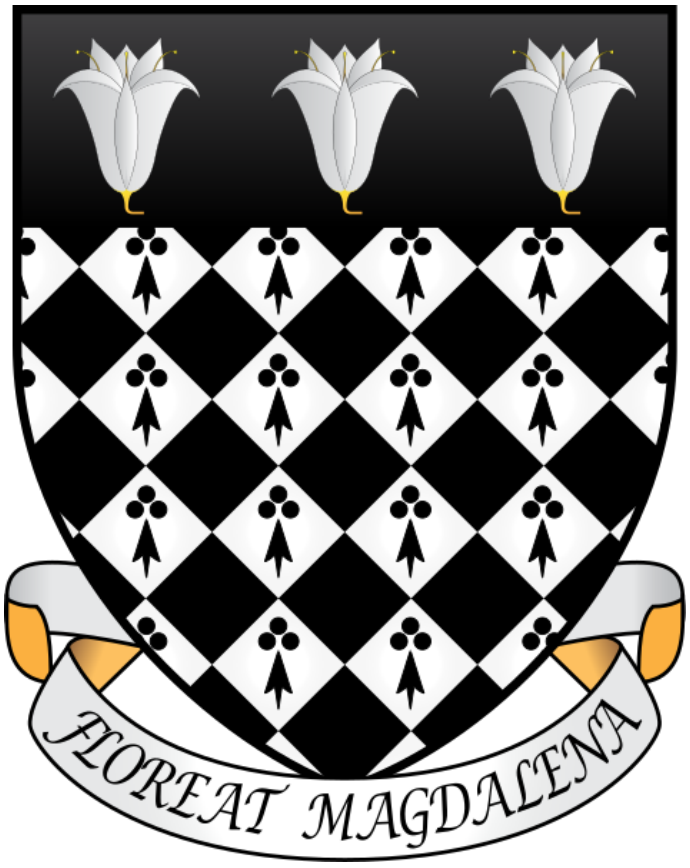
Adventures in Low-Valent Germanium Chemistry



Firstly, eternal thanks to Simon Aldridge for giving me the opportunity to pursue an interesting project, and for the continual provision of advice, patience, and wide-ranging sporting opinions throughout its completion. Main group chemistry is lucky to have you.

Huge thanks is due to the crystallographers whose painstaking efforts enabled the characterisation of the compounds in this thesis. Dr. Christian “El Cid” Sindlinger and Dr. Jamie “James” Hicks, I can only apologise for the number of protonated carbene structures I excitedly forced you to run. Thanks also to the rising star of the crystallography scene, Caitilín “Caitlin” McManus, whose seminal contributions to the field in the collection of the genre-defining compound 7 will surely live long in the annals of chemistry.

Thanks also for the advice and friendship from various other members of the Aldridge group over the years, as well as many other miscellaneous CRL gremlins. Particular thanks go to former Fuzzy Ducks’ player of the week and best Part II 16-17 Alex “Davies” Davies, whose efforts in cracking open the terphenyl project were greatly appreciated. For their scientific advice or lab companionship or even both, I’d also like to thank: Andrey “Wizard” Protchenko, Arnab “the Professor” Rit, Tom “I’m done” Hood, AK“GK”VK, Molly “PT” Kemp, Christian “OUFC ultra” Friedmann, Lewis “5 across” Wales, Steven “MNR” Lau, Kedar “decidedly non-trivial” Abhyankar, Anna “^{18}F Queen” Booth, Lorenzo “the Italian Stallion” Piola and Haoyu “drunktank” Niu.

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Thanks also to the many others who provided welcome distraction when it was often direly needed. Thanks to the many pals I made through dancing, in the OUDC Beginners team, Rock N Roll team, and Flight Club. Thanks to the machinists (Baz, LH, GC, AF and various other minor characters) for a silly year and excellent friendship besides. Thanks to Andrew and related pals for the musical vibes, and many in the math/post rock scene for four ridiculous ArcTanGents and many more good times. Thanks to the many undergrads it was a privilege to get to teach through various means, for the provision of much needed lighthearted youthful banter.

Miscellaneously, thanks to (Sir) Ben Stokes for his last minute inspiration, and to Damian Painton for making me realise chemistry is actually quite interesting, way back when.

Finally, thanks to my parents for their support throughout my education, and to my brother for getting a PhD before me and so meaning I had to finish out of sibling rivalry if nothing else.

This thesis explores the use of boryl, terphenyl and amido ligands in a variety of interesting areas of low-valent germanium chemistry.

In Chapter 1, a general introduction to the state of the art in this field is provided. The ligands that have proven pivotal in recent decades in germanium chemistry are introduced, and the developments that they have facilitated are then described. Finally, the field of germanium cations is introduced.

In Chapter 2, the general methods deployed in this thesis' work are described; modified literature procedures for the syntheses of a variety of starting materials that were used in this work are also detailed.

In Chapter 3, the synthesis of novel germylium-ylidenes is examined, utilising a strategy of chloride abstraction from chlorogermylenes substituted by a combination of N-heterocyclic carbene and anionic ligand. The structural characterisation of the first isolable germylium-ylidenes featuring boryl, terphenyl, primary amido, and borylamido ligands is reported, and the influence of these ligands on the structure of these compounds is discussed in detail. For instance, concerning terphenyl-substituted cations, the effect of subtle variation in ligand steric bulk is explored, in terms of changing the degree of aggregation, and leading to secondary interactions with the ligand peripheries.

In Chapter 4, the reactivity of these germylium-ylidenes is then explored. The first activation of E-H bonds by isolable germylium-ylidenes is reported, as well as novel onward reactivity of some of the products as a result of their charge. For instance, oxidative addition of certain cations with ammonia leads to a subsequent elimination. Attempts towards the synthesis of multiple bonds is described, and the novel compounds this leads to discussed; for instance, reaction of a boryl-substituted cation with trimethylsilylazide leads to the formation of the first germylium azide.

In Chapter 5, the synthesis of compounds featuring boryl-substituted germanium-transition metal bonds is investigated, and the first examples of such compounds for the cases of molybdenum, cobalt and iron are reported.

In Chapter 6, conclusions are drawn from the work of this thesis, and suggestions for future work are made.

Abbreviations

In Chapter II, known compounds synthesised in this work are numbered **2.1**-**2.45**, though may be referred to elsewhere using abbreviated names which are defined in the text. In Chapters I, III, IV and V, further known compounds referred to are either numbered **x.y**, where x refers to the chapter in which they are first mentioned and y is dependent on the order the compounds appear in the chapter, or they are denoted by abbreviated names which are defined in the text. In the case of Chapter VI, this numbering scheme is applied to hypothetical target compounds.

Novel compounds synthesised in the work presented in this thesis are numbered in the order they appear (**1**-**18**) or using labelling derived therefrom.

NHC^{plane}, B^{plane} and Ar^{plane} refer to the least squares planes defined by the central 5/6-membered ring of NHC, boryl and terphenyl ligands, respectively.

Ad = Adamantyl

Ar = Aryl

Ar* = 2,6-$[C(H)Ph_2]_2$-4-MeC_6H_2

Ar** = 2,6-$[C(H)Ph_2]_2$-4-$^{i}PrC_6H_2$

ATR = Attenuated Total Reflectance

ax. = axial

br. = broad

calc. = calculated

COD = 1,5-cyclooctadiene

COSY = homonuclear Correlation Spectroscopy

Cp = Cyclopentadienyl, C_5H_5

Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, C_5Me_5

d = doublet/days

DFT = Density Functional Theory

Dipp = Diisopropylphenyl, 2,6-$^{i}Pr_2C_6H_3$

DMAP = 4-dimethylaminopyridine

DOSY = Diffusion-Ordered Spectroscopy

eq. = equatorial

equiv. = equivalent

ESI = Electrospray Ionisation

Et = Ethyl

Fc = Ferrocenyl, $(C_5H_5)Fe(C_5H_4)$

Fp = $[Cp(CO)_2Fe]^-$

h = hours

HBpin = Pinacolborane, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane

HMBC = Heteronuclear Multiple Bond Correlation

HMDS = Hexamethyldisilazane, $(Me_3Si)_2N$

HOMO = Highest Occupied Molecular Orbital

HSQC = Heteronuclear Single Quantum Coherence/ Correlation

i = ipso

^{i}Pr = isopropyl, $CH(CH_3)_2$

IR = Infrared

J = coupling constant

L = Ligand

LUMO = Lowest Unoccupied Molecular Orbital

m/m = meta/multiplet

Me = Methyl

Mes = Mesityl, 2,4,6-$Me_3C_6H_2$

Mes* = Supermesityl, 2,4,6-$^tBu_3C_6H_2$

min = minutes

mol = moles

MS = Mass Spectrometry

NBO = Natural Bond Orbital

^{n}Bu = normal-butyl, $CH_2CH_2CH_2CH_3$

NHC = N-Heterocyclic Carbene

NHI = N-Heterocyclic Imine

NHO = N-Heterocyclic Olefin

NMR = Nuclear Magnetic Resonance

o = ortho

OTf^- = triflate (trifluoromethanesulphonate, $F_3CSO_3^-$)

p = para

Ph = Phenyl

ppm = parts per million

p-tol = 4-MeC_6H_4

q = quartet

R = general substituent

RT = Room Temperature

s = singlet

sept = septet

t = triplet

Tripp = Triisopropylphenyl, 2,4,6-$^iPr_3C_6H_2$

^{t}Bu = tertiary-butyl, $C(CH_3)_3$

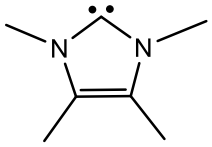
THF = Tetrahydrofuran

UV = Ultraviolet

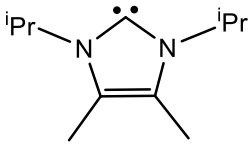
WCA = Weakly Coordinating Anion

δ = NMR chemical shift

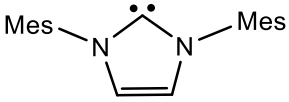
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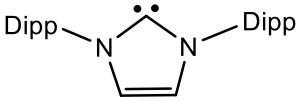
IPrMe:



IMes:

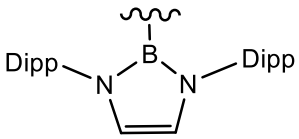


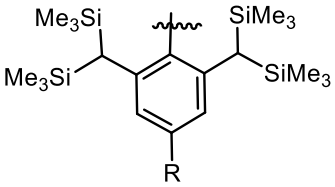
IDipp:



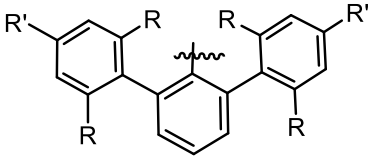
(Note: Saturated carbenes denoted by additional S in front of the name of the unsaturated analogue, e.g. SIDipp)

B^{Dipp}:

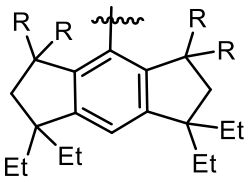




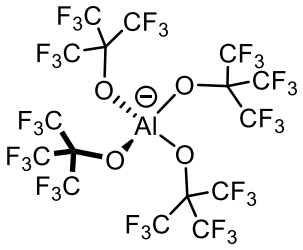
Tbt: R = CH(SiMe$_3$)$_2$
Bbt: R = C(SiMe$_3$)$_3$
Tbb: R = ^{t}Bu



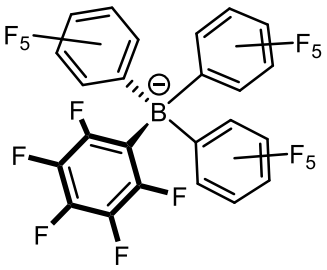
Ar^{Mes}: R = R' = Me
Ar^{Dipp}: R = ^{i}Pr, R' = H
Ar^{Tripp}: R = R' = ^{i}Pr
Ar^{Bu}: R = R' = ^{t}Bu



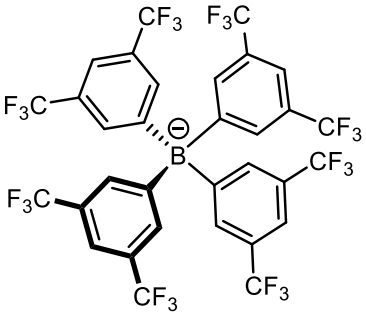
Eind: R = Et
EMind: R = Me



[Al(OR^F)$_4$]$^-$



[BArF$_{20}$]$^-$



[BArF$_{24}$]$^-$

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Chapter I

Introduction

1.1 The chemistry of germanium

Germanium is an element of group 14, occupying an intriguing position as a heavier congener of carbon. Since its discovery in 1886,[1–3] it has found widespread application in solid state chemistry as a semiconductor.[4] For example, germanium was used in the first ever transistor.[5] Its organometallic chemistry had until recently remained relatively understudied and unspectacular. However, in recent decades, the development of new ligands has rapidly expanded the field by enabling the synthesis of a series of landmark germanium compounds. These have provided remarkable insight into the chemistry of the heavier members of the main group, and in particular the comparisons with both their lighter congeners[6] and transition metals.[7] The traditional views of the relationships between these groups of elements have thus been challenged.

Carbon's ability to form multiple bonds with itself and with other lighter main group elements underpins the field of organic chemistry.[8] Furthermore, multiple bonds between carbon and certain transition metals are crucial in the field of olefin metathesis, and have been the subject of two Nobel Prizes.[9,10] However, the heavier main group elements have a decreased desire for maximal bonding (the "inert pair effect"), and when they do so a preference for single bonds over multiple bonds.[11,12] As such, they were once considered incapable of multiple bond formation (the "double bond rule").[13] Hence, examples of such bonds that have been stabilised by novel ligands in recent decades are of considerable interest.[14,15]

In terms of kinetics, transition metal complexes often feature partially filled d-orbitals with energetically accessible occupied and unoccupied frontier orbitals, while thermodynamically the $M^{n+}/M^{(n+2)+}$ oxidation states can often be cycled between with ease. Hence they are capable of processes such as oxidative addition, reductive elimination and migratory insertion, and therefore play central roles in catalysis.[16] However, main group compounds generally lack the open coordination

sites, modest frontier orbital separations and convenient redox states needed for such reactivity.[7,17] There is nevertheless a great incentive to find main group compounds that can act as "transition metal-like" catalysts, given that they tend to be cheaper, more abundant and less toxic than transition metals, and so the development of ligands to enable this has become a hot topic of research.[7,18,19]

Within this landscape, the field of heavier group 14 cations occupies an intriguing position,[20–22] with examples of landmark reactivity in terms of both multiple bond formation[23] and bond activation[24] being achieved thus far in the case of germanium. However, the application of the ligands that have proven so crucial in the development of other areas of germanium chemistry has largely yet to be achieved in the case of germanium cations, which could have potentially fascinating results.

1.2 Ligands in main group chemistry

The history of germanium compounds is intertwined with that of the ligands that have been used to stabilise them. The first organogermanium (IV) compound, tetraethylgermanium, was synthesised by Winkler in 1887, via the reaction of germanium tetrachloride with diethylzinc.[25] However, it was not until the 1970s that organogermanium (II) compounds were isolated in Lappert's pioneering studies,[26] utilising simple anionic amido[27–31] and alkyl[32–36] ligands. Since then, the development of well-designed ligands has led to increasingly interesting low-valent germanium chemistry, primarily through bulky ligands providing kinetic stabilisation against oligomerisation and other unintended processes. Weird and wonderful compounds previously only observed at low temperature in inert matrices, in the gas phase, in space,[37] or very transiently in solution, can now be stabilised at ambient conditions with the choice of an appropriate ligand.

1.2.1 N-heterocyclic carbenes

Carbenes feature divalent carbon atoms in the +2 oxidation state with 6 valence electrons: the two unshared electrons either occupy a single orbital and possess antiparallel spins (singlet) or occupy two separate orbitals with parallel spins (triplet).[38]

A linear system would feature sp-hybridisation and therefore contain degenerate non-bonding p-orbitals, and so possess a triplet ground state. Any bending at the carbenic centre would remove the

degeneracy and change the hybridisation of the bonding orbitals from sp to more-sp^2 like: one non-bonding p-orbital remains unhybridised (p_π), while the other acquires more s-character (σ). If the energy gap between the σ- and p_π-orbitals is sufficient to outweigh the interelectronic repulsion then a singlet state ($^1A_1$) results. Though H_2C (methylene) is a triplet,[39] there are few substituents able to stabilise triplet ground states, and although they have been kinetically stabilised in solution with bulky groups capable of delocalisation, none have been isolated in the crystalline state.[40] The singlet state, however, can be stabilised by both inductive and mesomeric effects: σ-withdrawing (electronegative) substituents stabilise the non-bonding σ-orbital by increasing the s-character, while not affecting the p_π-orbital, thus increasing the σ-p_π gap; π-donor substituents interact with the p_π-orbital, raising it in energy and so also increasing the σ-p_π gap.[38]

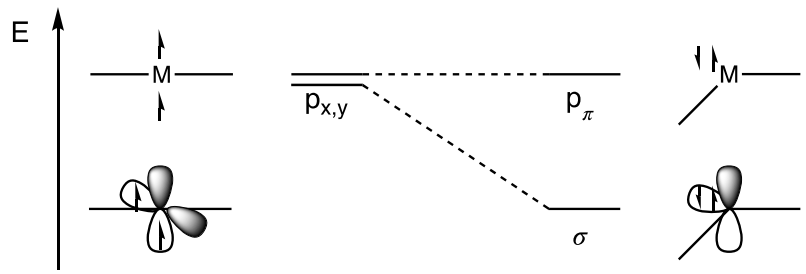


Figure 1.1: Change in σ-p_π gap upon bending

Although Wanzlick and Öfele studied N-heterocyclic carbenes (NHCs) in the 1960s in solution and bound to transition metals,[41–43] the first fully characterised crystalline carbene (**1.1**) was not reported until 1991 by Arduengo, via deprotonation of the corresponding imidazolium salt.[44] The nitrogen atoms provide the required "push-pull" combination of mesomeric donation and inductive withdrawal to moderate both the electrophilic (raise LUMO (p_π) energy) and nucleophilic (lower HOMO (σ) energy) reactivity of the carbene. While bulky N-substituents and an unsaturated backbone were initially thought to be necessary for stabilisation, the syntheses of the stable 1,3,4,5-tetramethylimidazol-2-ylidene (I-Me_4)[45] and first saturated imidazolin-2-ylidene[46] (SIMes) proved otherwise, although calculations have shown that unsaturation does lead to some increased stability due to cyclic electron delocalisation.[47] Alder introduced flexible acyclic diamino carbenes in 1996 (**1.2**),[48] as well as expanded ring 6-membered NHCs (with 7- and even 8-membered ring systems subsequently being synthesised,

1.3).[49–51] Abnormal carbenes (aNHC, also known as mesoionic or remote carbenes)[52–54] featuring only one N-substituent predictably act as stronger donors. These can be combined with normal carbenes in ditopic carbanionic carbenes (**1.4**).[55,56] Cyclic alkyl amino carbenes (CAACs)[57–60] feature a higher energy HOMO and lower energy LUMO compared to traditional NHCs, and are thus both stronger σ-donors and π-acceptors. This ambiphilicity has been accentuated even further with the development of 6-membered[61] and bicyclic[62] analogues. Remarkably, recently a carbene of the form R(H)C (**1.5**) has even been isolated.[63]

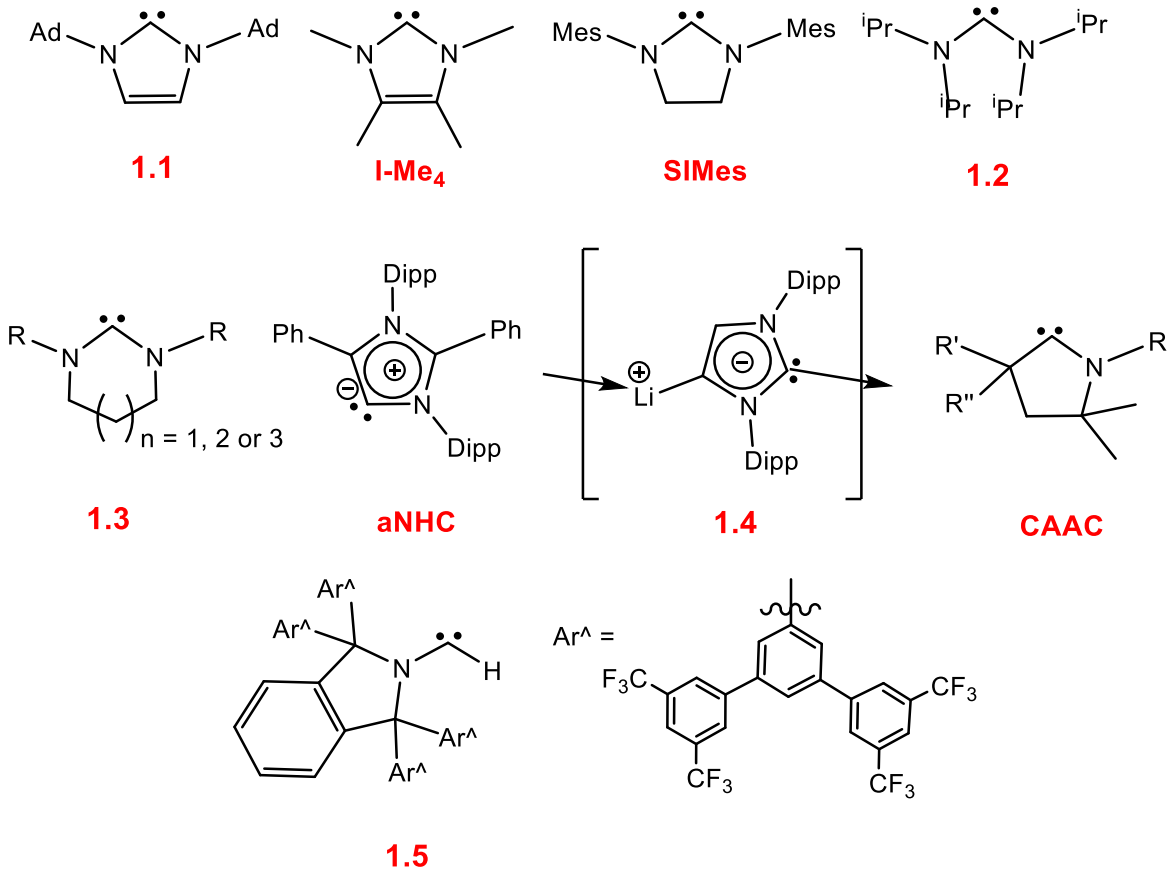


Figure 1.2: Common classes of NHCs and variations therein

NHCs have found three main applications – as organocatalysts in their own right,[64] coordinated to transition metals (and f-block elements),[65] and coordinated to low-valent main group species.[66] NHCs act primarily as neutral strong σ-donors (with a small degree of π-acceptor character for certain NHCs) and in transition metal chemistry have been applied as substitutes for phosphines.[67,68] A wide variety of transition metal catalysts for important processes now incorporate NHCs,[69] for example later generations of the Grubbs' olefin metathesis catalyst.[70]

