aromatic CH).  $^{13}C$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_C$  24.5, 24.6, 26.2, 26.3 (CHMe $_2$  of Dipp and NDipp), 29.4, 31.6 (CHMe $_2$  of Dipp and NDipp), 124.4, 124.5, 124.5, 126.7, 128.1, 129.5, 131.6 (m-C/p-C of Dipp and NDipp, NCH), 137.6, 140.6, 141.3, 146.2, 147.9 (o-C of Ar, i-C and o-C of Dipp and NDipp), 172.5 (i-C of Ar).  $^{11}B$  NMR (128 MHz, benzene- $d_6$ , 298 K):  $\delta_B$  50.6.

**Generation of {(Me $_3$ Si) $_2$ Ge}B(NDippCH) $_2$  (**8**) (as co-crystallite with [Li{N(SiMe $_3$ ) $_2$ }(thf)] $_2$ )**: Solid (thf) $_2$ Li[B(N(Dipp)CH) $_2$ ] (0.048 g, 0.089 mmol) was added to a solution of **7** (0.034 g, 0.086 mmol) in benzene- $d_6$  (0.5 mL) at room temperature forming a dark purple solution (having only one set of boryl ligand signals, see NMR data below). The solution was transferred into a two-section crystallisation tube and all volatiles removed *in vacuo*. The resulting oily residue was dissolved in a small amount of hexane and the tube was sealed under vacuum. The solvent was evaporated into the second arm, and the tube was stored in a freezer at  $-30^\circ C$  allowing slow diffusion of hexane vapour onto the product mixture. At first, colourless block crystals of the lithium amide were formed; repeating this procedure several times resulted in formation of purple-blue elongated plates of **8**·2[Li{N(SiMe $_3$ ) $_2$ }(thf)] $_2$  co-crystals. Attempts to remove the lithium amide co-product at this stage using [Et $_3$ NH]Cl were unsuccessful, due to competing formation of HN(SiMe $_3$ ) $_2$  and a germanium-containing product tentatively assigned as Ge{B(N(Dipp)CH) $_2$ }[N(SiMe $_3$ ) $_2$ ](H)Cl. As such, *in situ* generated **8** was used for further E-H insertion chemistry and the amide co-product removed from the less reactive Ge<sup>IV</sup> products by the use of [Et $_3$ NH]Cl. Data for **8** (*in situ* prepared):  $^1H$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.12 (18H, s, SiMe $_3$ ), 1.11 (12H, two overlapping d, CHMe $_2$ ), 1.38 (12H, d,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$ ), 3.17 (2H, sept,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$ ), 3.18 (2H, sept,  $^3J_{HH} = 6.9$  Hz, CHMe $_2$ ), 6.26 (2H, s, NCH), 6.28 (1H, br s, GeH), 7.13-7.17 (4H, m, m-CH of NDipp + C $_6$ D $_5$ H), 7.23 (2H, t,  $^3J_{HH} = 7.7$  Hz, p-H of NDipp).  $^{11}B\{^1H\}$  (128 MHz, benzene- $d_6$ , 298 K):  $\delta_B$  25.0. Crystallographic data (for **8**·2[Li{N(SiMe $_3$ ) $_2$ }(thf)] $_2$ ):  $C_{72}H_{158}GeBLi_4N_7O_4Si_{10}$ ,  $M_r = 1578.11$ , monoclinic,  $P2_1/c$ ,  $a = 10.4972(1)$ ,  $b = 15.0574(2)$ ,  $c = 63.1948(7)$  Å,  $\beta = 92.395(1)^\circ$ ,  $V = 9979.9(2)$  Å $^3$ ,  $Z = 4$ ,  $\rho_c = 1.050$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 1.54180$  Å. 221896 reflections collected, 20919 independent [ $R(int) = 0.100$ ], which were used in all calculations.  $R_1 = 0.1070$ ,  $wR_2 = 0.2412$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.1122$ ,  $wR_2 = 0.2431$  for all unique reflections. Max. and min. residual electron densities 2.16 and  $-0.79$  e Å $^{-3}$ . CCDC reference: 1474316.

**C-H activation product 9, formed from 6-Mes**: A solution of **6-Mes** (0.020 g, 0.026 mmol) was dissolved in benzene- $d_6$  and the resulting solution maintained at room temperature for 12 h. Over this period a colour change from green to colourless was observed, and the solution was shown by  $^1H$  NMR to consist of >95% of one product. Cooling a concentrated solution in hexane to  $-30^\circ C$  led to the formation of single crystals suitable for X-ray diffraction. Yield: 0.012 g, 60%.  $^1H$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_H$  0.81 (6H, d,  $^3J_{HH} = 7.0$  Hz, CHMe $_2$  of

NDipp), 1.02 (6H, d,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$  of NDipp), 1.06 (6H, d,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$  of NDipp), 1.12 (6H, d,  $^3J_{\text{HH}} = 7.0$  Hz,  $\text{CHMe}_2$  of NDipp), 1.61 (3H, s, Me of Mes), 1.83 (1H, d,  $^3J_{\text{HH}} = 13.2$  Hz,  $\text{GeCH}_2$ ), 1.96 (3H, s, Me of Mes), 2.19 (3H, s, Me of Mes), 2.28 (3H, s, Me of Mes), 2.34 (1H, d,  $^3J_{\text{HH}} = 13.1$  Hz,  $\text{GeCH}_2$ ), 2.41 (3H, s, Me of Mes), 2.93 (2H, sept,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$  of NDipp), 3.12 (2H, sept,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$  of NDipp), 4.11 (1H, s, GeH), 6.06 (2H, s, NCH), 6.71 (1H, s, m-H of Mes), 6.74 (2H, s, m-CH of Mes), 6.79 (1H, s, m-CH of Mes), 7.06–7.21 (9H, overlapping m, m-CH of Dipp and aromatic CH of Ar).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{C}}$  19.9 ( $\text{GeCH}_2$ ), 21.2, 21.6, 21.6 (2H, sept,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$  of NDipp), 4.11 (1H, s, GeH), 6.06 (2H, s, NCH), 6.71 (1H, s, m-H of Mes), 6.74 (2H, s, m-CH of Mes), 6.79 (1H, s, m-CH of Mes), 7.06–7.21 (9H, overlapping m, m-CH of Dipp and aromatic CH of Ar).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{C}}$  19.9 ( $\text{GeCH}_2$ ), 21.2, 21.6, 21.6 (2H, sept,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$  of NDipp), 4.11 (1H, s, GeH), 6.06 (2H, s, NCH), 6.71 (1H, s, m-H of Mes), 6.74 (2H, s, m-CH of Mes), 6.79 (1H, s, m-CH of Mes), 7.06–7.21 (9H, overlapping m, m-CH of Dipp and aromatic CH of Ar).  $^{11}\text{B}$  NMR (128 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{B}}$  26.4. Crystallographic data:  $\text{C}_{50}\text{H}_{61}\text{BGeN}_2$ ,  $M_r = 773.45$ , monoclinic,  $P2_1/c$ ,  $a = 17.0681(1)$ ,  $b = 12.4848(1)$ ,  $c = 20.4526(1)$  Å,  $\beta = 98.737(1)^\circ$ ,  $V = 4307.7(1)$  Å $^3$ ,  $Z = 4$ ,  $\rho_{\text{c}} = 1.293$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 1.54180$  Å. 49486 reflections collected, 8975 independent [ $R(\text{int}) = 0.025$ ], which were used in all calculations.  $R_1 = 0.0289$ ,  $wR_2 = 0.0728$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0313$ ,  $wR_2 = 0.0750$  for all unique reflections. Max. and min. residual electron densities 0.30 and  $-0.32$  e Å $^{-3}$ . CCDC reference: 1474317.