Various metrics are available to assess the steric[71] and electronic[72–75] profile of different NHCs. Sterically, the %-buried volume (%V_{bur}) measures the steric encumbrance of an NHC in the region around a metal centre,[76] as an analogue to the cone angle widely used for phosphines.[77] Electronically, the carbonyl stretching frequency of a transition metal fragment to which the NHC is bound (originally nickel,[78] more recently rhodium or iridium carbonyls)[79–81] can be measured to calculate the Tolman Electronic Parameter (TEP), with the value correlating inversely with the electron density at the metal centre (and so ligand donor strength).[82] As well as having quite a narrow range (ca. 2030-2070 cm^{-1}) and so not providing much differentiation between NHCs, this parameter only measures the overall donor strength, and thus doesn't deconvolute the σ-donor and π-acceptor effects. The ^{31}P NMR chemical shift of (NHC)PPh adducts[83] and the ^{77}Se shift of (NHC)Se adducts[84,85] have proven useful as a means of independently assessing π-acceptor characteristics.[86]

The first NHC complex of germanium was Arduengo's (IMes)GeI_2 in 1993.[87] Most of the early NHC-stabilised main group species were also simple Lewis base/acid adducts,[88] and many examples of (NHC)$GeCl_2$ species have been synthesised by simple combination of the free NHC and $GeCl_2$·dioxane.[89–91] Independently unstable main group halides, such as $SiCl_2$, have also been trapped by NHC coordination.[92–94] The field has rapidly grown in recent years[66,95–97] and the syntheses of many interesting NHC-stabilised compounds have been achieved. For example, the reduction of NHC adducts of main group halides allows for the stabilisation of homonuclear diatomics in the formal oxidation state (0)[98,99] (including phosphorus,[100] boron,[101] arsenic,[102] silicon,[103] germanium (**1.6**),[90] and tin).[104] As well as the obvious kinetic stabilisation, these compounds have also been calculated to be stabilised by dispersion forces between the bulky NHC substituents.[105] Germylones, that is, single germanium atoms in the zero oxidation state, have also been stabilised by the use of NHCs (**1.7**).[106–109] In addition, Rivard has utilised a donor-acceptor strategy with NHCs as the donor for the stabilisation of simple germanium molecules, e.g. GeH_2 (**1.8**),[110,111] H_2GeGeH_2[112] and H_2SiGeH_2.[113] Abnormal[114] and ditopic carbanionic NHCs[115] have also been recently coordinated to germanium species, while CAACs have been used to stabilise germylones (**1.9**)[116] and the first example of acyclic germanylidene anions.[117]

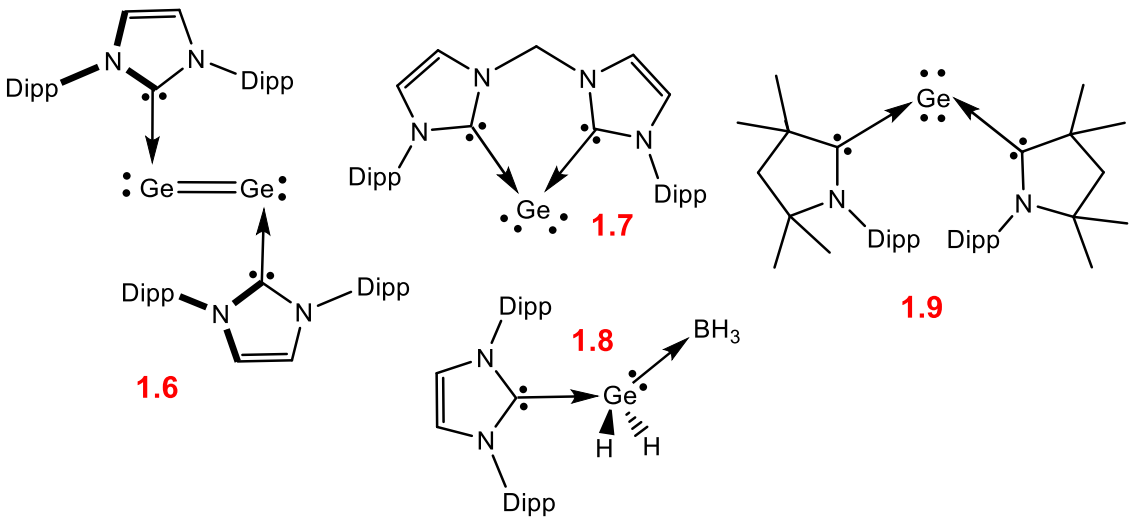
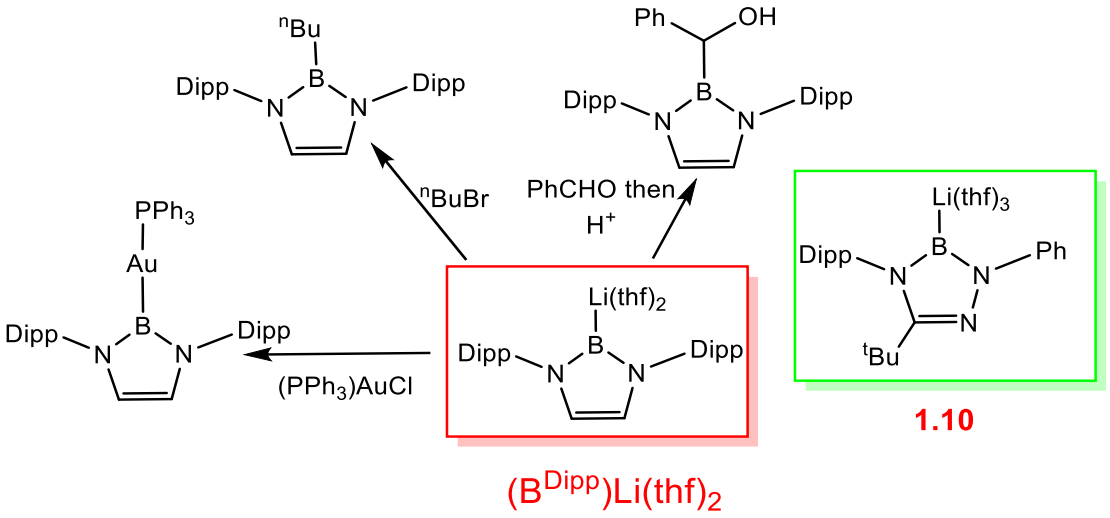


Figure 1.3: Novel germanium species stabilised by carbenes

1.2.2 Boryl ligands

In organic chemistry, the empty p-orbital of boron and its subsequent ability to accept a lone pair of electrons has led to the widespread use of its compounds as classic Lewis acids. Although transition metal boryl complexes have long been known,[118] the element's fundamental electron deficiency, combined with its low electronegativity, precluded the isolation of a nucleophilic boryl anion until 2006, when a boryllithium species ({B^{Dipp}}Li(thf)$_2$) was first isolated by lithium metal reduction of a bromoborane precursor.[119–121] By analogy with NHCs, a nitrogen-containing 5-membered ring structure with bulky flanking aryl groups (to prevent dimerisation of radical reduction intermediates) was deployed for this purpose.



Scheme 1.1: Reactivity of a boryl anion: nucleophilicity and transmetalation

This boryllithium reagent displays reactivity typical of a nucleophile towards organic substrates, and transmetalation enables the synthesis of boryl-substituted transition metal compounds.[122–124] Such transmetalation has also enabled the syntheses of many boryl-substituted main group species that will be discussed in this thesis. Notably, there are also many examples of the boryllithium acting as a reducing agent.[125–127] The boryl ligand is an extremely strong σ-donor:[128,129] this enables the stabilisation of electron-deficient complexes, and, through raising the energy of the HOMO, often renders species highly reactive. Although a variety of other boryllithiums have now been synthesised, for example featuring conjugated or saturated backbones or different aryl substituents,[120] as well as the triaza variant **1.10**,[130] within main group chemistry (B^{Dipp})Li(thf)$_2$ has been almost exclusively applied.[131]

An analogous anionic 5-membered ring system was reported incorporating gallium in 1999[132,133] and its use has been widely explored.[124] Although very different ligand systems were applied, anionic indium[134] and aluminium[135,136] nucleophiles have also recently been synthesised.

1.2.3 Terphenyl and related aryl ligands

Simple aryl substituents (the phenyl group and its alkyl-substituted analogues, Mes, Dipp, Tripp and Mes*) have long been utilised in organometallic chemistry (for example, the ubiquitous Ph_3P, West's first disilene $Mes_2Si{=}SiMes_2$,[137] and the first diphosphene Mes*P=PMes*).[138] Bulkier alternatives have been achieved by replacing methyls with $SiMe_3$ groups, in the form of the Tbb/Tbt/Bbt groups pioneered by Okazaki and Tokitoh.[139–141] Such rigid aryl groups provide inflexible steric shielding of the element centre (often described as "overcrowded"), and have enabled the synthesis of compounds inaccessible with simple aryl groups.[142–145]

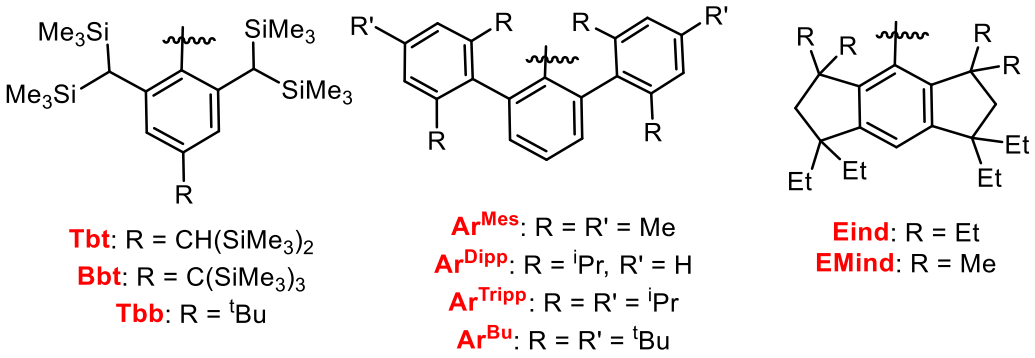


Figure 1.4: Popular aryl ligands in main group chemistry [Note: Ar^{Bu} only recently utilised][146]

Terphenyl ligands feature a central aryl ring with 2,6-disubstituted aryl groups. These aryl groups themselves have 2,6-alkyl substituents, so exhibit hindered rotation about the C^{Ar}-C^{Ar} bonds, and thus are perpendicularly disposed with respect to the central ring. This generates an overall concave steric pocket that surrounds the ligating ipso-carbon and helps protect low-valent element centres.[147] The flexibility of the flanking rings also facilitates the possibility of stabilising flanking aryl interactions with the element centre. As well as their use in transition metal chemistry[148] (for example, stabilising the first example of a quintuple bond between transition metals),[149] terphenyl ligands have (within the Power group especially)[150] been widely exploited for the stabilisation of low-valent main group complexes.[15,145,147]

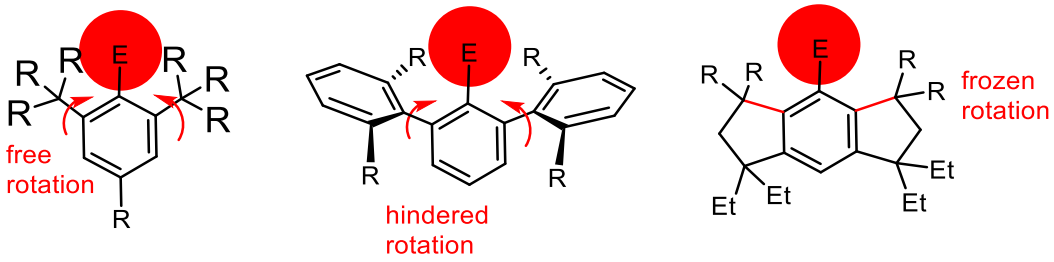


Figure 1.5: Illustration of the steric profile of different aryl ligands

Related substituted aryl ligands offer significant bulk without the associated flexibility of flanking aryl rings. The fused-ring Rind groups have been pioneered by the groups of Matsuo and Tamao, featuring "frozen rotation" that provides rigid steric crowding in the locality of the element centre without interrupting the space available for the element (to quote Matsuo and Tamao, "rind denotes the thick outer skin of some types of fruit for protection of the inside fruity flesh, which is in total agreement

with our research concept").[151,152] These have enabled the stabilisation of many novel main group species – most notably, the first example of a germanone (*vide infra*).[153,154]

1.3 Germylenes

Metallylenes (or tetrylenes) are the heavier analogues of carbenes discussed in **1.2.1**. Upon descending the group from carbon to germanium, the increased size of the orbitals for the heavier elements leads to a significantly reduced pairing energy. Moreover, due to the increasing number of inner nodes of the s- and p-orbitals with increasing principal quantum number, s/p hybridisation becomes less prevalent, and so the σ-p_π gap increases. The combination of these factors leads to increased stability of the singlet state relative to the triplet state – for H_2C the triplet state is the ground state by 9 kcal mol^{-1}, whereas for H_2Ge the singlet is lower in energy by 22 kcal mol^{-1}. Hence, germylenes are always singlets.[39,155]

Germylenes, as with carbenes, were initially considered only as reactive intermediates, generated *in situ* and studied via the use of matrices at low temperatures, in the gas phase,[156–159] or very transiently in solution.[160–165] Simple germylenes (e.g. Me_2Ge) polymerise rapidly in solution at ambient conditions, though can be stabilised with the use of donors (e.g. $GeCl_2$ is unstable but $GeCl_2$·dioxane is a stable and convenient starting material for germanium chemistry).[166,167] However, the use of bulky and electron-donating ligands has nevertheless enabled the isolation of two-coordinate germylenes.[124,145]

Germanium, tin and lead metallylenes stabilised by alkyl[32,33,35,168] (**1.11**, which is dimeric in the solid state,[34,36] *vide infra*) or amido (**1.12**)[28,31] donors were first studied in solution by Lappert in the 1970s. The first crystallographically characterised examples of germylenes stabilised by amido (**1.13**, 1980),[30] phenoxide (**1.14**, 1980),[169] alkyl (**1.15**, 1991)[170] and aryl (**1.16**, 1996)[171] groups eventually followed. Many early germylenes were also synthesised featuring Cp* ligands, such as Cp^*_2Ge[172,173] or Cp*GeX (X = amido, aryl, alkyl etc.).[174,175] In general, the synthesis of stable germylenes is usually accomplished via salt metathesis between the deprotonated ligand and commercially available $GeCl_2$·dioxane, or transamination/ligand exchange with $\{(Me_3Si)_2N\}_2Ge$. Other methods used involve the synthesis of a Ge^{IV} precursor, followed by reduction in the case of halide complexes, or photolysis and loss of e.g. an

alkyne.[145] The synthetic routes to other metallylenes are similar, although the synthesis of silylenes was initially hindered by a lack of Si^{II} precursors. The first silylene was not reported until 1994,[176] and the first acyclic silylene not until 2012 (*vide infra*).[125] More recently, this problem has been overcome through the use of (IDipp)$SiCl_2$, from which metathesis chemistry enables the synthesis of silylenes with liberation of free carbene.[93]

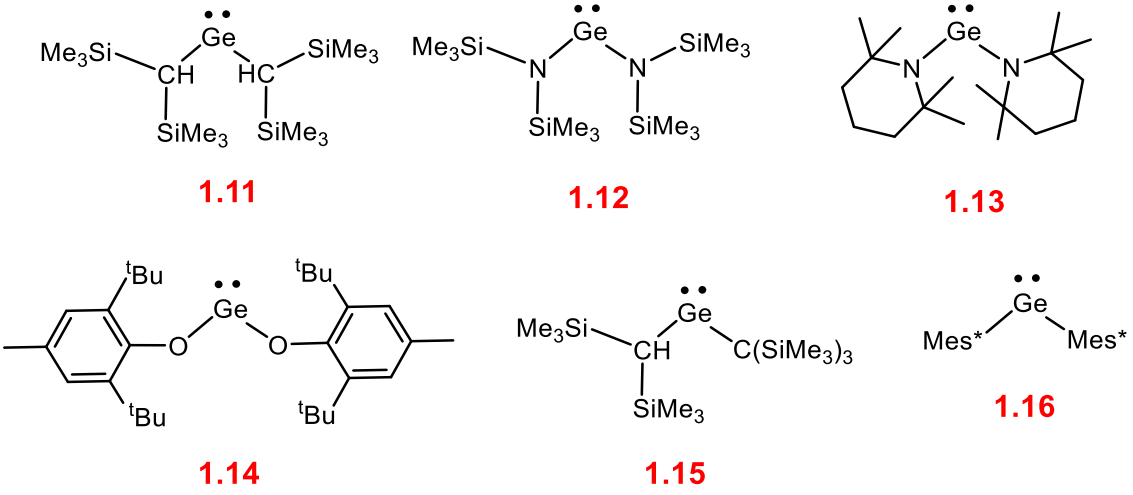


Figure 1.6: Early examples of isolable germylenes

A wide variety of N-heterocyclic germylenes[124,145,177] have also been reported, beginning with Veith's 4-membered ring system in 1982 (**1.17**);[178,179] 5-membered ring saturated (**1.18**),[180,181] unsaturated (**1.19**)[181] and benzannulated systems[182–185] (**1.20**, including ditopic versions with germylenes on either side of the aromatic ring,[186] and bis(germylenes) separated by a linker)[187] have followed, as well as recent examples with modifiable silyl groups on the backbone (**1.21**).[188] 6-membered ring systems with naphthalenediyl backbones (**1.22**)[189] and 7-membered ring systems (**1.23**)[190] have also been synthesised. Interestingly, the 6-membered example **1.24** actually reacts more like the betaine resonance form **1.24-B** (*vide infra*, Scheme 1.14).[191]