**Ar<sup>Mes</sup>Ge(Si(SiMe<sub>3</sub>)<sub>3</sub>(H)<sub>2</sub> (10):** A solution of **5-Mes** (0.050 g, 0.079 mmol) in toluene (5 mL) in a J Young's ampoule was degassed by three freeze-pump-thaw cycles before being treated with H<sub>2</sub> at ca. 4 atm pressure. The yellow solution was stirred at room temperature for 3 h before being concentrated *in vacuo*. Colourless X-ray quality crystals of **10** were acquired after crystallization at 5 °C in toluene. Yield 0.035 g, 70%. Elemental microanalysis: calc. for  $\text{C}_{33}\text{H}_{54}\text{GeSi}_4$  (**10**): C 62.39, H 8.57%; meas. C 62.25, H 8.43%.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{H}}$  0.13 (27H, s, SiMe<sub>3</sub>), 2.15 (12H, s, o-Me of Mes), 2.27 (6H, s, p-Me of Mes), 3.90 (2H, s, GeH<sub>2</sub>), 6.89 (4H, s, m-CH of Mes), 6.90 (2H, d,  $^3J_{\text{HH}} = 7.7$  Hz, m-CH of Ar), 7.20 (1H, t,  $^3J_{\text{HH}} = 7.8$  Hz, p-CH of Ar).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{C}}$  2.7 (SiMe<sub>3</sub>), 21.5 (p-Me of Mes), 22.2 (o-Me of Mes), 128.7 (m-C of Ar), 128.8 (m-C of Mes), 129.2 (p-C of Ar), 136.0 (o-C of Mes), 136.6 (o-C of Ar), 137.1 (p-C of Mes), 141.9 (i-C of Mes), 149.9 (i-C of Ar). Crystallographic data:  $\text{C}_{33}\text{H}_{54}\text{GeSi}_4$ ,  $M_r = 635.73$ , monoclinic,  $P2_1/n$ ,  $a = 11.4294(2)$ ,  $b = 19.3548(3)$ ,  $c = 16.4991(3)$  Å,  $\beta = 91.052(2)^\circ$ ,  $V = 3649.2(1)$  Å $^3$ ,  $Z = 4$ ,  $\rho_{\text{c}} = 1.157$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 1.54180$  Å. 39740 reflections collected, 10397 independent [ $R(\text{int}) = 0.041$ ], which were used in calculations.  $R_1 = 0.0849$ ,  $wR_2 = 0.2450$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0936$ ,  $wR_2 = 0.2560$  for all unique reflections. Max. and min. residual electron densities 2.46 and  $-1.99$  e Å $^{-3}$ . The structure was refined as a 2-component twin (BASF = 0.235). CCDC reference: 1474318.

**Ar<sup>Mes</sup>Ge(Si(SiMe<sub>3</sub>)<sub>3</sub>(H)(NH<sub>2</sub>) (11):** A solution of **5-Mes** (0.050 g, 0.079 mmol) in toluene (5 mL) was degassed by three freeze-pump-thaw cycles before being treated with NH<sub>3</sub> at ca. 1 atm pressure. The solution immediately turned colourless and the solution was concentrated *in vacuo*. X-ray quality crystals of **11** were obtained after crystallization at room temperature. Yield 0.038 g, 74%.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{H}}$   $-0.06$  (2H, br d,  $^3J_{\text{HH}} = 4.8$  Hz, GeNH<sub>2</sub>), 0.19 (27H, s, SiMe<sub>3</sub>), 2.13 (6H, s, o-Me of Mes), 2.19 (6H, s, o-Me of Mes), 2.22 (6H, s, p-Me of Mes), 5.10 (1H, t,  $^3J_{\text{HH}} = 5.5$ , GeH), 6.85 (2H, d,  $^3J_{\text{HH}} = 8.4$  Hz, m-CH of Ar), 6.86 (2H, s, m-CH of Mes), 6.89 (2H, s, m-CH of Mes), 7.20 (1H, t,  $^3J_{\text{HH}} = 7.6$  Hz, p-H of Ar).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{C}}$  3.5 (SiMe<sub>3</sub>), 21.5 (p-Me of Mes), 22.2 (o-Me of Mes), 128.7 (m-C of Ar), 128.8 (m-C of Mes), 129.2 (p-C of Ar), 136.0 (o-C of Mes), 136.6 (o-C of Ar), 137.1 (p-C of Mes), 141.9 (i-C of Mes), 149.9 (i-C of Ar). Crystallographic data:  $\text{C}_{33}\text{H}_{53}\text{GeNSi}_4$ ,  $M_r = 648.71$ , orthorhombic,  $P2_12_12_1$ ,  $a = 11.539(2)$ ,  $b = 16.640(3)$ ,  $c = 19.115(4)$  Å,  $V = 3670.3(12)$  Å $^3$ ,  $Z = 4$ ,  $\rho_{\text{c}} = 1.174$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 1.54180$  Å. 66419 reflections collected, 7602 independent [ $R(\text{int}) = 0.041$ ], which were used in all calculations.  $R_1 = 0.0485$ ,  $wR_2 = 0.1114$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0616$ ,  $wR_2 = 0.1200$  for all unique reflections. Max. and min. residual electron densities 0.64 and  $-0.54$  e Å $^{-3}$ . CCDC reference: 1474319.

**{(Me<sub>3</sub>Si)<sub>2</sub>N}{(HC(Dipp)N)<sub>2</sub>Ge(H)GeH<sub>2</sub>{B(NDippCH)<sub>2</sub> (12):** A sample of **8** and [(thf)Li{μ-N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (generated *in situ* from solid Li{B(N(Dipp)CH)<sub>2</sub>(thf)<sub>2</sub> (0.096 g, 0.178 mmol) and a solution of Ge{N(SiMe<sub>3</sub>)<sub>2</sub> (0.070 g, 0.178 mmol) in C<sub>6</sub>H<sub>6</sub> (1.0 mL)) was dried *in vacuo* for 2 h and then transferred into a 20 mL J Young's ampoule. After addition of hexane (2.0 mL), the solution was degassed by three freeze-pump-thaw cycles and the ampoule back-filled with 1 atm of H<sub>2</sub>. The resulting mixture was stirred at room temperature for 6 h during which time

the colour gradually changed from purple to red, then orange, and finally yellow. Solid [Et<sub>3</sub>NH]Cl (0.025 g, 0.180 mmol) was then added, and the mixture stirred for 5 min prior to removal of volatiles *in vacuo*. The resulting residue was extracted with hexane (1.0 mL), concentrated to a small volume and stored at  $-30$  °C for 2 d yielding colourless blocks of **12**. Yield 0.022 g, 23% based on germanium. Elemental microanalysis: calc for  $\text{C}_{58}\text{H}_{93}\text{B}_2\text{Ge}_2\text{N}_5\text{Si}_2$  (**12**): C 64.39, H 8.75, N 6.50%; meas. C 64.30, H 8.65, N 6.46.  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{H}}$   $-0.04$  (18H, br s, SiMe<sub>3</sub>), 0.93 (6H, d,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CHMe}_2$ ), 1.10 (18H, three overlapping d,  $\text{CHMe}_2$ ), 1.17 (6H, d,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CHMe}_2$ ), 1.30 (6H, d,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CHMe}_2$ ), 1.43 (12H, d,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CHMe}_2$ ), 1.73 (1H, d,  $^3J_{\text{HH}} = 2.6$  Hz, BNGeH), 2.53 (1H, dd,  $^2J_{\text{HH}} = 12.0$  Hz,  $^3J_{\text{HH}} = 2.6$  Hz, BGeH<sub>2</sub>H<sub>β</sub>), 2.87 (2H, sept,  $^3J = 6.8$  Hz,  $\text{CHMe}_2$ ), 2.93 (2H, sept,  $^3J = 6.8$  Hz,  $\text{CHMe}_2$ ), 3.38 (sept,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CHMe}_2$ ), 3.44 (2H, sept,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CHMe}_2$ ), 4.92 (1H, d,  $^2J_{\text{HH}} = 12.0$  Hz, BGeH<sub>2</sub>H<sub>β</sub>), 6.16 (2H, s, NCH), 6.29 (2H, s, NCH), 7.05 (2H, two overlapping d,  $^3J_{\text{HH}} = 7.4$  Hz, m-CH of NDipp), 7.14–7.18 (6H, m, m-CH of NDipp + C<sub>6</sub>D<sub>5</sub>H), 7.19–7.26 (4H, m, p-CH of NDipp).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{C}}$  3.8 (br s, SiMe<sub>3</sub>), 5.9 (br s, SiMe<sub>3</sub>), 22.8 ( $\text{CHMe}_2$ ), 23.2 ( $\text{CHMe}_2$ ), 24.3 ( $\text{CHMe}_2$ ), 24.5 ( $\text{CHMe}_2$ ), 26.2 ( $\text{CHMe}_2$ ), 26.5 ( $\text{CHMe}_2$ ), 26.9 ( $\text{CHMe}_2$ ), 28.2 ( $\text{CHMe}_2$ ), 28.4 ( $\text{CHMe}_2$ ), 28.7 ( $\text{CHMe}_2$ ), 29.1 ( $\text{CHMe}_2$ ), 122.6 (NCH), 122.8 (NCH), 123.5 (m-CH of NDipp), 123.7 (m-CH of NDipp), 124.2 (m-CH of NDipp), 124.3 (m-CH of NDipp), 128.2 (p-CH of NDipp, overlapping with C<sub>6</sub>D<sub>5</sub>H), 140.0 (i-C of NDipp), 140.3 (i-C of NDipp), 145.4 (o-C of NDipp), 145.8 (o-C of NDipp), 146.2 (o-C of NDipp), 146.7 (o-C of NDipp).  $^{11}\text{B}$  NMR (128 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{B}}$  27.9. Crystallographic data:  $\text{C}_{58}\text{H}_{93}\text{B}_2\text{Ge}_2\text{N}_5\text{Si}_2$ ,  $M_r = 1083.38$ , monoclinic,  $P2_1$ ,  $a = 12.8186(1)$ ,  $b = 16.3303(2)$ ,  $c = 14.8112(1)$  Å,  $\beta = 92.057(1)^\circ$ ,  $V = 3098.5(1)$  Å $^3$ ,  $Z = 2$ ,  $\rho_{\text{c}} = 1.161$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 1.54180$  Å. 18762 reflections collected, 10632 independent [ $R(\text{int}) = 0.020$ ], which were used in all calculations.  $R_1 = 0.0263$ ,  $wR_2 = 0.0731$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0267$ ,  $wR_2 = 0.0734$  for all unique reflections. Max. and min. residual electron densities 0.32 and  $-0.47$  e Å $^{-3}$ . CCDC reference: 1474320.