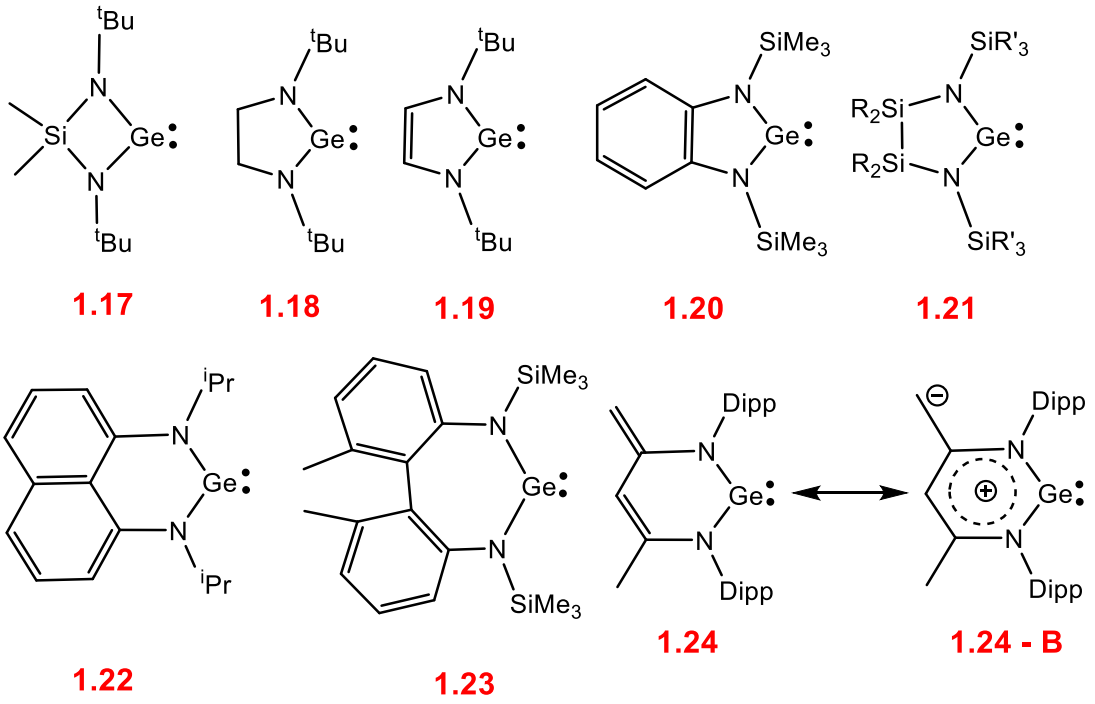


Figure 1.7: N-heterocyclic germylenes

Cyclic chelating monoanionic N-donors provide additional stabilisation due to intramolecular coordination, and the germylene being three-coordinate enables greater flexibility in terms of the additional modifiable exocyclic group (X). They have been deployed in the case of 4-, 5-, and 6-membered rings: amidinate/guanidinate (**1.25/1.26**),[192–197] aminotroponiminate (**1.27**)[198–201] as well as non-annulated versions (**1.28**),[202] and β-diketiminate (**1.29**),[203] respectively. The β-diketiminate (NacNac) system is particularly amenable to derivatisation (see labelling scheme in Figure 1.8),[204] with a wide variety of X substituents achieved at germanium, primarily via salt metathesis from halide derivatives, including X = Cl,[205] F,[206] I,[207] H[208] (which can insert unsaturated molecules such as CO_2 or alkynes into the Ge-H bond),[209,210] OH,[211] Me, ^{n}Bu,[212] O^{t}Bu,[213] OAr,[214] PH_2, $P(SiMe_3)_2$,[215] PPh_2,[213] CCPh,[216] NHAr,[217] $N(SiMe_3)_2$, NMe_2, $NHNH_2$,[218] N_3,[219,220] $OPPh_2$, $OP(O)Ph_2$,[221] PCO,[222] $\{CpFe(CO)_2\}$[223] etc. Y is usually Me or ^{t}Bu, but can be replaced by NMe_2 to give a more electron-rich system.[224] Z is ordinarily H, but can be altered to, for example, an aryl group,[225] while bulk can also be added via backbone annulation.[226,227] R is usually Dipp, but can be modified to, for example, C_6F_5.[228] Dinuclear[191] and trinuclear[229] complexes have also been made. A chlorogermylene example could be reduced to form the first example of a neutral, monomeric germanium (I) radical.[230]

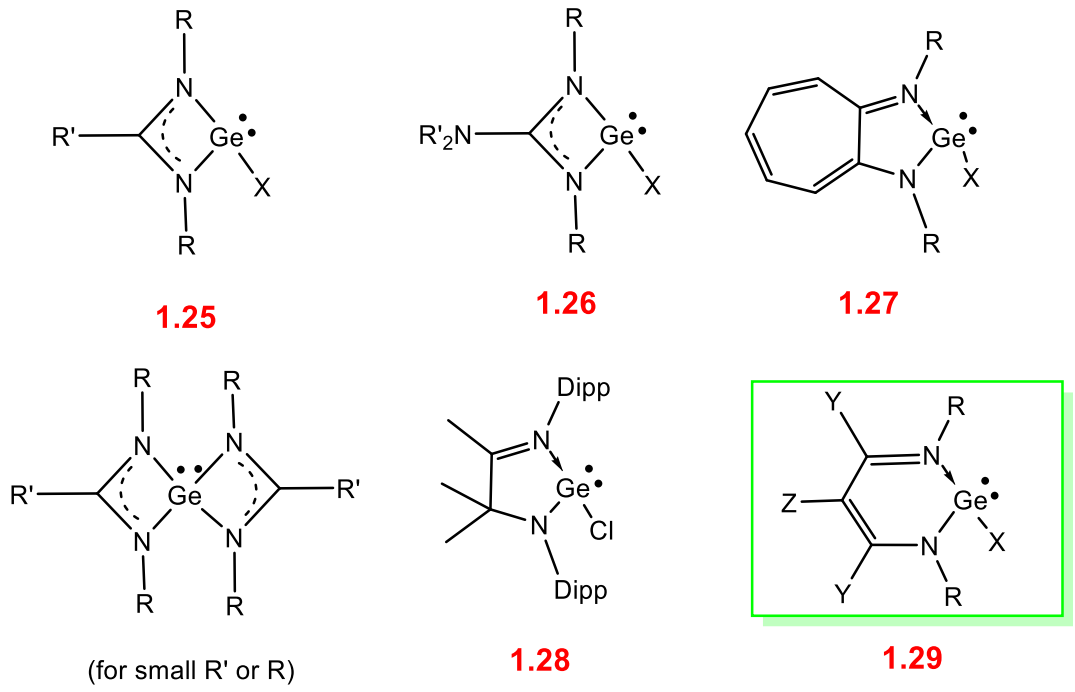


Figure 1.8: Germylenes featuring chelating monoanionic ligands

Analogous to the development of NHCs, cyclic alkyl amino germylenes have also recently been reported.[231,232] Baceiredo and Kato utilised a phosphanylidene phosphorane substituent to generate a reactive N,P-heterocyclic germylene.[233] A variety of interesting acyclic germylenes have been synthesised recently employing amido groups. Thus, for example, bulky amides have been utilised by Jones to synthesise the first examples of two-coordinate amido-stabilised chlorogermylenes,[234,235] as well as the first two-coordinate hydridogermylenes (**1.30**).[236]

As compared to carbenes, the relative lack of a need for π-stabilisation results in a much wider array of non-amido substituents for germylenes. Various additional examples of aryl-substituted germylenes have been synthesised (e.g. (Tbt)(Tripp)Ge).[153,237–239] Homoleptic germylenes have been made substituted by the related classes of N-heterocyclic olefin (NHO, IDippCH),[240] N-heterocyclic imine (NHI, IDippN),[241] and boryloxy ($B^{Dipp}O$) ligands.[242] Chalcogenolate (oxygen-, sulphur- and selenium-substituted terphenyl,[243] or sulphur-substituted alkyl)[244] ligands have also been utilised. Although phosphido-substituted germylenes have been known since 1995,[245,246] the increasing barrier to planarisation at phosphorus means that only recently could Izod deploy bulky substituents and observe π-donation from phosphorus to a germylene (**1.31-P**).[247,248] No π-donation was observed from the corresponding arsenide ligands,[249] with the diarsagermylene (**1.31-As**) instead featuring a flanking aryl

interaction to stabilise the low-valent germanium centre.

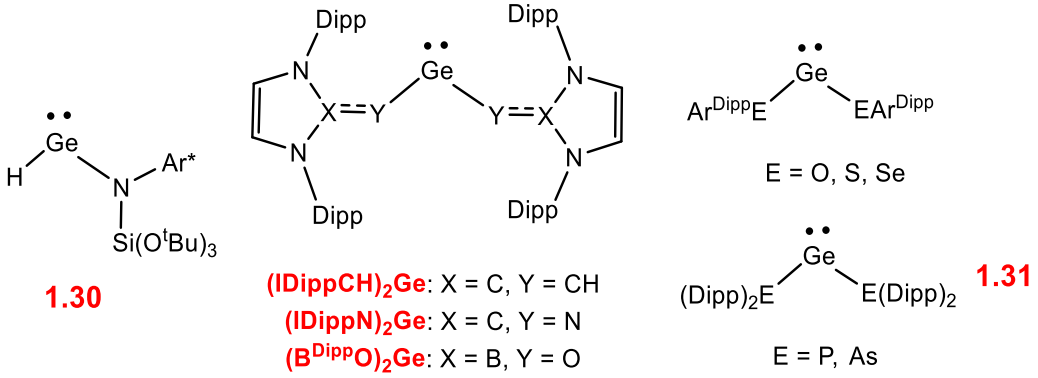


Figure 1.9: Recent examples of acyclic germylenes

The use of boryl and terphenyl ligands has been crucial in the synthesis of novel metallylenes (Figure 1.10). The first two-coordinate acyclic silylenes featured boryl or silyl groups, paired with an amido ligand;[125,250] analogous boryl-/amido-substituted germylenes have also been synthesised.[125,251] Interestingly, bis(boryl) silylenes and germylenes are unknown, as are bis(terphenyl) silylenes. However, bis(terphenyl) germylenes (as well as stannylenes and plumbylenes) are known. $(Ar^{Mes})_2Ge$,[252] $(Ar^{Dipp})_2Ge$,[253] and very recently $(Ar^{Tripp})_2Ge$[254] have all been synthesised (with modified terphenyls with additional substituents on the central ring also being deployed),[255] along with their heavier metallylene analogues.[252–254] Attempts to form a bis(terphenyl) stannylene with the recently synthesised extremely bulky terphenyl Ar^{Bu} failed, suggesting this ligand is excessively sterically encumbering to be used as a substituent for homoleptic metallylenes.[146] The existence of bis(terphenyl) germylenes but not bis(boryl) germylenes despite the more sterically encumbering 6-membered central ring of terphenyl ligands is indicative of the greater donor strength of the boryl ligand, which is too destabilising higher up the group. This is borne out by the calculated singlet-triplet gaps of −0.27 kJ mol^{-1}, 17.9 kJ mol^{-1} and 39.2 kJ mol^{-1} for bis(boryl) silylene, germylene and stannylene, respectively.[125] Consistently, only the bis(boryl) stannylene[125] and plumbylene[256] are isolable species.

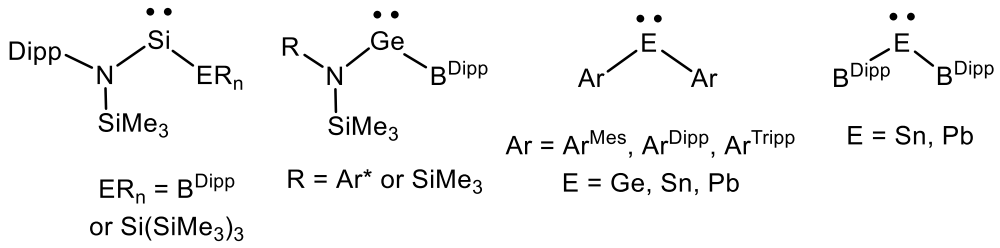


Figure 1.10: Boryl- and terphenyl-substituted germylenes

The accessibility of terphenyl $(ArGeCl)_n$[252,257,258] species permits the formation of heteroleptic terphenyl-substituted germylenes via salt metathesis.[259] Accordingly, following the synthesis by Power of $(Ar^{Mes})Ge(Ge^tBu_3)$,[260] a series of germylenes of the form $(Ar^{Mes/Dipp})Ge(ER_n)$ could be synthesised within the Aldridge group (Figure 1.11). Among these, $(Ar^{Dipp})Ge(B^{Dipp})$ can only be isolated at low temperature, while $(Ar^{Mes})Ge(B^{Dipp})$ undergoes facile intramolecular C-H activation at room temperature, whereas $(Ar^{Mes})Ge(ER_n)$ for various ER_n can be readily synthesised, again illustrating the strong donor capabilities of the boryl group.[251]

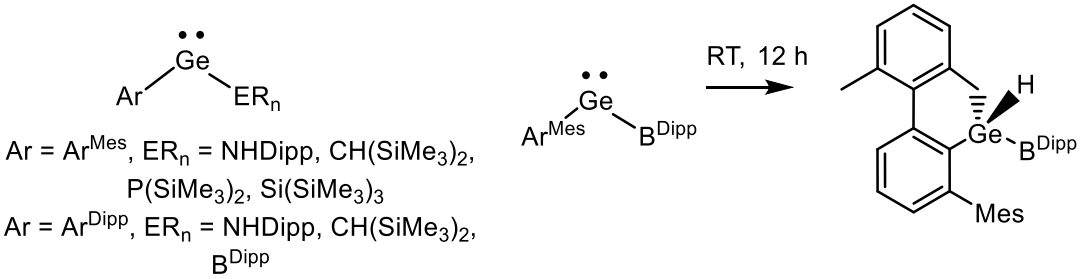


Figure 1.11: Heteroleptic terphenyl-substituted germylenes

Extensive attempts, by Marschner in particular,[261] towards the synthesis of purely silyl-substituted germylenes have mostly been thwarted by the propensity of substituents to migrate towards the germanium centre,[262] though the free germylene can be trapped by coordination of a base.[263–265]

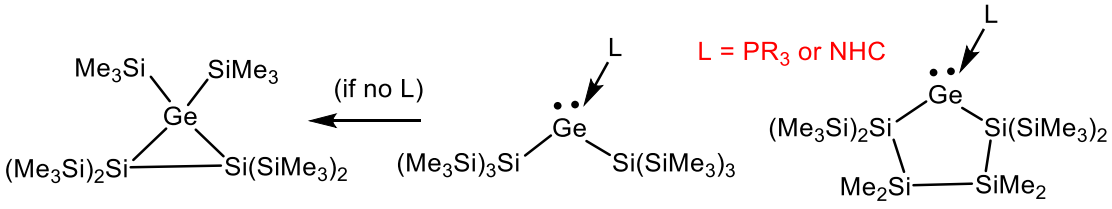


Figure 1.12: Silyl-substituted germylenes

1.4 Multiple bonding in group 14

1.4.1 Homonuclear multiple bonding

Descending group 14, the decreasing tendency for s/p hybridisation (as well as weaker bond strengths) leads to a reduced desire to attain the formal group oxidation state (the "inert pair effect"), while the greater size of the elements leads to an increasing preference for single bonds over multiple bonds (π-bond strengths, C=C = 65 kcal mol^{-1}, Si=Si = 25 kcal mol^{-1}, as compared to bond strengths in H_3C-CH_3 and H_3Si-SiH_3 of 88 kcal mol^{-1} and 74 kcal mol^{-1} respectively).[11,12] Consequently, multiply-bonded heavy group 14 species were for many years thought to be unobtainable (the "double bond rule").[13]

Nevertheless, the first homonuclear multiply-bonded group 14 species were synthesised by Lappert in the 1970s, who used kinetic stabilisation provided by bulky alkyl substituents to prevent oligomerisation in the landmark heavy alkene analogue $\{(Me_3Si)_2HC\}_2Sn{=}Sn\{CH(SiMe_3)_2\}_2$,[32,33] and later corresponding germanium compound, **(1.11)$_2$**.[32,34,36] Both of these systems are monomeric in solution, illustrating the sometimes subtle borderline between germylenes and digermenes. The first example of a heavier main group molecule to retain its homonuclear double bond in solution was West's disilene, $Mes_2Si{=}SiMes_2$, reported in 1981.[137]

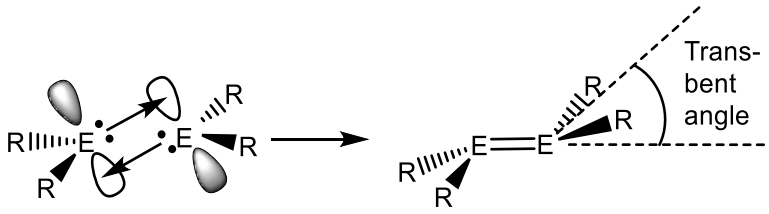


Figure 1.13: Valence bond description of digermenes

Lappert's digermene features a short (2.347(2) Å) Ge=Ge bond and a trans-bent geometry (trans-bent/fold angle = 32°), which is also observed in other digermenes, in contrast to the planar structure of ethene.[34,36] A valence bond explanation for this bending involves the Carter-Goddard-Malrieu-Trinquier (CGMT) model, in which double bond formation is explained using singlet-triplet energy gaps of the constituent metallylenes ($\Delta E_{S\text{-}T}$), on the basis that a classical planar σ+π double bond, requiring the interaction of triplet states, will not be formed when the singlet state is much more stable than the triplet. Hence, if $E_{\sigma+\pi}$ (the sum of σ- and π-bond energies) is greater than $4\Delta E_{S\text{-}T}$ then a planar bond

results; if less, then a trans-bent bond will be formed. If $E_{\sigma+\pi} < 2\Delta E_{S\text{-}T}$ then the fragments will remain as monomers – the "inert pair" is too stabilised to become involved in bonding. Thus, a trans-bent geometry occurs when $\frac{1}{4}E_{\sigma+\pi} < \Delta E_{S\text{-}T} < \frac{1}{2}E_{\sigma+\pi}$. As a consequence, as group 14 is descended, and simultaneously bond strengths decrease and the singlet state becomes more stable, planar geometries are progressively less favoured. The singlet metallylene monomers instead minimise repulsion between their lone pairs by dimerising in a bent fashion, forming polar dative (or "paw-paw") bonds[36,39,266–270] (or remain as metallylene monomers if $\Delta E_{S\text{-}T}$ is sufficiently large, or for steric reasons).

	$\Delta E_{S\text{-}T}$	$\frac{1}{4}E_{\sigma+\pi}$	$\frac{1}{2}E_{\sigma+\pi}$	Expected structure
$H_2C{=}CH_2$	−9	43	86	Planar
$H_2Si{=}SiH_2$	18-21	18-19	35-38	Trans-bent (borderline)
$H_2Ge{=}GeH_2$	22	15-17	30-35	Trans-bent
$H_2Sn{=}SnH_2$	23	15-17	30-35	Trans-bent
$H_2Pb{=}PbH_2$	41	12-15	25-30	Doubly bridged

Table 1.1: Predicted structure of heavier ethene analogues[39] (energies in kcal mol^{-1})

From a molecular orbital viewpoint, one can explain the trans-bending in terms of a 2nd order Jahn-Teller distortion. Bending leads to two opposing effects: a weakening of the σ- and π-bonds, and a stabilising mixing of the π- and σ*-levels (as well as the σ- and π*-orbitals, although these are farther apart in energy so this effect is less significant), which are of the same symmetry (b_u) in the trans-bent C_{2h} point group but not the planar D_{2h} point group. Thus, as group 14 is descended and bonding in general becomes weaker, the bonding and antibonding levels become closer in energy, and the increasing energetic gain of bending is more justified relative to the decreasing loss of bond weakening.[36,271,272] However, it should also be noted that recent theoretical work has suggested that a significant reason for stabilisation of group 14 multiple bonds is actually dispersion forces between the substituents, a contribution which had largely previously been neglected.[273–275]

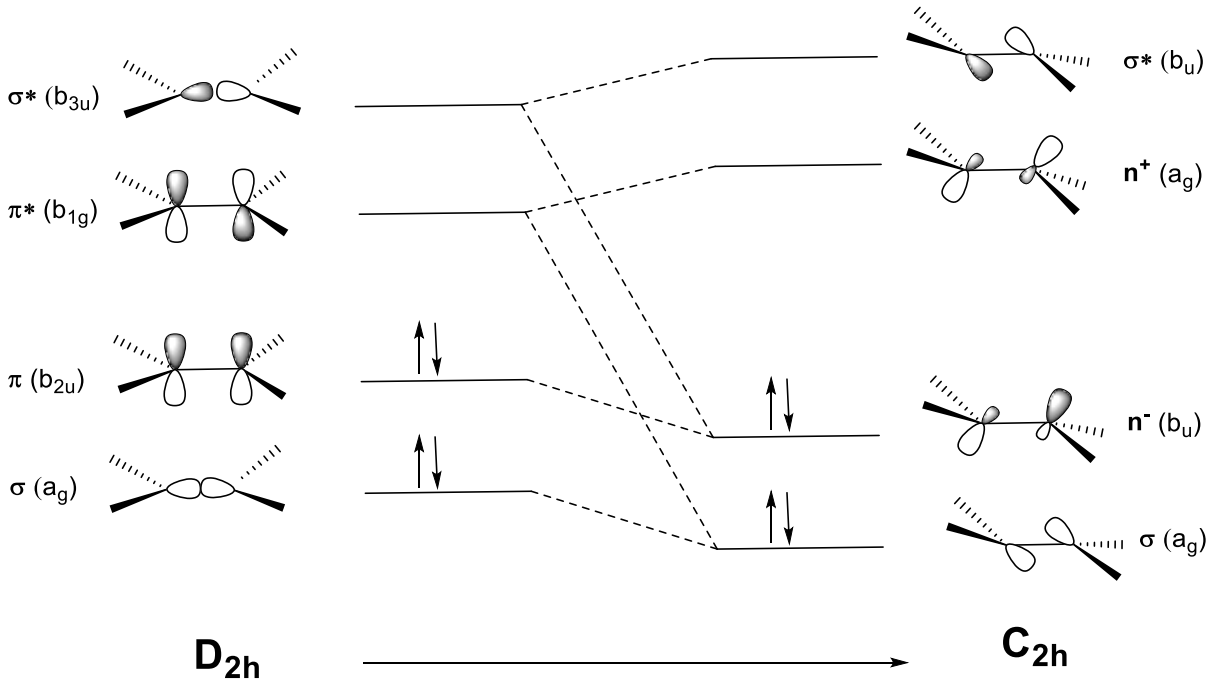


Figure 1.14: Digermene molecular orbital diagrams for planar and trans-bent geometries