**{(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>(H)I (13):** A sample of **8** and [(thf)Li{μ-N(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (generated *in situ* from solid Li{B(N(Dipp)CH)<sub>2</sub>(thf)<sub>2</sub> (0.048 g, 0.089 mmol) and a solution of Ge{N(SiMe<sub>3</sub>)<sub>2</sub> (0.034 g, 0.086 mmol) in C<sub>6</sub>H<sub>6</sub> (0.5 mL)) was added to solid [Me<sub>3</sub>NH]I (0.033 g, 0.178 mmol) in a two-section tube. The mixture was shaken until most of the ammonium salt dissolved and the colour of the reaction mixture changed from purple to yellow (~5 min). Volatiles were removed *in vacuo* and the remaining viscous yellow oil was analysed by multinuclear NMR showing the clean conversion of **8** into a new boryl-containing product, but that the LiI(thf), side-product was still present. Volatiles were again removed *in vacuo* and the residue was dried under dynamic vacuum for 2 h. Extraction with pentane (0.5 mL) left a significant amount of white powder (LiI). The extract was concentrated to a small volume; crystallisation was initiated by freezing with liquid nitrogen and continued at room temperature, yielding colourless blocks of **13** suitable for X-ray crystallography. Yield: 0.052 g, 78%. Elemental microanalysis: calc for  $\text{C}_{32}\text{H}_{55}\text{BGeIN}_3\text{Si}_2$  (**13**): C 51.36, H 7.41, N 5.62%; meas. C 50.98, H 7.68, N 5.72. Crystallographic data:  $\text{C}_{32}\text{H}_{55}\text{BGeIN}_3\text{Si}_2$ ,  $M_r = 748.29$ , monoclinic,  $P2_1/c$ ,  $a$   $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{H}}$  0.15 (18H, s, SiMe<sub>3</sub>), 1.10 (12 H, two overlapping d,  $\text{CHMe}_2$ ), 1.38 (6H, d,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$ ), 1.42 (6H, d,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$ ), 3.09 (2H, septet,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$ ), 3.23 (2H, septet,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CHMe}_2$ ), 5.57 (1H, br s, GeH), 6.23 (2H, s, NCH), 7.11–7.16 (4H, overlapping m, m-H of Ar + C<sub>6</sub>D<sub>5</sub>H), 7.23 (2H, t,  $^3J_{\text{HH}} = 7.7$  Hz, p-H of Ar).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{C}}$  4.1 (SiMe<sub>3</sub>), 23.0 ( $\text{CHMe}_2$ ), 23.5 ( $\text{CHMe}_2$ ), 26.6 ( $\text{CHMe}_2$ ), 26.8 ( $\text{CHMe}_2$ ), 29.0 ( $\text{CHMe}_2$ ), 29.0 ( $\text{CHMe}_2$ ), 122.8 (NCH), 124.0 (m-CH of Ar), 124.1 (m-CH of Ar), 128.6 (p-CH of Ar), 138.7 (ipso-C of Ar), 145.8 (o-C of Ar), 146.2 (o-C of Ar).  $^{11}\text{B}\{^1\text{H}\}$  (128 MHz, benzene- $d_6$ , 298 K):  $\delta_{\text{B}}$  22.4. Crystallographic data:  $\text{C}_{35}\text{H}_{55}\text{BGeIN}_3\text{Si}_2$ ,  $M_r = 748.29$ , monoclinic,  $P2_1/c$ ,  $a = 17.5711(2)$ ,  $b = 10.95490(10)$ ,  $c = 19.7672(2)$  Å,  $\beta = 92.6450(9)^\circ$ ,  $V = 3800.93(7)$  Å $^3$ ,  $Z = 4$ ,  $\rho_{\text{c}} = 1.308$  g cm $^{-3}$ ,  $T = 150$  K,  $\lambda = 1.54180$  Å. 41698 reflections collected, 7919 independent [ $R(\text{int}) = 0.031$ ], which were used in all calculations.  $R_1 = 0.0218$ ,  $wR_2 = 0.0458$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0243$ ,  $wR_2 = 0.0477$  for all unique reflections. Max. and min. residual electron densities 0.46 and  $-0.46$  e Å $^{-3}$ . CCDC reference: 1474321.