Digermenes with a variety of substituents have been synthesised, usually either by photolysis of cyclotrigermanes, reductive coupling of dihalodigermanes, or dimerisation of germylenes.[276,277] Aryl-substituted digermenes of the form $Ar_2Ge=GeAr_2$ with Ar = Mes,[278] 2,6-dimethylphenyl,[279] 2,6-diethylphenyl,[280] Dipp[281] retain their double bonds in solution. However, with bulkier substituents, as in the case of Ar = Tripp[282] or Ar = 2-^{t}Bu-4,5,6-Me_3C_6H,[283] or in the case of crowded hetero-substituted digermenes such as (Tbt)(Mes)Ge=Ge(Mes)(Tbt),[284,285] (Bbt)(Br)Ge=Ge(Br)(Bbt),[286] (Eind)(Br)Ge=Ge(Br)(Eind)[287] and (Tripp)(Fc)Ge=Ge(Fc)(Tripp),[288] equilibria are observed in solution between the digermene and corresponding germylenes, as evidenced by, for example, germylene trapping reactions or UV-Vis spectroscopy. Of course, further increase in the bulk of the aryl ligands results in the formation of germylenes that are monomeric in the solid state (e.g. $(Mes^*)_2Ge$,[171] (Tbt)(Tripp)Ge[237] or $(Ar^{Mes})_2Ge$).[252] Hetero-substituted digermenes almost always exist as the *E* isomer, though judicious variation of substituents by Masamune enabled the crystallographic characterisation of *Z*-(Dipp)(Mes)Ge=Ge(Mes)(Dipp), which in solution was found to undergo *E*-*Z* isomerism.[289] In related work, Weidenbruch found that minor variation of cyclic aminosilyl substituents resulted in the crystallisation of either a germylene or a digermene (of either *E* or *Z* constitution).[290–292]

(Ar^{Mes})GeCl and (Ar^{Dipp})GeCl dimerise in the solid state,[252,258] though the bulkiest case of (Ar^{Tripp})GeCl has been found to crystallise simultaneously as the monomer and dimer.[259] The decreasing propensity for multiple bonding down the group can be illustrated by the fact that these germanium examples dimerise through weak element-element bonds, while their tin analogues do so via chloride bridges. Metathesis reactions with (Ar^{Tripp})GeCl enable the synthesis of digermenes of the form (R)(Ar^{Tripp})Ge=Ge(Ar^{Tripp})(R) for R = Me, Et, Ph,[259] while (Ar^{Dipp})GeCl can be used to access alkynyl-substituted digermenes;[293] all of these retain their double bond in solution. Tetrakis(trialkysilyl)digermenes have also been synthesised with a variety of silyl groups.[294,295] These exhibit significantly more planar structures than their aryl-substituted analogues, which can be rationalised on the basis of a small ΔE_{S-T} brought about by the electropositive substituents. In such cases, steric relief is often achieved by twisting about the Ge-Ge bond instead. A comparison of digermenes with disilenes and distannenes reveals the expected trends – greater trans-bending and a greater tendency to dissociate into monomers in solution upon descending the group. Indeed, the distannene ($^tBu_2MeSi)_2Sn=Sn(SiMe^tBu_2)_2$ is quite unique among that class in remaining dimeric in solution and having a relatively planar geometry, as a consequence of the electropositive silyl substituents.[296]

The synthesis of the first heavier alkyne analogue took somewhat longer; this was achieved in 2002, when Power reduced (Ar^{Dipp})GeCl to give the terphenyl-stabilised digermyne (Ar^{Dipp})GeGe(Ar^{Dipp}).[297] Whereas alkynes are linear and possess a triple bond, this compound was found to be trans-bent (Ge-Ge-C_{Ar} angle = 128.67(8)°) and have a bond length more consistent with a double bond (2.2850(4) Å).[298] Further examples of trans-bent digermynes have since been synthesised stabilised by various other ligands, including other substituted terphenyls,[299] Bbt,[300] Tbb,[301] and bulky amido groups. Intriguingly, use of the amido group N($SiMe_3$)(Ar*) results in an extremely long, single Ge-Ge bond (2.7093(7)Å);[302] however, when the steric bulk is increased even further by use of the N(Si^iPr_3)(Ar^{**}) ligand, a multiple bond results (2.3568(3) Å).[303] This counterintuitive result can be explained by planarisation at nitrogen occurring in the former case to enable N-Ge π-bonding; this is then impossible once the bulk of the ligand is increased.

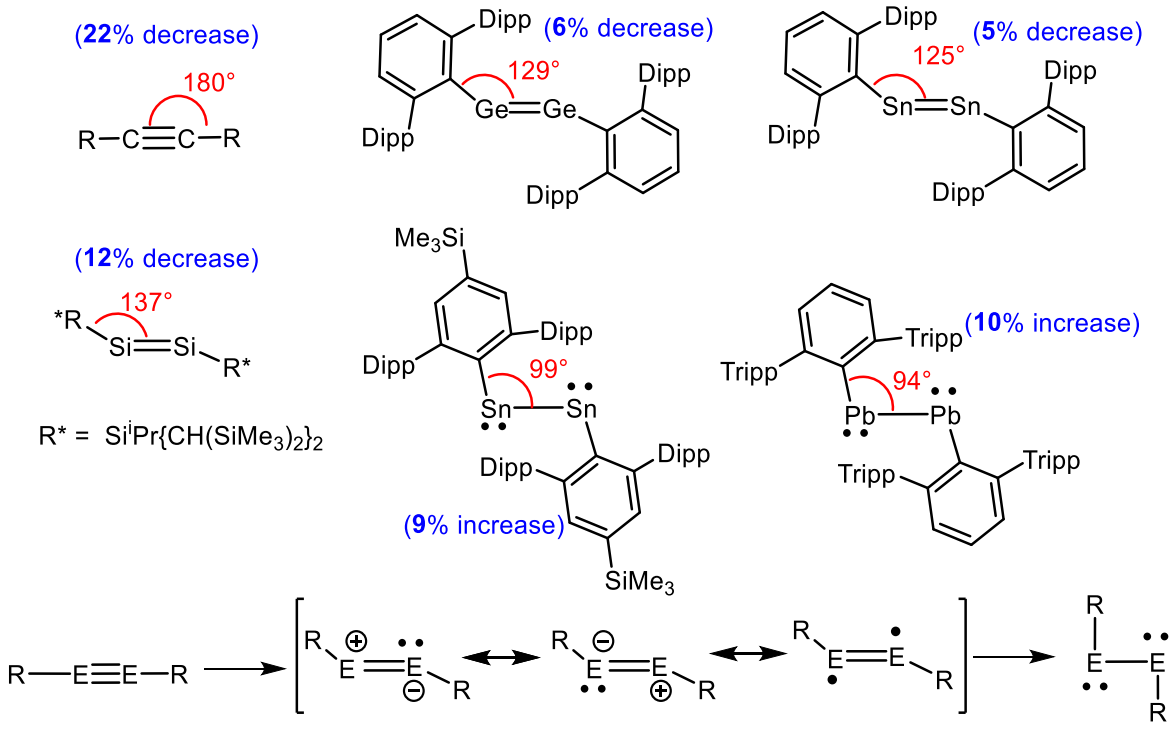


Figure 1.15: Illustration of degree of trans-bending in heavier alkyne analogues (values in blue are the % change of the bond length relative to a single bond for that element)[272,304]

Analogous heavier alkynes have been synthesised in the case of tin, (Ar^{Dipp})SnSn(Ar^{Dipp}),[305] and lead, (Ar^{Tripp})PbPb(Ar^{Tripp}).[306] No terphenyl-substituted disilyne has been achieved, despite favourable computational predictions regarding their stability,[307,308] with C-C insertion products isolated upon attempted reduction of Si^{IV} precursors;[309] however, disilynes have been synthesised substituted by bulky silyl groups,[310] as well as more recently aryl[311] and alkyl[312] groups. The bond order decreases and degree of trans bending increases down the group, with the degree of trans-bending in (Ar^{Tripp})PbPb(Ar^{Tripp}) approaching 90° and the bond length surpassing that of a typical single bond (though this is in part contributed to by relativistic effects). Of note is the fact that for distannynes, minor variation in substituents has been observed to lead to large changes in structure.[299,304,313] This has been rationalised by calculations which indicate that the multiply-bonded and more highly trans-bent singly-bonded forms are extremely close in energy (ca. 5 kcal mol^{-1}),[314–317] and hence that minor crystal packing effects can lead to the adoption of considerably different structures in the solid state (with more uniformly multiply-bonded structures thought to be adopted in solution).

Similar explanations as for alkene analogues can be used to justify the trans-bending. Thus, from a valence bonding perspective, one can consider that a linear geometry requires the interaction of

quartet states of the RE monomers (i.e. all unpaired electrons), and that as the group is descended the energetic gain from a linear geometry is reduced and the relative stability of the doublet state increases, such that $E_{2\pi} < 2\Delta E_{D\text{-}Q}$. Hence a trans-bent bonding mode via the interaction of doublet monomers becomes more favourable.[318–320] The situation in the middle-ground is somewhat contentious (continuing the controversy over alternative bonding descriptions of the "triply-bonded" isoelectronic $Na_2[(Ar^{Tripp})GaGa(Ar^{Tripp})]$ species),[321–324] with the convenient description utilising "paw-paw" bonds and an additional π-bond not correlating with the fully trans-bent σ-bonded form that results upon further bending.[14]

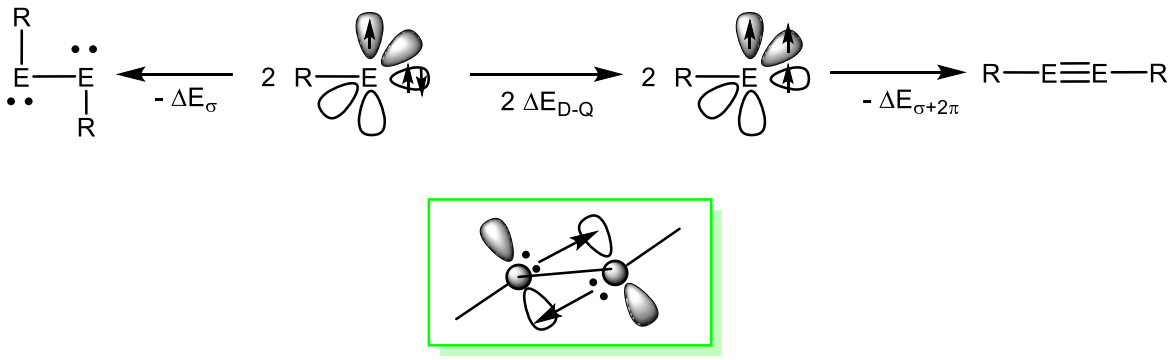


Figure 1.16: Valence bond description of trans-bending

As an alternative rationale, the bending in these systems can also be explained by a 2nd order Jahn-Teller distortion.[272] Bending (from $D_{\infty h}$ to C_{2h}) results in a stabilising mixing of the (in plane) π- and σ*-orbitals (both now of b_u symmetry), which increasingly outweighs the bond weakening down the group. Furthermore, the mixing leads to an accumulation of non-bonded electron density at the tetrel centre, causing further bending due to interelectronic repulsion. For silicon, the HOMO-1 is a slipped π-bond, whereas for germanium this is more accurately described in terms of lone pair character, thereby explaining the reduction in bond order.[325] In the more extreme trans-bent form adopted by diplumbynes and some distannynes, the HOMO and LUMO as shown in Figure 1.17 are inverted, and so a singly-bonded form results. Tin exists at the borderline, hence the wide variation in trans-bending seen for distannynes.[325] It is also important to note that, as with the alkene analogues, the stability of heavier alkynes has also been shown to be influenced by dispersion force effects between the substituents.[326]

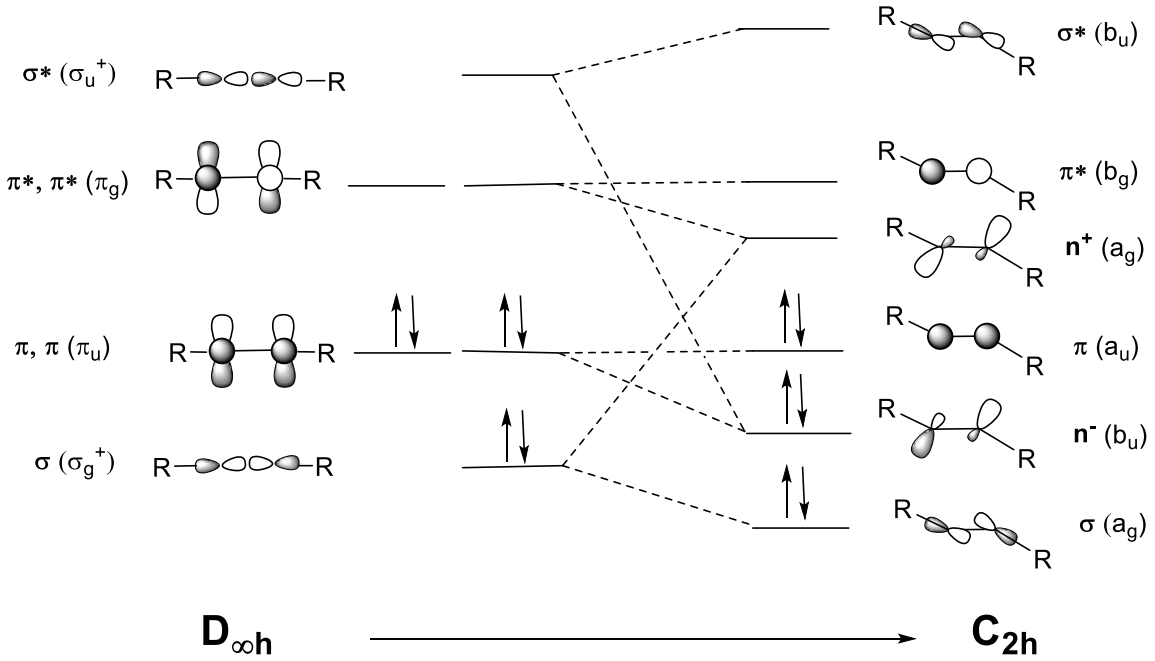


Figure 1.17: Digermyne molecular orbital diagrams for planar and trans-bent geometries

An interesting caveat to these trans-bent structures for REER species comes via the use of boryl groups at germanium, which leads instead to the isolation of a heavier analogue of vinylidene (H_2CC), $(B^{Dipp})_2GeGe$.[327] H_2GeGe is more stable than trans-bent HGeGeH,[318] and that boryl substituents but not terphenyl lead to adoption of this structure can be justified by two factors: firstly, the less sterically imposing nature of the boryl groups, given the 5- rather than 6-membered central ring size and also the longer Ge-B vs. Ge-C bond lengths; secondly, the digermyne to digermavinylidene conversion can be considered as a formal disproportionation of Ge^{I} to Ge^{0} and Ge^{II}, and boryl groups have been shown to lead to such disproportionations due to their ability to stabilise higher oxidation states.[328]

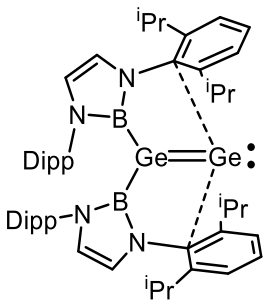


Figure 1.18: A boryl-substituted digermavinylidene

1.4.2 Heteronuclear multiple bonding

In addition to the factors disfavouring the formation of homonuclear multiple bonds, heteronuclear multiple bonds involving germanium often feature large electronegativity differences,[15,329] and the

resulting polarity favours oligomerisation processes and other unintended reactivity. For example, for C=X descending the chalcogens, the (Pauling) electronegativity differences are 0.89, 0.03 and 0 (for O, S and Se, respectively), whereas for Ge=X they are 1.43, 0.57 and 0.54, respectively.[330] Nevertheless, Tokitoh successfully employed a combination of bulky aryl Tbt and Tripp groups to stabilise the first examples of compounds featuring three-coordinate Ge=X bonds (X = S,[331,332] Se,[332,333] Te),[143,334] usually synthesised via a direct reaction of the germylene and elemental chalcogen, or via dechalcogenation of tetrachalcogenagermolanes with PPh_3. However, the analogous germanone (X = O) was found to undergo intramolecular cyclisation with the Tbt ligand, illustrating its higher reactivity (Figure 1.19).[335] As well as other unintended reactivities,[171,336] many attempts towards the synthesis of germanones have also resulted in the formation of dimeric oxo-bridged compounds instead.[285,288,337–353] It was not until 2012 that the first isolable example of a three-coordinate germanone was reported, $(Eind)_2Ge=O$, from the reaction of an Eind-substituted germylene and Me_3NO.[153] Such bonds have also been accessed with less bulky groups, but only through the coordination of further neutral donors (e.g. NHCs) at germanium (**1.32**).[354–356] Related molecules analogous to common organic functional groups have also been synthesised, for example heavier analogues of carboxylic acids.[357]

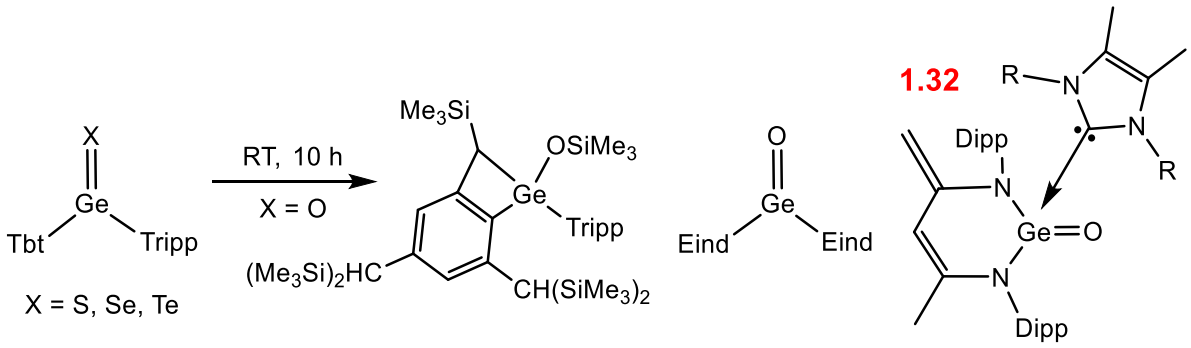
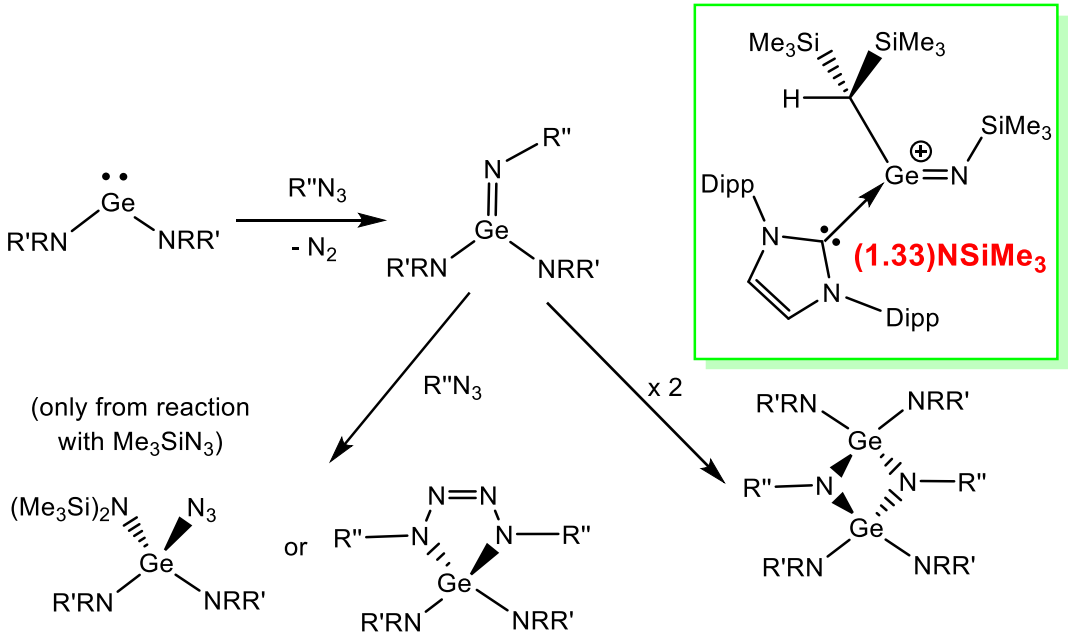


Figure 1.19: Heavier ketone analogues

Isolable Ge=N moieties have been accessed via the reactions of germylenes with azides. Interestingly, the reactions of bis(amido) and related germylenes give a variety of different products depending on the substituents at germanium and nitrogen.[182,233,358–362] The doubly-bonded germa-imine is initially formed, but is generally only isolable when there is a bulky group at nitrogen, otherwise dimerisation or reaction with further azide can occur. In the case of trimethylsilylazide, this can result in the formation of either a tetrazole via [3+2] cycloaddition or an azide/amide via 1,2-addition, with the

latter usually occurring in the case of more polarised bonds.[182,233,360] The formation of two of these different products for the same set of substituents has yet to be observed for germanium, but such isomerism/equilibria has been seen for gallium[363] and tin.[364] Resonance/conjugation effects have also been exploited to stabilise germa-imines featuring less steric bulk at nitrogen,[365–370] as well as the more recent strategy utilised by the Aldridge group of electrostatically disincentivising aggregration using cationic systems (**{1.33}NSiMe$_3$**).[23]



Scheme 1.2: Reactivity of germylenes with azides

Following the synthesis of the first compound featuring a Ge=P bond in the 1980s (**1.34**),[371,372] the use of the dianionic germanium reagent **1.35**[373,374] has enabled the synthesis of an additional example (**1.36-P**),[375] as well as the first example of a compound containing a Ge=As bond (**1.36-As**), reported as recently as 2018.[376] However, analogous compounds featuring antimony and bismuth have thus far eluded isolation. Heteronuclear triple bonds are challenging targets given the availability of only one substituent to stabilise the bond. Thus, for example, attempts by Hinz and Goicoechea to increase the steric bulk of amido ligands to stabilise RGe≡P against dimerisation reached the limit of activation of the ligand periphery by the transient germaphosphyne upon generation.[377]

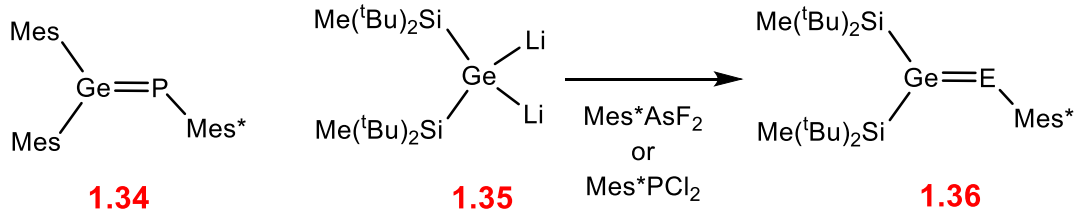


Figure 1.20: Multiple bonds between germanium and the heavier members of group 15

Compounds featuring Ge=C moieties (germenes) have been stabilised by a combination of steric bulk and resonance stabilisation/conjugation (e.g. one of the first examples, **1.37**).[283,378–383] A similar electrostatic strategy as for germa-imines has also been applied within the Aldridge group (**{1.33}CH{SiMe$_3$}**).[23]

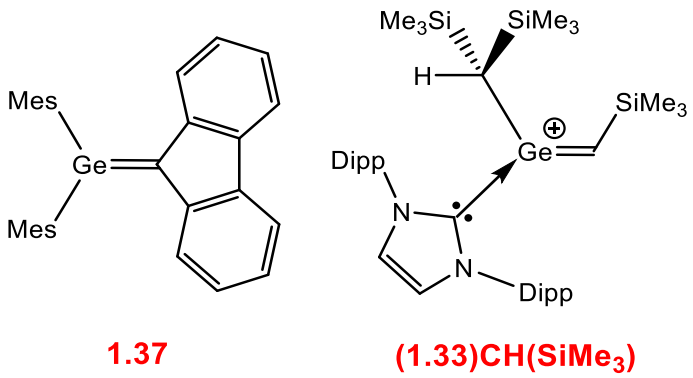
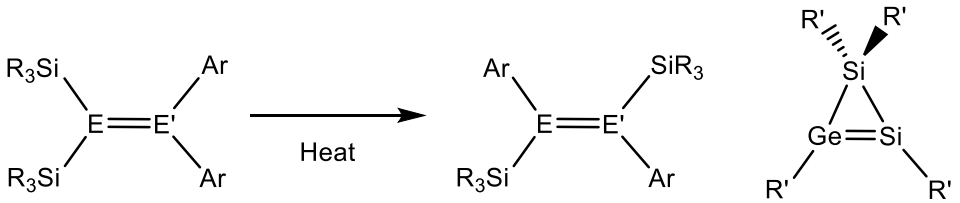


Figure 1.21: Stabilisation strategies for germenes

Initial attempts to synthesise heteronuclear heavy alkene analogues[384] were frustrated by various rearrangements. For example, the germasilene $Mes_2Ge{=}SiMes_2$ rearranges to the silylgermylene $MesGe(SiMes_3)$,[385,386] and the germastannene $Mes_2Ge{=}SnTripp_2$ dissociates to the respective germylene and stannylene and then recombines to give the cyclic germadistannirane.[387] However, the introduction of bulkier groups (e.g. $Tripp_2Ge{=}SnTripp_2$),[388] and especially electropositive silyl groups (e.g. the cyclic disilagermirene **1.38**)[389] stabilises the alkene species, which (if acyclic) display trans-bent geometries as per their homonuclear analogues. Utilising the dianionic germanium reagent **1.35**, acyclic germasilenes[373] and germastannenes[390] have been accessed, while analogous dilithio silicon reagents could be reacted with Mes_2GeCl_2 to form germasilenes of the form $Mes_2Ge{=}Si(SiR_3)_2$.[391,392] These unsymmetrical species can undergo isomerisation on heating to the corresponding symmetrical versions.[390,392] Hetero-vinylidene analogues have been stabilised by NHCs.[393–395] Heteronuclear "heavy allene analogues" have been synthesised, although their (typically) bent structures has led to

considerable debate as to whether they are in fact better described as metallylene-stabilised E(0) adducts.[396–399]



E = Si, E' = Ge, R_3Si = Si^tBu_3, Ar = Mes, 100°C for 24 h
E = Ge, E' = Sn, R_3Si = $SiMe^tBu_2$, Ar = Tripp, 50°C for 40 h

R' = $SiMe^tBu_2$

1.38

Figure 1.22: Heteronuclear heavy alkene analogues

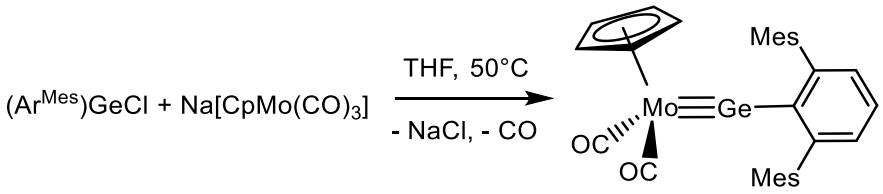
Finally, with regard to group 13, Ge=Ga and Ge=In containing species have been isolated,[400] but those containing Ge=B bonds have only been proposed as reactive intermediates.[401] The range of multiple bonds synthesised for the other heavier members of group 14 is similar,[15,329] with predictably more examples for silicon and less for tin. For example, Brook's silene in 1981 acted as the first landmark in the field of group 14 heteronuclear multiple bonding,[402–404] and examples of (in contrast to germanium) Si=B[405] and Si=Sb moieties[406] have since been isolated. On the other hand, no tin analogue of a ketone has yet been reported.

A variety of reactivities across heteronuclear germanium double bonds have been observed. Common is the addition of polar E-H bonds such as water and alcohols across the multiple bond,[378,381,382] while germenes have been found to undergo cycloaddition reactions with alkynes and carbonyl groups.[407] The replication of the reactivity capable across transition metal-heteroatom multiple bonds[408] with main group systems is a keen topic of interest; for example, Si=N bonds have been recently found to undergo cycloaddition with CO_2.[409,410]

1.4.3 Multiple bonding between germanium and transition metals

Transition metal carbenes ($M=CR_2$) and carbynes ($M\equiv CR$) have been studied since the 1960s,[9] and widely applied in alkene and alkyne metathesis.[10] Hence, there is considerable interest in exploring the chemistry of their heavier analogues, which were unknown until relatively recently.[411,412]

Germyl complexes featuring single bonds between germanium and transition metals have long been known.[413] Doubly-bonded germylene complexes were first reported in 1976,[414] and have been applied in catalysis; they have, however, been less widely utilised in this regard than the more recently accessed silylene complexes.[415–420] Initial examples of such compounds typically consisted of an independently unstable germylene fragment that could only be isolated on coordination to a metal.[421,422] More recently, though, by analogy with the wide variety of NHC-coordinated transition metal complexes, a variety of isolable germylene (primarily N-heterocyclic or amidinato-stabilised)[423] metal complexes have been synthesised and applied in catalysis (for example, an analogue of the Grubbs' catalyst featuring a germylene as an ancillary ligand).[424] Such NHGes feature less N-E π-donation than NHCs, thus enhancing their π-acceptor behaviour with respect to the metal.[425]

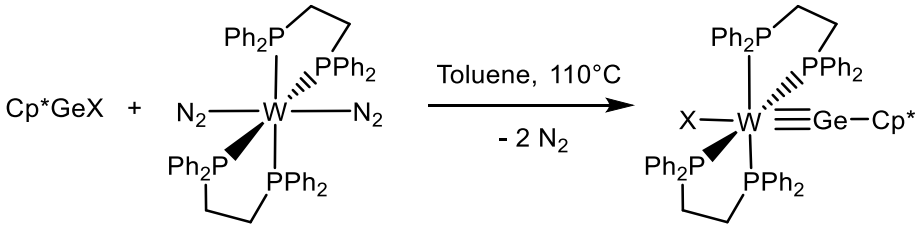


Scheme 1.3: Power's salt metathesis route to the first germylyne

The first germylyne featuring a triple bond between germanium and a transition metal was reported by Power in 1996.[426] A simple salt metathesis strategy was utilised in reacting the terphenyl-substituted chlorogermylene (Ar^{Mes})GeCl with the anionic molybdenum fragment Na[CpMo(CO)$_3$]; accompanying CO elimination directly generated the germylyne (Scheme 1.3). X-ray crystallography revealed a short Mo-Ge bond length of 2.271(1) Å and near-linear coordination at germanium (Mo-Ge-C_{Ar} angle = 172.2(2)°). The same approach was again applied by Power in reacting (Ar^{Tripp})GeCl with Na[CpM(CO)$_3$] (M = Cr, Mo, W).[427] Interestingly, in the case of molybdenum the germylyne was again synthesised directly, whereas for chromium and tungsten the singly-bonded metallo-germylene was first made, which could then be converted to the germylyne through heating or photolysis. Jones applied a similar strategy to synthesise a molybdenum germylyne supported by a bulky amido ligand (via initial metallo-germylene formation).[428] In a related method, a germylenoid, shown to behave as a chlorogermylene in solution, was reacted with Li[CpMo(CO)$_3$] to synthesise a trisyl (C(SiMe$_3$)$_3$) substituted germylyne (**1.39**).[429] As well as group 6, the salt metathesis approach has also been applied

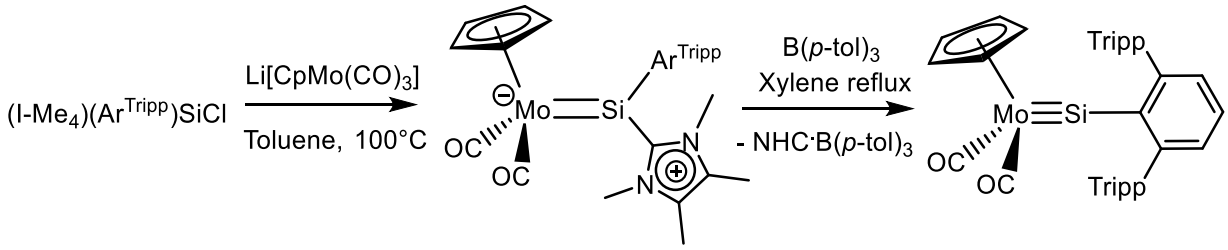
recently to group 5 to synthesise complexes featuring the first bonds between group 14 elements and niobium.[430]

In 2000, Filippou pioneered a new synthetic strategy: the oxidative addition of a chlorogermylene to a transition metal, with loss of labile N_2 ligands, to generate a Cp*-substituted germylyne.[431,432] This method has been subsequently applied with terphenyl substituents,[433] and enabled the formation of the first stannylyne[434] and plumbylyne complexes.[435] The method can also be applied with PMe_3 as the labile ligand,[436] which facilitated the synthesis of a compound containing the first multiple bond between rhenium and a group 14 element.[437]



Scheme 1.4: Filippou's addition-elimination route to germylynes [X = Cl, Br, I]

The use of E^{IV} hydride precursors enables a wider range of group 14 fragments to be coordinated to transition metal centres. This has been employed particularly to synthesise silylenes and silylynes,[438] as for silicon there are fewer available Si^{II} precursors. Concerning germanium, the dehydrogenation of a hydrido(hydro)germylene by either MesNCO[439] or an NHC[440] has been utilised as an alternative route to a trisyl-substituted tungsten germylyne. NHC-stabilised E^{II} precursors have also been deployed. The reaction of (IDipp)$GeCl_2$ with Li[Cp*$W(CO)_3$],[441] followed by photolysis then halide abstraction, enabled the synthesis of the cationic germylyne [Cp*$(CO)_2$W≡Ge(IDipp)][$BArF_{24}$].[442] Furthermore, the reaction of an NHC-coordinated terphenyl chlorosilylene with Li[CpMo$(CO)_3$] generated a terphenyl-substituted zwitterionic silylene, from which the NHC could be abstracted with a strong Lewis acid to generate the first example of a silylyne as recently as 2010.[443]



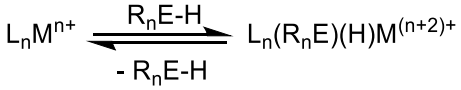
Scheme 1.5: Filippou's synthesis of the first silylyne

Although the majority of germylynes are formally 18 valence electron complexes, a number of these have been oxidised to form 17 valence electron open-shell species.[433] Metal-bound halide ligands have also been abstracted to form cationic complexes, or replaced by a variety of other groups.[444] Thermolysis of germylynes has resulted in the formation of M≡Ge-Ge≡M chains.[445] Metallylynes are electrophilic at the group 14 element and display Fischer-type reactivity. Thus, silylynes have been reacted with a variety of nucleophiles,[446] and shown to undergo cycloaddition with alkynes.[438] Germylynes coordinate NHCs at germanium,[429] and have been shown to add alcohols across the triple bond,[447] as well as react with arylaldehydes[447] and α,β-unsaturated ketones[448] via initial cycloaddition.

Thus, although germylynes have been synthesised featuring a variety of metals, they are still relatively underexplored. Of particular note is the lack of any compounds featuring bonds between heavier group 14 elements and transitions metals substituted by boryl ligands.

1.5 Small molecule activation and catalysis

The involvement of transition metals in processes such as oxidative addition, reductive elimination and metathesis has been established for many years, and has led to widespread application of these metals in catalysis.[16] Although such reactivity involving main group elements is considerably less well-known, huge strides have been made in this field in recent decades.[7,19]



Scheme 1.6: Oxidative addition and reductive elimination at transition metal centres

In situ-generated germylenes and other metallylenes have long been known to be capable of E-H bond activation – for instance, silanes have been employed since the 1960s as "silylene/germylene

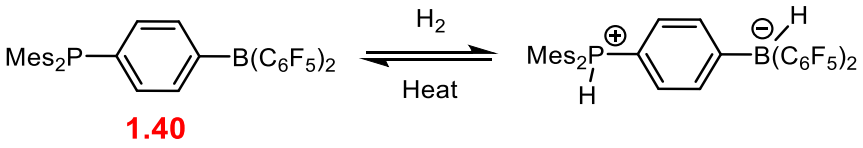
traps".[386,449–454] From the 1980s, Lappert investigated the addition reactions of his stable germylenes towards polar bonds such as organic acids and anhydrides,[455] and alcohols.[456]

A breakthrough came in 2005, when the digermyne (Ar^{Dipp})GeGe(Ar^{Dipp}) was reported by Power as the first isolable main group molecule to activate dihydrogen under ambient conditions, yielding a mixture of the digermene (Ar^{Dipp})HGeGeH(Ar^{Dipp}) (the major product with 1 equivalent of H_2), the digermane (Ar^{Dipp})H_2GeGeH_2(Ar^{Dipp}) and the primary germane $Ar^{Dipp}GeH_3$ (the latter two in a ratio of 85:13 and 65:35 for 2 and 3 equivalents of H_2, respectively).[457] Interestingly, this product ratio starkly differs from that resulting from the analogous chemistry with tin, where the only products obtained are, depending on the steric bulk of the terphenyl ligand, exclusively (Ar^{Dipp})Sn(μ_2-H)$_2$Sn(Ar^{Dipp}) or (3,5-$^{i}Pr_2Ar^{Tripp}$)SnSnH_2(3,5-$^{i}Pr_2Ar^{Tripp}$).[458–460] Remarkably, the activation of dihydrogen by (Ar^{Dipp})SnSn(Ar^{Dipp}) has recently been shown to be reversible.[461]

Other digermynes have also been utilised: both singly-[302] and multiply-bonded[303] digermynes substituted by bulky amido ligands have been reported by Jones to be capable of the activation of a single equivalent of dihydrogen. The boryl-substituted digermavinylidene (B^{Dipp})$_2$GeGe reacts with 2 equivalents of H_2 to give the symmetric 1,2-diboryl-digermane (B^{Dipp})H_2GeGeH_2(B^{Dipp}).[327] A variety of further reactivities have also been shown for digermynes,[325,462,463] including C-H activation,[464–466] C=C insertion,[467] cycloadditions with alkenes, alkynes and related species[301,466,468–472] and reactivity with other unsaturated molecules.[473–475] Notably, terphenyl-substituted distannynes are capable of the reversible binding of ethylene.[476] Interestingly, whereas the bonding models proposed in **1.4.1** would suggest increasing reactivity on descending the group, this is not borne out experimentally, with a greater reactivity observed for digermynes as compared to distannynes. The predominant theory is that the greater singlet diradicaloid character of digermynes leads to their unexpectedly high reactivity.[325]

A further landmark in main group small molecule activation came shortly after in 2006 when Stephan reported the phosphinoborane **1.40** to be capable of the reversible activation of dihydrogen.[477] Such Frustrated Lewis Pairs (FLPs) featuring donor and acceptor orbitals on different atoms have since found

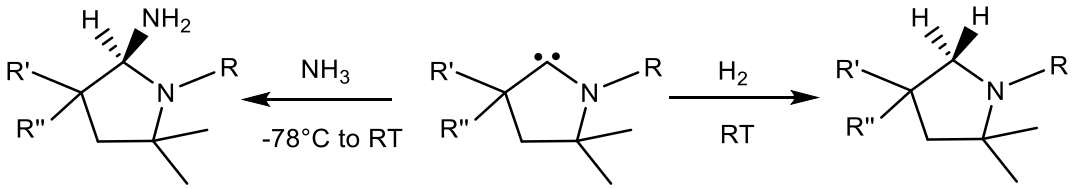
wide-ranging applications in bond activation and catalysis.[478,479]



1.40

Scheme 1.7: Reversible dihydrogen activation by an FLP

In 2007, Bertrand reported the facile splitting of dihydrogen and ammonia utilising both cyclic and acyclic alkyl amino carbenes.[58] The activation of NH_3 is especially interesting, as the first example of ammonia addition by a transition metal was not achieved until 2005,[480] due to the favourability of competing Werner-type adduct formation. A saturated NHC has even been shown to be capable of reversible ammonia activation.[481] CAACs and their analogues have since been found to activate a wide variety of bonds, including Si-H, B-H, C-H and C-F bonds.[59,60,482]



Scheme 1.8: Small molecule activation by CAACs

In the course of the reaction of transition metals with dihydrogen, the primary interaction is between a vacant orbital at the metal and the σ-bonding orbital of the H-H bond. If sufficient accompanying back-donation from a filled d-orbital into the anti-bonding σ*-orbital of the H-H bond occurs, then homolytic bond cleavage results. The MO interactions between heavier alkyne analogues and H_2 are also symmetry allowed:[460] the initial interaction is thought to be a similar synergistic interaction of the H_2 σ-bonding MO with the LUMO of the heavier alkyne, and of the π-bonding HOMO of the heavier alkyne with the σ*-antibonding MO of H_2. In the case of carbenes and metallylenes (EX_2), the situation is again similar, with the donor orbital the E-centred lone pair HOMO, and the acceptor the LUMO, a vacant perpendicular orbital of π-symmetry.[483,484]

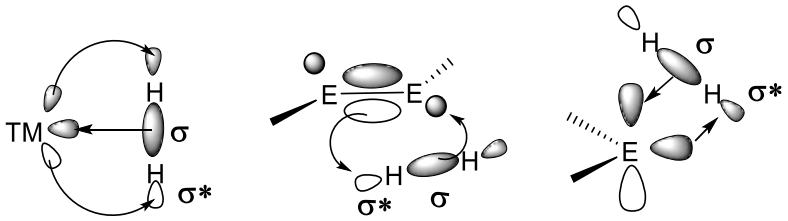


Figure 1.23: Frontier orbital interactions of transition metals, digermynes and metallylenes with dihydrogen

A smaller HOMO-LUMO gap (which correlates with the singlet-triplet gap) thus increases the kinetic accessibility of potential E-H bond activation by metallylenes,[484] so the factors affecting its magnitude have been extensively investigated.[38] The situation is essentially the inverse of the discussion regarding carbene stabilisation in **1.2.1** (and, hence, there are opposing requirements in terms of stabilising metallylenes while also eliciting from them interesting reactivity). So, a wider angle between the X substituents implies greater HOMO p-orbital character, a higher HOMO energy and a smaller HOMO-LUMO gap. This is usually caused by sterically imposing substituents. However, a counterintuitive example was recently presented by Power in which Ar^{Tripp}-supported metallylenes displayed smaller inter-ligand angles than their less sterically encumbered analogues, due to greater (attractive) dispersion forces between ligands with more peripheral alkyl groups.[254]

The inter-ligand angle is also influenced by electronic effects. Electropositive, σ-donating X substituents (e.g. boryl or silyl) lead to a higher contribution of s-orbital character in the bonding of the central element with these ligands (Bent's rule),[485] and hence a higher p-character of the lone pair and a higher HOMO energy. Conversely, electron-withdrawing groups lead to more p-orbital character in bonding to the ligands, and so to higher s-character in the lone pair and a lower HOMO energy.[38,251] The HOMO-LUMO gap can also be tuned via variation of the LUMO energy, with π-donor substituents causing elevation of the LUMO due to greater E-X π* character.[486] Thus, variation of substituent σ- and π-characteristics can be used to control the HOMO-LUMO separation and therefore reactivity. Hence, for example, while alkyl amino carbenes react with H_2 and CO, diamino carbenes (with a lower energy HOMO and higher energy LUMO) do not.[58] More subtle modifications have been employed by Power, who appended various electron-withdrawing or donating groups onto terphenyl ligands, resulting in the expected effects on the orbital energies and inter-ligand angles of the derived germylene

complexes.[255]