**{(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>(H)<sub>2</sub> (14):** Solid K[Et<sub>3</sub>BH] (0.020 g, 0.144 mmol) was added to a solution of Ge{B(N(Dipp)CH)<sub>2</sub>(N(SiMe<sub>3</sub>)<sub>2</sub>(H)I) (0.060 g, 0.080 mmol) in C<sub>6</sub>H<sub>6</sub> (0.5 mL) and the reaction progress was monitored by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy. After 3 d at 70 °C the transformation was complete (the use of excess K[Et<sub>3</sub>BH] was found to be required to drive the reaction to completion). All volatiles were removed *in vacuo* and the residue extracted with hexane. The extract was concentrated to a very small volume, crystallisation was initiated by

repeated freezing with liquid N<sub>2</sub> and continued at room temperature yielding colourless blocks of **14** suitable for X-ray crystallography. Yield 0.043 g, 86%. Recrystallized samples of the product were subject to slight contamination with unreacted K[Et<sub>3</sub>BH] (as evident from <sup>11</sup>B spectrum) leading to microanalytical results reproducibly low in carbon and nitrogen, but high in hydrogen. <sup>1</sup>H NMR (400 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>H</sub> 0.02 (s, 18 H, SiMe<sub>3</sub>), 1.13 (d, <sup>3</sup>J = 6.9 Hz, 12 H, CHMe<sub>2</sub>), 1.36 (d, <sup>3</sup>J = 6.9 Hz, 12 H, CHMe<sub>2</sub>), 3.18 (septet, <sup>3</sup>J = 6.9 Hz, 4 H, CHMe<sub>2</sub>), 4.63 (s, 2 H, GeH), 6.29 (s, 2 H, NCH), 7.14–7.16 (m, 4 H, *m*-H of Ar + C<sub>6</sub>D<sub>5</sub>H), 7.23 (t, <sup>3</sup>J = 7.7 Hz, 2 H, *p*-H of Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>C</sub> 3.7 (SiMe<sub>3</sub>), 23.4 (CHMe<sub>2</sub>), 26.3 (CHMe<sub>2</sub>), 28.9 (CHMe<sub>2</sub>), 122.2 (NCH), 123.8 (*m*-CH of Ar), 127.8 (*p*-CH of Ar), 139.3 (*ipso*-C of Ar), 146.0 (*o*-C of Ar). <sup>11</sup>B NMR (128 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>B</sub> 26.4. Crystallographic data: C<sub>32</sub>H<sub>58</sub>BGeN<sub>3</sub>Si<sub>2</sub>, *M<sub>r</sub>* = 622.39, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 18.3603(2), *b* = 19.6644(1), *c* = 21.2377(2) Å, β = 102.896(1)°, *V* = 7474.4(1) Å<sup>3</sup>, *Z* = 8, ρ<sub>c</sub> = 1.106 g cm<sup>-3</sup>, *T* = 150 K, λ = 1.54180 Å. 90649 reflections collected, 15570 independent [*R*(int) = 0.031], which were used in all calculations. *R*<sub>1</sub> = 0.0292, *wR*<sub>2</sub> = 0.0739 for observed unique reflections [*I* > 2σ(*I*)] and *R*<sub>1</sub> = 0.0326, *wR*<sub>2</sub> = 0.0770 for all unique reflections. Max. and min. residual electron densities 1.16 and -0.46 e Å<sup>-3</sup>. CCDC reference: 1474322.