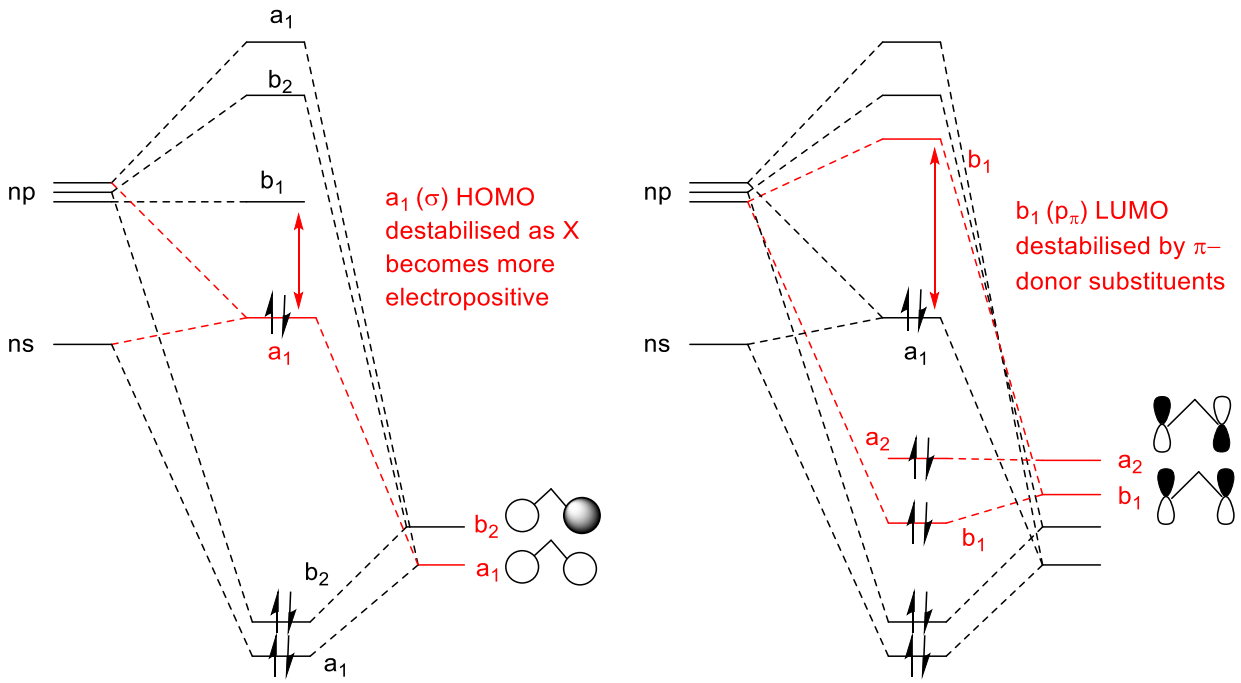
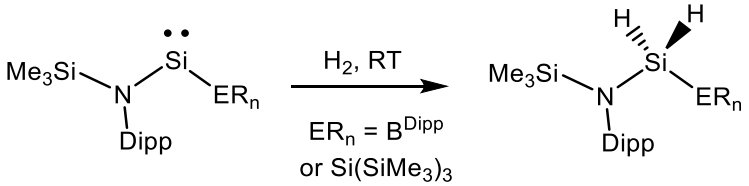


Figure 1.24: Effects on the frontier orbitals of σ-donors (left) and π-donors (right)

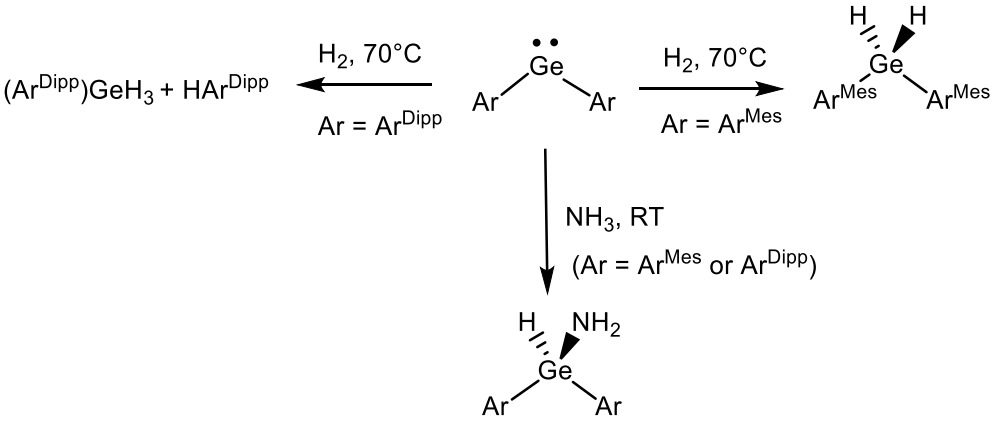
Of course, there are also differences in descending the group that impact on bond activation processes: kinetically, the singlet-triplet/HOMO-LUMO gap increases down the group, disfavouring oxidative addition; thermodynamically, weaker bond strengths and a decreasing propensity for hybridisation result in a more stable +2 oxidation state down the group, disfavouring oxidative addition but favouring reductive elimination if the +4 state can be accessed.[17]

Predictably, boryl, silyl and terphenyl substituents have been prominent in the history of isolable metallylenes capable of bond activation. Acyclic silylenes featuring a single α-boryl or silyl group have narrow HOMO-LUMO gaps and are notably capable of the activation of H_2, as well as undergoing C-H activation of peripheral ligand moieties on heating.[125,250]



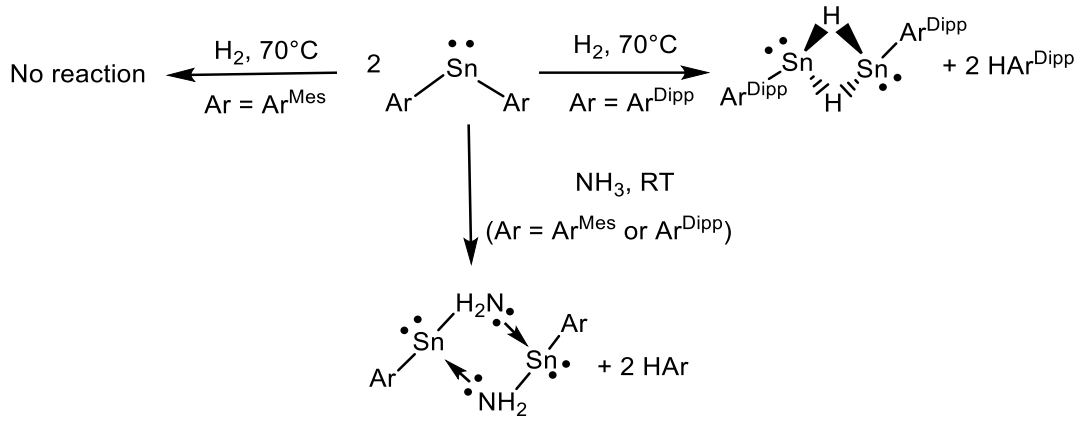
Scheme 1.9: Dihydrogen activation by acyclic silylenes

Bis(terphenyl) germylenes have been found to activate a wide variety of E-H bonds; for example, their reactivity towards dihydrogen and ammonia was reported in 2009 (Scheme 1.10).[487] The contrasting reactivity of $(Ar^{Dipp})_2Ge$ and $(Ar^{Mes})_2Ge$ towards dihydrogen can be explained by the larger steric bulk of Ar^{Dipp} favouring arene elimination, generating $(Ar^{Dipp})GeH$ which is then capable of the addition of further H_2.[487] Computational studies of the mechanism of NH_3 addition indicate that this proceeds via initial coordination, with solvation of the coordinated NH_3 by a further equivalent.



Scheme 1.10: Small molecule activation by bis(terphenyl) germylenes

This reactivity can be contrasted with that of the corresponding stannylenes;[487,488] $(Ar^{Mes})_2Sn$ is unreactive towards dihydrogen, while the reactions of $(Ar^{Dipp})_2Sn$ with H_2 and both stannylenes with NH_3 result in the formation of Sn^{II} products via an arene elimination route (which is concerted, rather than via a Sn^{IV} intermediate).[487,488] These differences have been rationalised in terms of the increased HOMO-LUMO gap down the group (kinetically disfavouring the reaction of $(Ar^{Mes})_2Sn$ and $(Ar^{Dipp})SnH$ with H_2), as well as the greater size and weaker bond strengths associated with tin leading to a thermodynamic bias towards the +2 oxidation state. The smaller inter-ligand angle of $(Ar^{Mes})_2Sn$ results in a larger HOMO-LUMO gap compared to the bulkier ligand case, hence its lack of reactivity.[462]

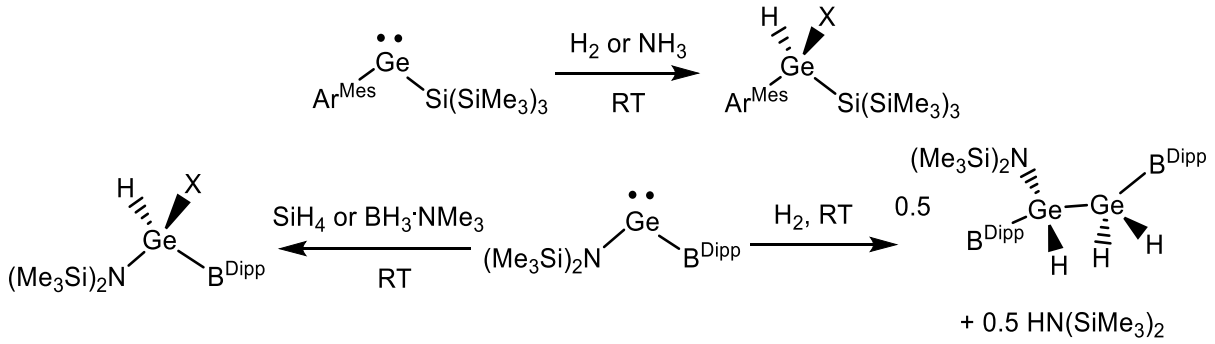


Scheme 1.11: Small molecule activation by bis(terphenyl) stannylenes

Additional examples illustrate further the similarities and differences between the bis(terphenyl) germanium and tin systems. The reaction of $(Ar^{Mes})_2Ge$ with inorganic acids (HCN, HN_3, HBF_4) leads to the E^{IV} products, as does that of $(Ar^{Mes})_2Sn$ with HBF_4;[489] however, with water and methanol, the reactivity is analogous to that with ammonia, with the Ge^{IV} oxidation product, $(Ar^{Mes})_2GeH(OR)$, being obtained - in contrast to the (dimeric) Sn^{II} product $(Ar^{Mes})Sn(\mu_2\text{-}OR)_2Sn(Ar^{Mes})$.[490] Both $(Ar^{Mes})_2Ge$ and $(Ar^{Mes})_2Sn$ also react with PH_3; in contrast to the situation with NH_3, a mixture of the oxidative addition $(Ar^{Mes})_2EH(PH_2)$ and arene elimination products $(Ar^{Mes})E(\mu_2\text{-}PH_2)_2E(Ar^{Mes})$ are observed for both elements (in a 80:20 and 68:32 ratio for germanium and tin, respectively).[491] While $(Ar^{Mes})_2Ge$ inserts irreversibly into the M-C bonds of gallium trialkyls and zinc dialkyls, these reactions are reversible in the case of $(Ar^{Mes})_2Sn$.[492,493] Interestingly, $(Ar^{Mes})_2Ge$ has been shown to reversibly activate P_4,[494] activate hydrazines,[495] and form adducts with isocyanides, which can then undergo C-H activation.[496,497] Very recently, the reversible activation of alkynes[498] and olefins[499] by bis(terphenyl) germylenes has also been demonstrated. However, bis(terphenyl) stannylenes have also been reported to undergo unique reactivity, such as C-H bond metathesis.[500]

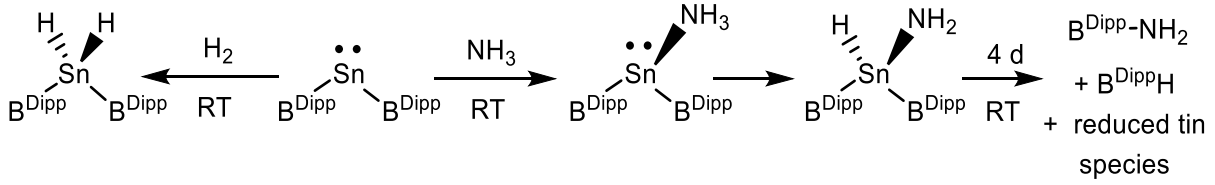
Germylenes of the form $(Ar^{Mes})Ge(ER_n)$, meanwhile, have reactivity strongly influenced by the nature of E.[251] Thus, $(Ar^{Mes})Ge(B^{Dipp})$ features a very small HOMO-LUMO separation of 119 kJ mol^{-1} and undergoes facile intramolecular C-H activation (see Figure 1.11), while the slightly less reactive $(Ar^{Mes})Ge\{Si(SiMe_3)_3\}$ ($\Delta E_{HOMO\text{-}LUMO}$ = 134 kJ mol^{-1}) reacts cleanly under ambient conditions with H_2 and NH_3. Amido-substituted $(Ar^{Mes})Ge(NHDipp)$ ($\Delta E_{HOMO\text{-}LUMO}$ = 275 kJ mol^{-1}), by contrast, is inert to oxidative E-H bond activation. However, the boryl-substituted amidogermylene $(B^{Dipp})Ge\{N(SiMe_3)_2\}$

($\Delta E_{HOMO\text{-}LUMO}$ = 180 kJ mol^{-1}) reacts with boranes, silanes and dihydrogen. The mechanism of dihydrogen activation is postulated to initially be similar to that for $(Ar^{Dipp})_2Ge$, with the starting material then reacting with the proposed $(B^{Dipp})GeH_3$ intermediate to furnish the observed product.[251]



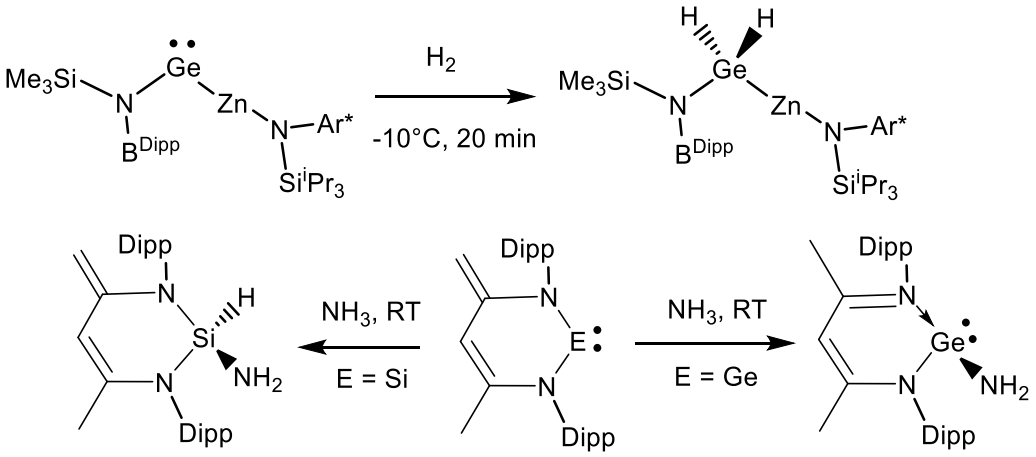
Scheme 1.12: Small molecule activation by heteroleptic terphenyl- or boryl-substituted germylenes

The contrasting reactivity of bis(boryl) and bis(terphenyl) stannylenes is indicative of the greater donor strength of the boryl group. Thus, addition of dihydrogen to $(B^{Dipp})_2Sn$ provided the first example of single-site activation of H_2 at tin to yield a Sn^{IV} dihydride; furthermore, addition of NH_3 results in a Sn^{IV} compound that persists for 4 days, before reductive elimination of an amido-functionalised boryl group. A similar situation is observed for the water activation product, $(B^{Dipp})_2SnH(OH)$, which eliminates to form $B^{Dipp}H$, $B^{Dipp}OH$ and tin metal on heating at elevated temperatures.[486]



Scheme 1.13: Bond activation by a bis(boryl) stannylene

Of course, other ligand systems have been employed to effect bond activation processes by metallylenes (Scheme 1.14). Arguably the most reactive germylene was recently synthesised by Jones, who utilised an extremely electropositive zinc substituent to enable the rapid sub-ambient activation of dihydrogen (within minutes at −10°C).[501] Meanwhile, the differing addition products of ammonia to heterocyclic silylene[502] and germylene[503] systems are indicative of the greater propensity of silicon to adopt the higher oxidation state (though neither of these compounds reacts with dihydrogen).



Scheme 1.14: Bond activation by metallylenes

In addition to those previously discussed, there are only a very limited number of examples of reductive elimination or reversibility that have been observed at group 14 centres. Wesemann among others has illustrated elimination of dihydrogen from Sn^{IV} hydrides (often base-triggered),[504–511] while Power has shown irreversible loss of dihydrogen/arenes from Sn^{IV} hydrides upon extended thermolysis.[146,512,513] Silylenes have been reported by Baceiredo and Kato,[514] and Power,[515] to reversibly bind ethylene. Furthermore, Baceiredo and Kato's phosphine-coordinated amidosilylenes have been observed to reversibly activate silanes and phosphines,[516,517] while NHI/silyl-substituted silylenes have been shown to be concealed via reversible intramolecular C=C bond activation.[518] Notable is the paucity of examples of reversibility for germanium,[18,19,511] other than a recent case utilising a cationic metallo-germylene reported by Tobita (*vide infra*, Scheme 1.19).[24]

These examples of oxidative addition and reductive elimination at main group element centres thus potentially pave the way for redox-based main group catalysis.[18,19] A striking example of this is the observation that the digermyne (Bbt)GeGe(Bbt) was found to act as a catalyst for the regioselective cyclotrimerisation of alkynes, even demonstrating superior selectivity to traditional transition metal catalysts for this reaction.[519] Though there are not many examples of redox-based catalysis, catalysis using germanium compounds that proceeds instead via a constant oxidation state insertion/metathesis pathway is more established.[520–525] A notable case is the use by Jones of bulky amido-stabilised germanium hydrides[526] for the hydroboration of carbonyls[527] and CO_2.[528]

1.6 Group 14 cations

1.6.1 Weakly coordinating anions

In a similar fashion to the advances in ligand design that have enabled the synthesis of novel (predominantly neutral) main group species, the isolation and application of cations previously thought of only as unstable transient intermediates has required the use of increasingly sophisticated anions. Thus any discussion of cations first requires a discussion of the anions that are paired with them.