{(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>H(SiH<sub>3</sub>)} (**15**): An *in situ* generated 1:1 mixture of **8** and Li{N(SiMe<sub>3</sub>)<sub>2</sub>(thf)<sub>2</sub>} (0.086 mmol of each) in benzene-d<sub>6</sub> (0.5 mL) was degassed by three freeze-pump-thaw cycles and exposed to an atmosphere of SiH<sub>4</sub> at room temperature. The tube was shaken for 1 min, during which time the colour changed from purple to light yellow. In order to remove the lithium amide, solid [Et<sub>3</sub>NH]Cl (12.3 mg, 0.089 mmol) was then added to the reaction mixture and the tube agitated for a further 5 min until the crystals of [Et<sub>3</sub>NH]Cl disappeared and a fine powder of LiCl formed. The <sup>1</sup>H NMR spectrum at this point showed replacement of the SiMe<sub>3</sub> signal of the lithium amide dimer (δ<sub>H</sub> = 0.36 ppm) by that attributed to the neutral amine HN(SiMe<sub>3</sub>)<sub>2</sub> (δ<sub>H</sub> = 0.09 ppm). Volatiles were then removed *in vacuo*, the residue dissolved in hexane (0.5 mL) and the resulting solution transferred into a crystallisation tube. Concentration of the solution and storage at -30 °C produced colourless crystals of **15** suitable for X-ray crystallography. Yield: 0.014 g, 24%. <sup>1</sup>H NMR (500 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>H</sub> 0.11 (s, 18H, SiMe<sub>3</sub>), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CHMe<sub>2</sub>), 6.26 (s, 2H, NCH), 1.11 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, CHMe<sub>2</sub>), 1.33 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6 H, CHMe<sub>2</sub>), 1.42 (d, <sup>3</sup>J = 6.9 Hz, 6H, CHMe<sub>2</sub>), 3.06 (d, <sup>3</sup>J<sub>HH</sub> = 3.4 Hz, 3H, SiH<sub>3</sub>), 3.09 (septet, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CHMe<sub>2</sub>), 3.29 (septet, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CHMe<sub>2</sub>), 4.88 (quartet, <sup>3</sup>J<sub>HH</sub> = 3.4 Hz, 1H, GeH), 7.12–7.18 (m, 4H, *m*-CH of NDipp + C<sub>6</sub>D<sub>5</sub>H), 7.23 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H, *p*-H of NDipp). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>C</sub> 4.6 (SiMe<sub>3</sub>), 23.0 (CHMe<sub>2</sub>), 23.6 (CHMe<sub>2</sub>), 26.5 (CHMe<sub>2</sub>), 26.9 (CHMe<sub>2</sub>), 28.8 (CHMe<sub>2</sub>), 28.8 (CHMe<sub>2</sub>), 122.6 (NCH), 124.1 (*m*-CH of NDipp), 128.3 (*p*-CH of NDipp), 139.4 (*i*-C of NDipp), 146.2 (*o*-C of NDipp), 146.3 (*o*-C of NDipp). <sup>11</sup>B{<sup>1</sup>H} (160 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>B</sub> 27.1. <sup>29</sup>Si{<sup>1</sup>H} (99 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>Si</sub> -87.3. Crystallographic data: Crystallographic data: C<sub>32</sub>H<sub>58</sub>BGeN<sub>3</sub>Si<sub>3</sub>, *M<sub>r</sub>* = 652.49, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 17.9877(4), *b* = 12.4887(2), *c* = 18.8621(4) Å, β = 118.119(3)°, *V* = 3731.1(2) Å<sup>3</sup>, *Z* = 4, ρ<sub>c</sub> = 1.160 g cm<sup>-3</sup>, *T* = 150 K, λ = 1.54180 Å. 42947 reflections collected, 7822 independent [*R*(int) = 0.044], which were used in all calculations. *R*<sub>1</sub> = 0.0444, *wR*<sub>2</sub> = 0.1177 for observed unique reflections [*I* > 2σ(*I*)] and *R*<sub>1</sub> = 0.0482, *wR*<sub>2</sub> = 0.1220 for all unique reflections. Max. and min. residual electron densities 2.75 and -0.73 e Å<sup>-3</sup>. CCDC reference: 1474323.