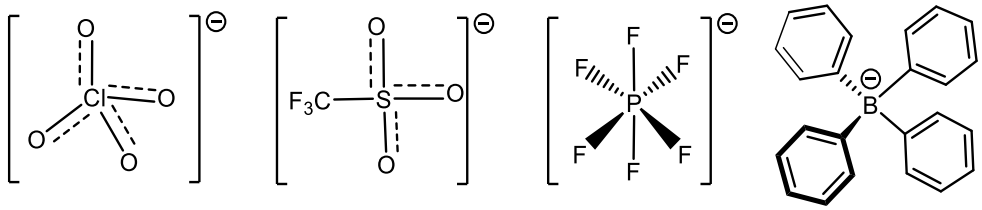


Figure 1.25: Common traditional WCAs: perchlorate, triflate (OTf^-), hexafluorophosphate, tetraphenylborate

Weakly coordinating anions (WCAs) are anions that display minimal interaction with their paired cation.[529] Traditional weakly coordinating anions include perchlorate, triflate, tetrafluoroborate, tetraphenylborate, and hexafluorophosphate (and antimonate). However, in reality these have been found to be reactive or coordinating towards the most reactive low-valent main group cations. Thus, the development of even more weakly coordinating anions has become a topic of keen interest. These tend to be voluminous, and feature a central electropositive atom with bulky peripheral moieties substituted by strongly electronegative atoms, to bury and delocalise the negative charge symmetrically over a large area of non-nucleophilic and chemically robust moieties, thus minimising any potential interaction between the anion and the cation. The large size of WCAs also leads to low lattice enthalpies, increasing their solubility in non-polar media (which are consequently less coordinating to low-valent cations) and reducing their likelihood of displacing loosely-bound Lewis bases. Thus, so-called "pseudo-gas phase" conditions are created.[21,529,530]

Over recent decades, some favoured WCAs have emerged for the stabilisation of main group cations, as detailed in Figure 1.26. In $[B(C_6F_5)_4]^-$ ($[BArF_{20}]^-$) and $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ ($[BArF_{24}]^-$),[531] the use of fluorinated aryl rings delocalises the negative charge, makes the rings electron-poor and unreactive to

electrophiles, and incorporates strong carbon-fluorine bonds that are extremely unlikely to be cleaved. However, there are nevertheless examples of coordination to transition metals by both; for example, $[BArF_{24}]^-$ through the aryl rings[532] and $[BArF_{20}]^-$ through fluorine.[533] In the $[Al(OC(CF_3)_3)_4]^-$ ($[Al(OR^F)_4]^-$) and related anions (often referred to as the "Krossing" anion due to extensive use by Ingo Krossing and his group),[534] the 36 fluorine atoms ensure a low and symmetric distribution of the negative charge on the surface of the anion. Carboranes have been employed widely by Reed,[535] with their halogenated analogues proving less coordinating and more resistant to oxidation (although coordination to low-valent centres via the halogens can still occur).[536,537] There are a variety of ways to generate reactive cations with WCA counteranions from suitable precursors: by halide abstraction by a metal (Li, Na, Ag etc.) salt to form an insoluble salt as the by-product; by hydride abstraction by a trityl ($[Ph_3C]^+$) salt to form a strong covalent bond (the Bartlett-Condon-Schneider reaction); by abstraction of e.g. a methyl group or a hydride by a Lewis acid to create the WCA in the process (e.g. $[MeB(C_6F_5)_3]^-$ or $[HB(C_6F_5)_3]^-$); or by protonation using a WCA-containing super acid (for example, Brookhart's acid, $[H(OEt_2)_2][BArF_{24}]$,[538] $[H(OEt_2)_2][BArF_{20}]$ (Jutzi's acid),[539] $[H(OEt_2)_2][Al(OR^F)_4]$[540] or $H[HCB_{11}Cl_{11}]$[541]).[529,530]

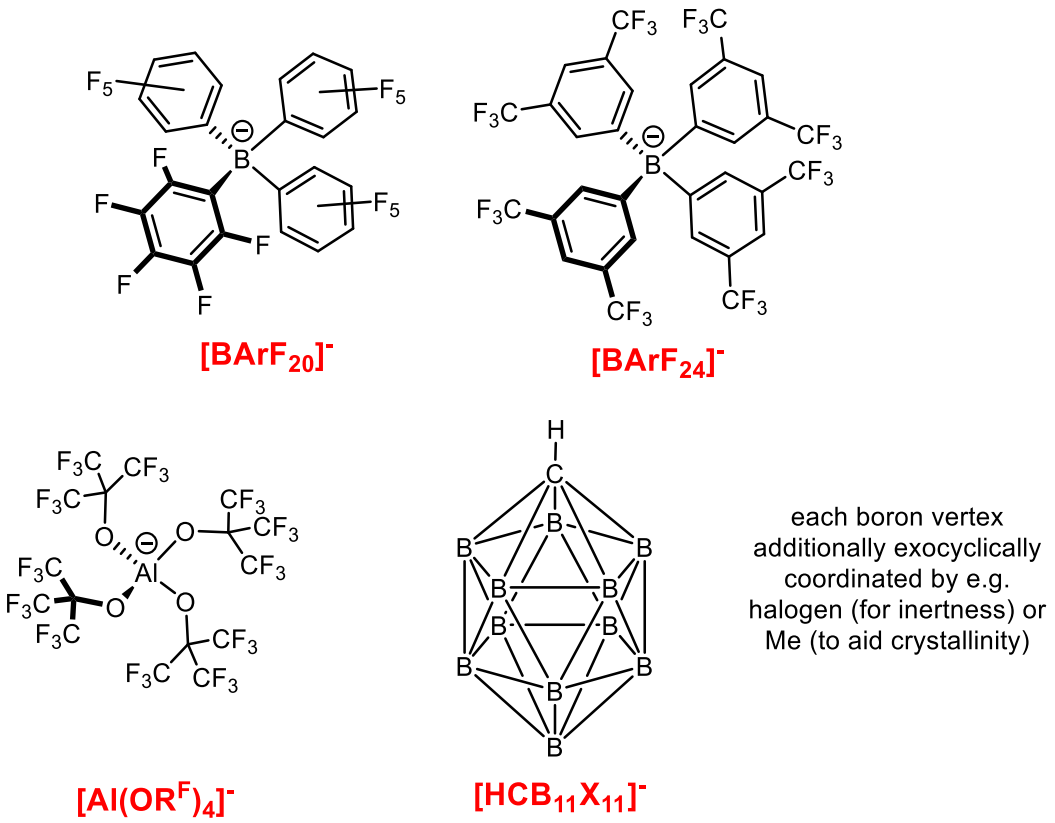


Figure 1.26: Common modern WCAs

1.6.2 Tetrylium cations

Carbocations have long been known both as important intermediates and also as isolated species in organic chemistry, with the trityl cation being first observed over 100 years ago.[542] Tetrylium ions, $[R_3E]^+$, the heavier analogues of carbenium ions ($[R_3C]^+$), are relatively easy to make (and identify by mass spectrometry) in the gas phase for these more electropositive elements. However, the electronegativity difference of C-Si bonds, combined with silicon's greater size and so inability to engage in conjugative or hyper-conjugative effects with aryl or alkyl substituents respectively, leads to a concentration of positive charge at silicon. This results in a high avidity of silylium ions for electron density, while the longer bonds to substituents further invite attack from nucleophiles (they have been described as having a "voracious appetite for nucleophiles").[543] Hence, in the condensed phase, interactions with the solvent, counteranion, and flanking groups of the ligand initially precluded the isolation of three-coordinate cations (the "silylium ion problem"),[544] with considerable debate and misidentification abounding (for instance, the claimed triethylsilylium cation which actually featured coordination from toluene).[536,545] After hints in 1997 from ^{29}Si NMR measurements of the existence of $[Si(Mes)_3][BArF_{20}]$,[546] in 2002 $[Si(Mes)_3][HCB_{11}Me_5Br_6]$ was the first truly three-coordinate silylium cation to be crystallographically characterised.[547] From these initial beginnings as academic curiosities, the pronounced Lewis acidity that so hindered the isolation of silylium cations has led to applications in small molecule activation and catalysis.[548–553]

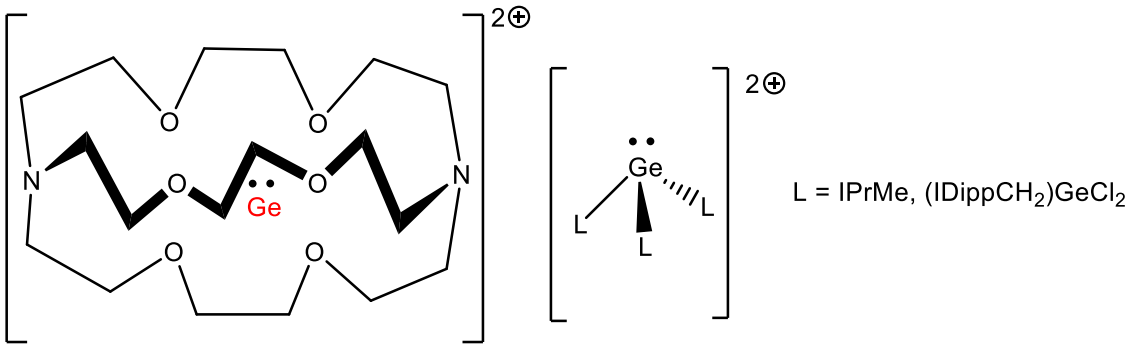
Unfortunately, in contrast to the other members of group 14, for germanium there is no convenient NMR probe of the element centre, preventing confident *in situ* characterisation of proposed species. The spin of germanium's only NMR-active nucleus ^{73}Ge is $\frac{9}{2}$ (as compared to $\frac{1}{2}$ for ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb) and it has a relatively large quadrupolar moment of −19.6 fm^2, while its natural abundance (7.76%) and (especially) its gyromagnetic ratio (−0.9332 x 10^7 rad T^{-1}s^{-1}) are low.[554] Thus definitive identification of a three-coordinate germylium cation could not be achieved[555] until the crystallographic characterisation of $[(^tBu_2MeSi)_3Ge][BArF_{20}]$ in 2003[556] (though a cyclotrigermenium cation, $[(^tBu_3SiGe)_3][BPh_4]$, was reported in 1997,[557] and a cationic cluster in 2002).[558] Aryl-substituted

examples have since followed.[511,559,560] The electrophilicity of germylium cations has been exploited in the case of a corrole-supported example, which was found to activate C-H bonds.[561]

1.6.3 Tetrylium-ylidenes

Group 14 cations in the +2 oxidation state, tetrylium-ylidenes, $[L_nRE]^+$, are intriguing as they combine the nucleophilic nature of metallylenes and the electrophilicity of cations, thus giving rise to Lewis ambiphilicity ideal for potential "transition metal-like" behaviour.[20,22] The plus of a positive charge in (constant oxidation state) main group catalysis has been illustrated by the aforementioned silylium ions,[548,549] and by the fact that a cationic aluminium complex was found to be a superior catalyst to neutral analogues for cyanosilylation of aldehydes.[562] In addition, a few rare but promising examples of catalysis by silylium-ylidenes[563] and germylium-ylidenes have been reported.[523,525] Regarding redox-based reactivity, kinetically, calculations have suggested a cationic charge can reduce the HOMO-LUMO gap at the group 14 centre.[24] Thermodynamically, a cationic system would be expected to have a greater disposition towards reductive elimination and a return to the more electron-rich +2 oxidation state.[511] However, the means used to stabilise tetrylium-ylidenes in the vast majority of cases lead to quenching of their potentially fascinating oxidative reactivity, and hence this possibility has been relatively under-explored, with just a few recent examples of bond activation processes having been reported.[23,24,511,523]

Early strategies to stabilise germylium-ylidenes utilised cyclopentadienyl-type ligands, capable of undergoing a haptotropic shift to mitigate the electron deficiency.[172,564] More recently, dications have been stabilised using a single multidentate ligand such as a cryptand (**1.41**),[565] azamacrocycle,[566] or anionic poly(pyrazolyl)borate,[567] or with multiple NHC (**1.42-NHC**),[89] bipyridine (bipy),[568] isocyanide[569] or small crown ether (12-crown-4)[566,570] ligands. An unusual example reported by Rivard features a dication coordinated by three IDippCH$_2$-ligated GeCl$_2$ moieties (**1.42-IDippCH$_2$**).[571]



1.41 **1.42**

Figure 1.27: Dications stabilised by multiple neutral donors (counteranions: OTf^-, I^- (IPrMe)/ $[GeCl_3]^-$ (IDippCH$_2$))

Monocationic $[L_nGeX]^+$ species (where X = Cl, usually, or less commonly another halide, H or Me) have been synthesised featuring a variety of multidentate neutral donors. For example, the reaction of $GeCl_2$ with the cyclophane $(p\text{-}C_6H_4CH_2CH_2)_3$ and $AlCl_3$ generates a cation stabilised by threefold internal η^6-coordination.[572] Though there are some such examples utilising halide abstraction, as well as salt metathesis, mostly, however, the coordination of the strong donor ligand to $GeCl_2$·dioxane leads to either halide ejection or autoionisation, to produce $[L_nGeCl]^+$ with Cl^- or $[GeCl_3]^-$ as the counteranion, respectively (given the coordinative saturation and consequent lack of empty orbitals, WCAs are not so necessary for such cations). Thus, while addition of 12-crown-4 to $GeCl_2$·dioxane generates a bis(crown ether) dication,[566,570] the use of larger crown ethers (15-crown-5 or 18-crown-6, or sulphur-containing analogues) instead leads to encapsulated $[GeCl]^+$ monocations.[570,573,574] The chloride substituent can subsequently be replaced by triflate, and then water or ammonia to generate coordinated dications.[575]

Tridentate ligands such as bis(imino)pyridines (**1.43**)[576] or triamines[577] have also been used, however more commonly the ligands involved are bidentate. Bidentate N-donors have been deployed in the case of bis(phosphazenyl) ligands,[578] iminopyridines (**1.44**)[579,580] and bipyridine (**1.45**),[577] as well as germanium-coordinated N-heterocyclic imines to generate an unusual germylene-germylium-ylidene (**1.46**).[581] Driess has utilised bis(NHC)[106] (**1.47**, X = Cl or N_3)[582] and bis(N-heterocyclic silylene) ligands;[583,584] the former case provides a rare example of exchange of the X moiety in these compounds (Scheme 1.15). Kinjo's imino-NHC ligands[585,586] combine C- and N-donors in one ligand (**1.48**). An intriguing recent example of a chlorogermylium-ylidene features both C,C- and N,N-coordinated Ge-Cl

moieties, with NMR and DFT evidence suggesting **1.49** is the predominant resonance structure.[587] Very recently, bifunctional PNNP[588] and NNNN[580] frameworks have been applied for the simultaneous coordination of two chlorogermylium-ylidene units.

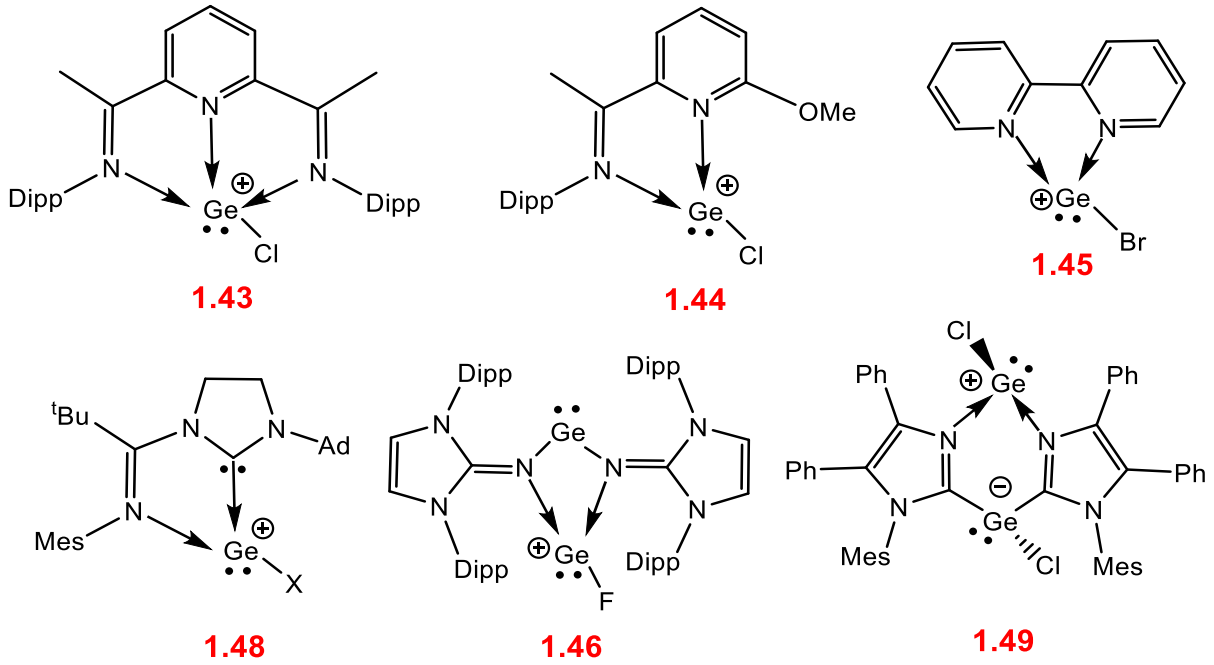
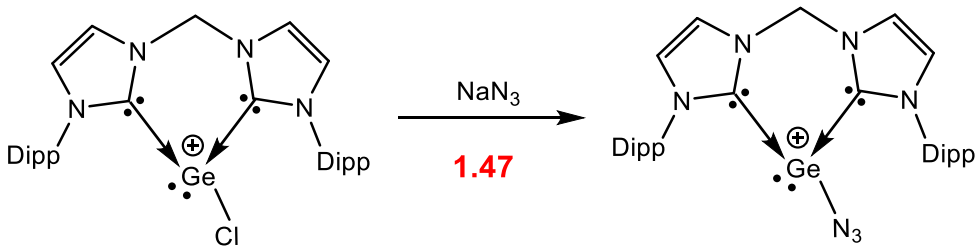


Figure 1.28: $[GeX]^+$ cations stabilised by multidentate neutral donors (counteranions: (top row) $[GeCl_3]^-$, $[GeCl_3]^-$, $[GeBr_3]^-$, (bottom row) $[GeCl_3]^-$ (X = Cl) or OTf^- (X = Me), $[BF_4]^-$, N/A)



Scheme 1.15: Bis(NHC) coordinated germylium-ylidenes (counteranions: Cl^- or $[BPh_4]^-$, N_3^- or $[BPh_4]^-$)

An anionic borate linker between the components of a bidentate ligand enables zwitterionic cations to be synthesised, and this has been done in the case of bis(NHC)[589]and bis(phosphine) ligands, **1.50** (accessed via salt metathesis).[590] These bis(NHC) borate ligands of Driess have enabled the synthesis of the first germylium-ylidene hydride (**1.51**),[589] hydride abstraction from which leads to formation of a dication additionally coordinated by a further equivalent of germylium-ylidene hydride.[589] Using a similar ligand, a phosphaketenyl germylium-ylidene was synthesised (**1.52**); photolysis of this species leads to a rare $[L_2Ge\text{-}GeL_2]^{2+}$ dication, as well as a germylium-ylidene-substituted diphosphene.[591] Interestingly, in toluene as opposed to THF, potassium salts of such ligands have been shown to

rearrange to a C,N-donor isomer, which has also been used to stabilise zwitterionic $[GeCl]^+$ and $[GeH]^+$ moieties (**1.53**).[592] Goicoechea provided an intriguing related example in this category, of an amido-substituted germylium-ylidene, coordinated by two ditopic carbanionic carbenes and thus forming an anionic complex overall (**1.54**).[115]

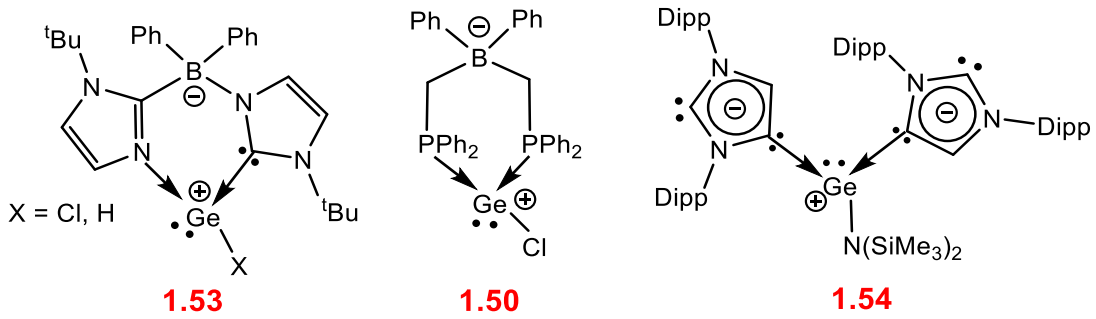
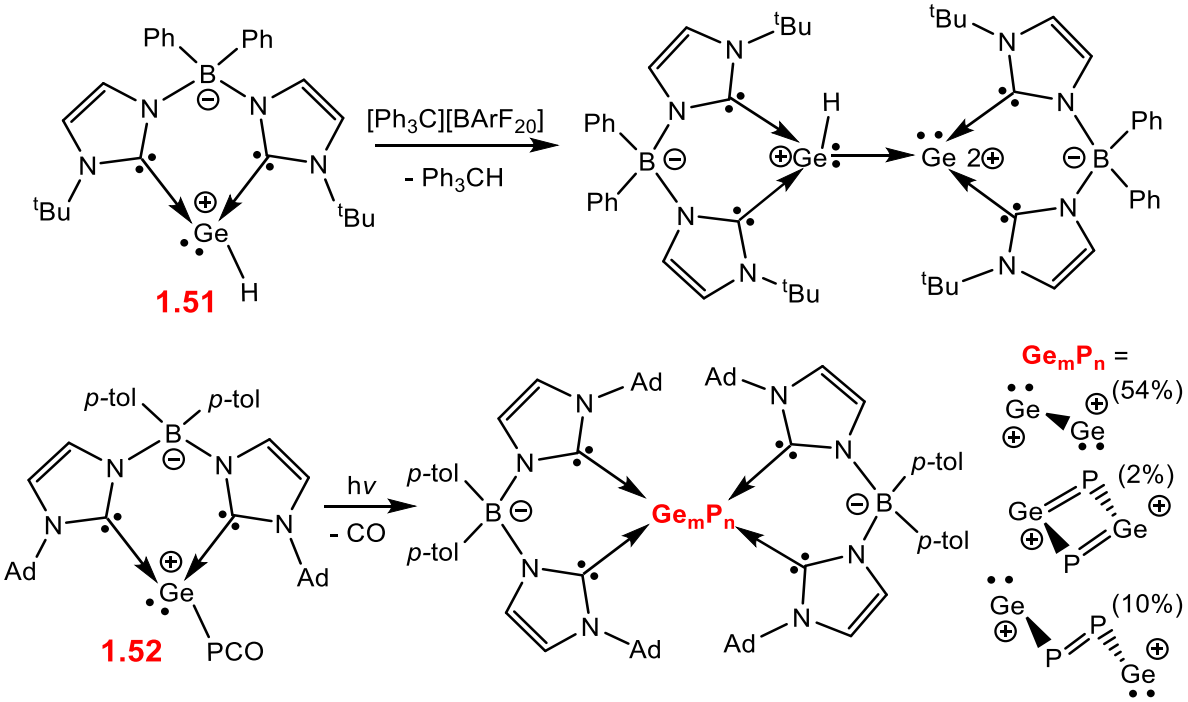


Figure 1.29: $[GeX]^+$ cations stabilised by anionic neutral donors (counteranion: K^+ (1.54))



Scheme 1.16: Reactions of zwitterionic germylium-ylidenes (counteranion: $[BArF_{20}]^-$ for top right)

In the limit of a very strongly donating, bulky ligand, then a two-coordinate $[LGeX]^+$ cation can be achieved. This is the case with the simultaneous σ- and π-donor carbodiphosphorane (**1.55**).[593] Interestingly, Baines reported the formation of $[(IPrMe)_2GeCl]^+$,[565] suggesting the IPrMe carbene is insufficiently bulky to stabilise a two-coordinate cation; IDipp has also been reported to fail for this purpose.[593] Rivard's trityl-substituted NHC ITr is the bulkiest NHC reported to date and possesses an extreme donor strength: its $\%V_{bur}$ and TEP values are 57.3% and 2034 cm^{-1}, respectively, as compared

to 45.4% and 2051.5 cm^{-1} for IDipp.[594] The umbrella-shaped canopy this ligand creates is able to stabilise an $[(ITr)GeCl]^+$ cation, **1.56** (synthesised by the obscure route of halide abstraction/metathesis of the $[(ITr)Tl][BArF_{24}]$ salt with $GeCl_2$·dioxane). However, this ligand alone appears insufficient to stimulate oxidative reactivity; furthermore, the electron-withdrawing chloride is not an ideal substituent for enhancing reactivity in these complexes.