{(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>H(BH<sub>2</sub>NMe<sub>3</sub>)} (**16**): To an *in situ* generated 1:1 mixture of {(Me<sub>3</sub>Si)<sub>2</sub>N}Ge{B(NDippCH)<sub>2</sub>} (**8**) and Li{N(SiMe<sub>3</sub>)<sub>2</sub>(thf)<sub>2</sub>} (0.086 mmol of each) in benzene-d<sub>6</sub> (0.5 mL) was added Me<sub>3</sub>NBH<sub>3</sub> (0.007 g, 0.089 mmol) and the NMR tube shaken for 10 min until the original purple coloration disappeared. Analysis of the boryl ligand backbone CH signals in the <sup>1</sup>H NMR spectrum at this point showed that one main product was formed in more than 70% yield. Volatiles were then removed *in vacuo*, the residue dissolved in hexane (1 mL) and the resulting solution transferred into a two-section crystallisation tube before being degassed and the tube sealed. Most of the solvent was evaporated into the second section of the tube leaving large colourless block-like crystals, which were washed with a small amount of cold hexane and dried. The <sup>1</sup>H NMR spectrum of this material showed that it retained some lithium amide, and it was therefore recrystallised from hexane again producing X-ray quality crystals of **16**. Yield: 0.020 g, 32%. Elemental microanalysis: calc. for C<sub>35</sub>H<sub>66</sub>B<sub>2</sub>GeN<sub>4</sub>Si<sub>2</sub> (**16**): C 60.52, H 9.72, N 7.96%; meas. C 60.63, H 9.60, N 8.08%. <sup>1</sup>H{<sup>11</sup>B} NMR (400 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>H</sub> 0.09 (9H, s, SiMe<sub>3</sub>), 0.39 (9H, s, SiMe<sub>3</sub>), 1.22 (12H, two overlapping d, CHMe<sub>2</sub>), 1.52 (12H, two overlapping d, CHMe<sub>2</sub>), 1.73 (9H, s, NMe<sub>3</sub>), 1.98 (1H, br d, <sup>2</sup>J<sub>HH</sub> = 8.0 Hz, BH<sub>2</sub>H<sub>β</sub>), 2.32 (1H, br d, <sup>2</sup>J<sub>HH</sub> = 8.0 Hz, BH<sub>2</sub>H<sub>β</sub>), 3.39 (2H, sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, CHMe<sub>2</sub>), 3.53 (2H, sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, CHMe<sub>2</sub>), 4.53 (1H, br d, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz, GeH), 6.29 (2H, s, NCH), 7.19 (6H, m, CH of NDipp + C<sub>6</sub>D<sub>5</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR

(100 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>C</sub> 4.9 (SiMe<sub>3</sub>), 5.9 (SiMe<sub>3</sub>), 23.2 (CHMe<sub>2</sub>), 23.6 (CHMe<sub>2</sub>), 26.6 (CHMe<sub>2</sub>), 26.9 (CHMe<sub>2</sub>), 28.5 (CHMe<sub>2</sub>), 28.9 (CHMe<sub>2</sub>), 53.4 (NMe<sub>3</sub>), 122.1 (NCH), 123.5 (*m*-CH of NDipp), 123.7 (*m*-CH of NDipp), 127.4 (*p*-CH of NDipp), 141.3 (*i*-C of NDipp), 146.7 (*o*-C of NDipp), 146.9 (*o*-C of NDipp). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, benzene-d<sub>6</sub>, 298 K): δ<sub>B</sub> 29.8 (3-coordinate boryl), -5.1 (BH<sub>2</sub>NMe<sub>3</sub>). Crystallographic data: C<sub>35</sub>H<sub>66</sub>B<sub>2</sub>GeN<sub>4</sub>Si<sub>2</sub>, *M<sub>r</sub>* = 693.32, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 14.0071(1), *b* = 17.8164(2), *c* = 16.3798(1) Å, β = 97.979(1)°, *V* = 4048.1(1) Å<sup>3</sup>, *Z* = 4, ρ<sub>c</sub> = 1.138 g cm<sup>-3</sup>, *T* = 150 K, λ = 0.71073 Å. 79616 reflections collected, 9170 independent [*R*(int) = 0.028], which were used in all calculations. *R*<sub>1</sub> = 0.0374, *wR*<sub>2</sub> = 0.0913 for observed unique reflections [*I* > 2σ(*I*)] and *R*<sub>1</sub> = 0.0485, *wR*<sub>2</sub> = 0.1053 for all unique reflections. Max. and min. residual electron densities 0.62 and -0.84 e Å<sup>-3</sup>. CCDC reference: 1474324.

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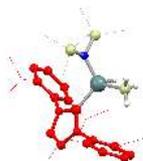
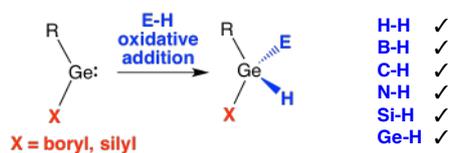
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## Entry for the Table of Contents

### FULL PAPER



#### E-H bond activation by Main Group compounds

*Matthew Usher, Andrey V. Protchenko, Arnab Rit, Jesús Campos, Eugene L. Kolychev, Rémi Tirfoin, and Simon Aldridge*

■■ - ■■

**A systematic study of structure and E-H bond activation chemistry by sterically encumbered germylene complexes**

A systematic study of the effects of the  $\alpha$ -substituents on the geometric/electronic structure and reactivity of acyclic germylene complexes reveals that wide R(X)Ge: angles, narrow HOMO-LUMO gaps and high reactivity towards E-H activation are associated with systems bearing boryl or silyl groups at X.