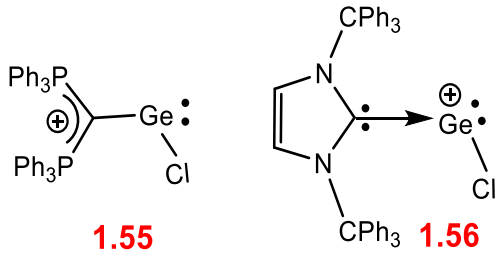


Figure 1.30: $[LGeCl]^+$ cations (counteranions: $[AlCl_4]^-$ and $[BArF_{24}]^-$)

There are however many examples of two-coordinate cations stabilised by incorporation into heterocycles, involving bidentate, monoanionic N-donor ligands featuring an additional N-donor to quench the electrophilicity of the cation (e.g. aminotroponiminate (**1.57**),[198,525] β-diketiminate (NacNac, **1.58**),[207,595,596] amido/imidazolin-2-iminato (**1.59**),[597] amido/imido (**1.60**)[598] etc.). The coordinative unsaturation as compared to $[L_nGeX]^+$ (n≥2) results in a greater need for WCA counteranions in these cases. This is illustrated by the weak coordination to **1.57** by triflate or $[\{CpZrCl_2\}(\mu_2\text{-}Cl)_3\{ZrCl_2Cp\}]^-$ anions, and phenyl group migration to the cation upon attempts to use tetraphenylborate as a counteranion.[198,525] Insufficiently bulky bidentate heterocyclic ligands may result in unavoidable solvent coordination; this is the case with a chiral bis(oxazoline) ligand used to synthesise a chiral cation (additionally coordinated by THF).[599] Chelating ligand scaffolds, however, disfavour oxidative reactivity. Electronically, N-donors act to raise the LUMO energy, while a cyclic system leads to a small N-Ge-N angle and a lower energy HOMO; sterically, there is little flexibility to accommodate further substituents following oxidative addition.

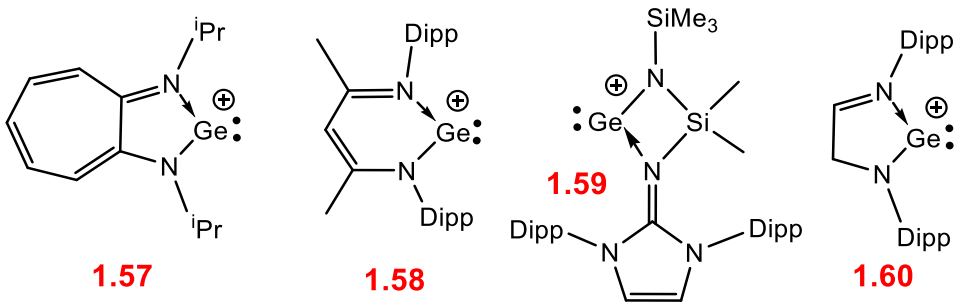


Figure 1.31: N,N-coordinated germanium cations (counteranions: vide supra, $[HO\{B(C_6F_5)_3\}_2]^-$, $[MeB(C_6F_5)_3]^-$, $[BArF_{20}]^-$)

There are as of yet no examples of a truly one-coordinate $[RGe]^+$ cation. A close attempt was synthesised by Jones and Krossing (**1.61**),[600] and features a single extremely bulky amide ligand as well as flanking stabilising interactions from an aryl group in the periphery of the ligand. While the electrophilicity of the cation could be demonstrated by the coordination of DMAP, the π-donor substituent appears to quench any potential for oxidative reactivity. Very recently, a similar strategy was applied by Hinz, who utilised a carbazolyl ligand to stabilise a "pseudo-one-coordinate" cation (**1.62**), again with the help of flanking aryl interactions.[601]

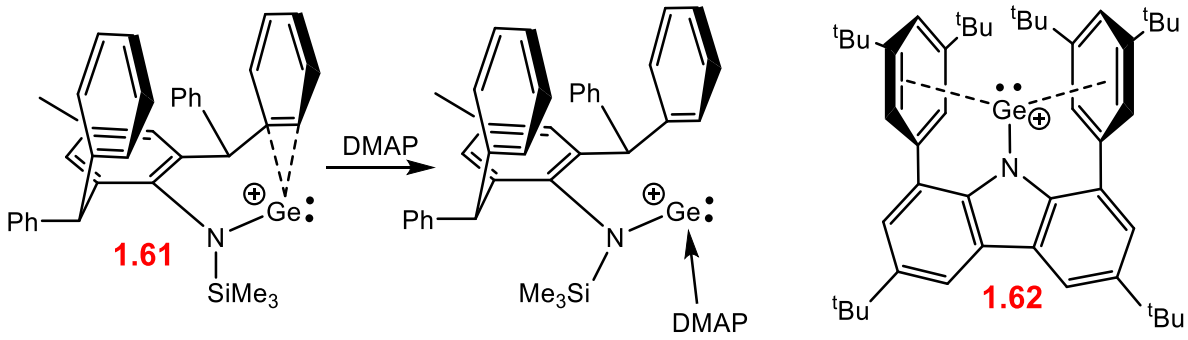


Figure 1.32: Quasi/Pseudo-one-coordinate cations (counteranion: $[Al(OR^F)_4]^-$ in both cases)

Of note is the relative lack of germanium cations stabilised by strong anionic σ-donors, such as terphenyl ligands. This is surprising given their widespread use in other aspects of germanium chemistry,[462] as well as in related main group compounds. Monomeric terphenyl-substituted $(Ar^{Tripp})E$ species featuring the group 13 elements, isoelectronic to tetrylium-ylidenes, have been synthesised with E = Ga,[602] In[603] and Tl;[604] notable are the subtle steric effects, as a slight reduction in terphenyl size results in $\{(Ar^{Dipp})E\}_2$ being dimeric in the solid state for all three elements (although these readily dissociate to the monomers in solution).[602,605–607] $\{(Ar^{Dipp})Ga\}_2$ is capable of the oxidative addition of H_2 and NH_3.[608] Notably, attempts to synthesise an aluminium analogue resulted in the isolation of its

cycloaddition product with toluene, illustrating its high reactivity.[609] Two-coordinate terphenyl-substituted group 13 cations in the +3 oxidation state have also been synthesised in the case of aluminium[610] and gallium.[611–613] Furthermore, group 15 (antimony and bismuth) cations isoelectronic to metallylenes have been synthesised featuring terphenyl substituents.[614]

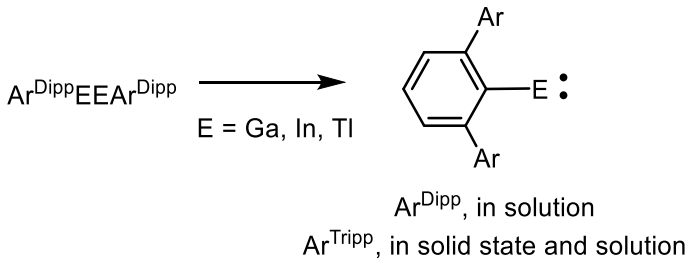
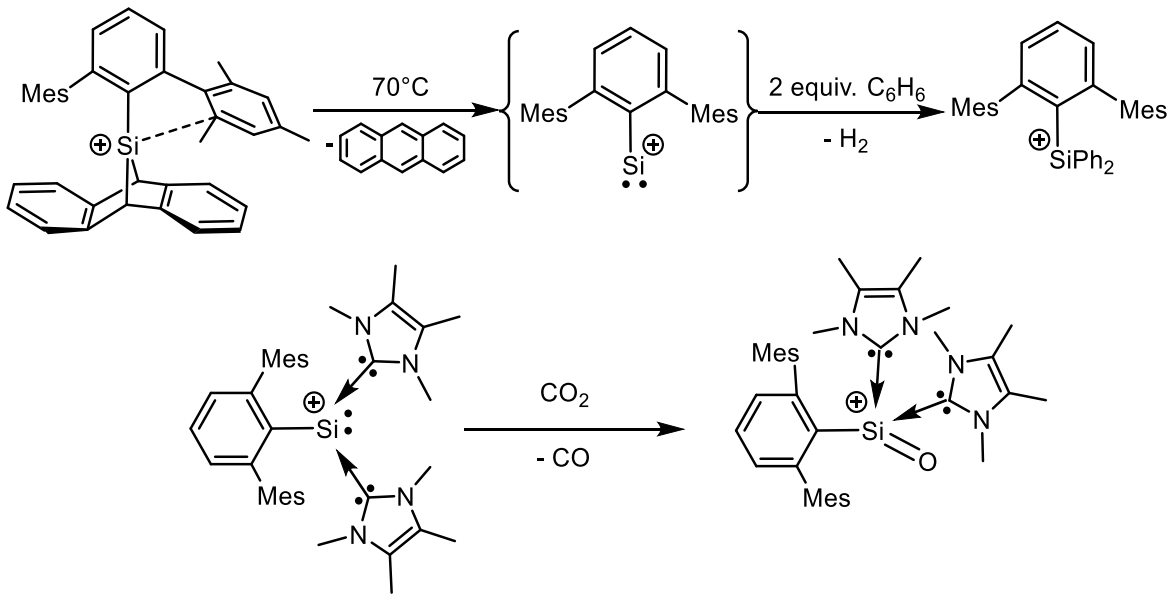


Figure 1.33: One-coordinate terphenyl-substituted group 13 species

Calculations have shown terphenyl ligands to be prime candidates for the stabilisation of silylium-ylidenes,[615] and a one-coordinate terphenyl-substituted silylium-ylidene ($[(Ar^{Mes})Si]^+$) could be generated *in situ* and shown to be extremely reactive,[616] while an NHC-stabilised version ($[(I\text{-}Me_4)_2(Ar^{Mes})Si]^+$) has been shown to have varied reactivity, including C-H activation of phenylacetylene, and reaction with CO_2 to give a silicon analogue of an acylium ion.[617–620] Terphenyl-substituted silylium cations have also been isolated, featuring distribution of the charge across the aryl rings.[621] There is also an example of silylium insertion into the flanking aryl ring of a terphenyl ligand.[622]



Scheme 1.17: Reactivity of terphenyl-substituted silylium-ylidenes (counteranion: $[BArF_{20}]^-$ or $[HCB_{11}H_5Br_6]^-$ (top) and Cl^- (bottom))

Two-coordinate terphenyl-stabilised stannylium-ylidenes, $[L(R)Sn]^+$, have been characterised in the solid state,[509] and their stabilising flanking aryl interactions studied *in situ*,[623] while a "quasi-one-coordinate" terphenyl-stabilised lead cation could be accessed featuring only a weak additional interaction from a toluene molecule.[624] Very recently, $[(Ar^{Tripp})Sn(benzene)]^+$ was generated via spontaneous dihydrogen elimination from $[(Ar^{Tripp})SnH_2]^+$ at ambient temperature; that $(Ar^{Tripp})SnH_3$ is much more stable is indicative of the greater propensity of cationic species for reductive elimination.[511]

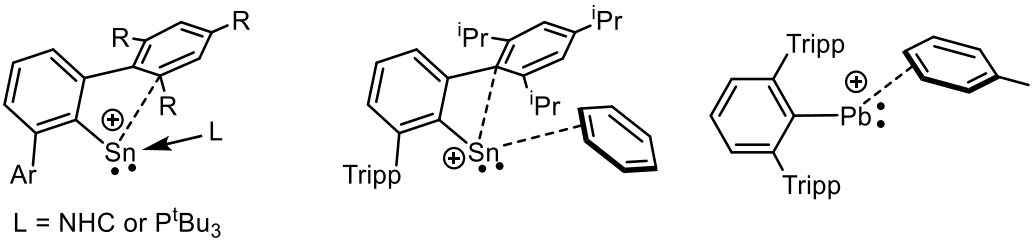
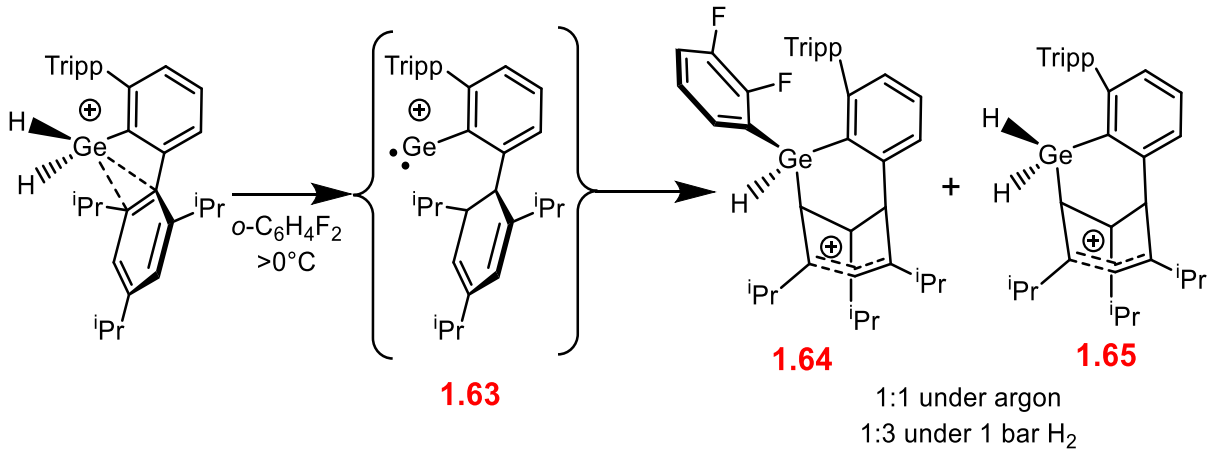


Figure 1.34: Terphenyl-substituted tetrylium-ylidenes (counteranions: $[HB(C_6F_5)_3]^-$, $[Al(OR^F)_4]^-$, $[MeB(C_6F_5)_3]^-$)

In the same study, the only example of terphenyl-substituted germanium cations can be found. $[(Ar^{Tripp})GeH_2]^+$ was also observed to be unstable at room temperature, generating initially the postulated intermediate **1.63** via hydrogenation of a flanking Tripp ring, followed by reaction with difluorobenzene solvent to yield a mixture of **1.64** and **1.65**. If instead $[(Ar^{Tripp})GeH_2]^+$ was generated under an atmosphere of dihydrogen, then an increase in the yield of **1.65** was observed, suggesting initial reaction with the aryl ring, followed by addition of H_2 instead of the solvent. However, no terphenyl-substituted germylium-ylidene could be isolated.[511]



*Scheme 1.18: In-situ reactivity of **1.63** (counteranion: $[Al(OR^F)_4]^-$)*

Compared to this relatively rich terphenyl chemistry, there are as of yet no group 14 cations substituted by boryl ligands. Although a free RE group 13 boryl species hasn't been obtained, the boryl-substituted aluminylene and gallylene have been trapped by coordination to iron carbonyl fragments (**1.66**).[625]

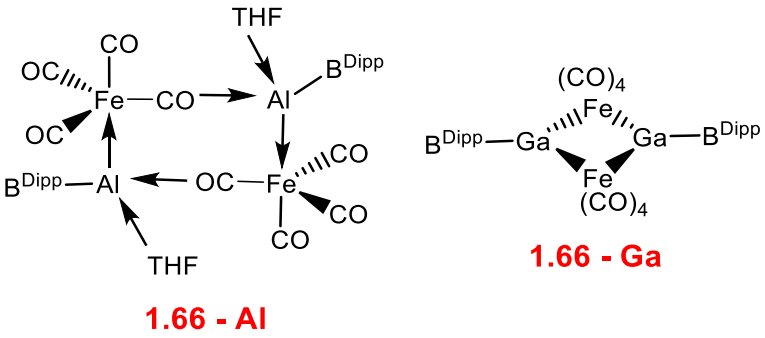


Figure 1.35: Boryl-substituted aluminylene and gallylene coordinated to iron carbonyl fragments

There are just a few further examples of germanium cations substituted by such strong anionic donors, in addition to the above terphenyl-substituted example. The mixed d/p-block cations **1.67** have been reported by Tobita, with calculations indicating significant delocalisation of the positive charge into the NHC ligands.[441] The monomeric cation **1.67-IDipp** has been found capable of the oxidative addition of H_2 at germanium, and (even more remarkably) of the reversible activation of silanes and boranes.[24] Other examples of cationic metallo-tetrylenes have been applied in the formation of novel multiple bonds; for example, $[\{Cp^*Cr(CO)_3\}Si(SIDipp)]^+$ was reacted with N_2O to form a rare example of a compound featuring a three-coordinate silicon centre with a Si=O bond, **1.68**.[626]

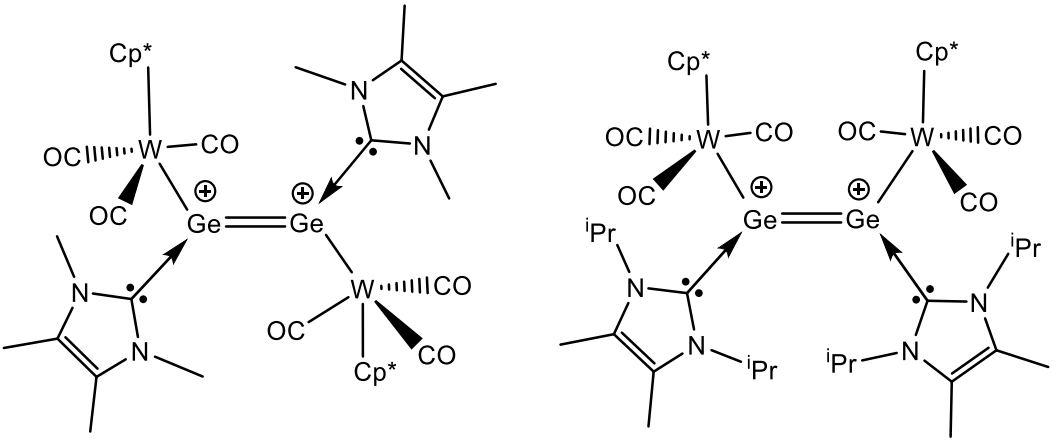
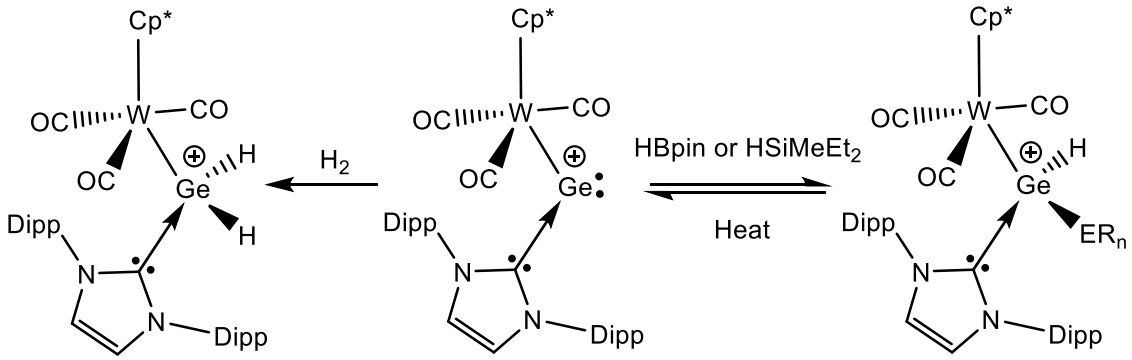
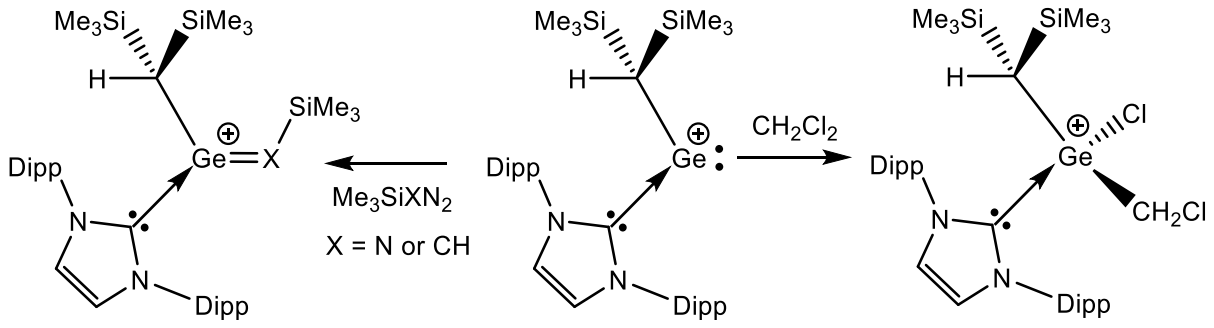


*Figure 1.36: Dimeric transition metal-substituted cations, **1.67-I-Me$_4$** and **1.67-IPrMe***



*Scheme 1.19: Bond activation by **1.67-IDipp** (counteranion: $[BArF_{24}]^-$)*

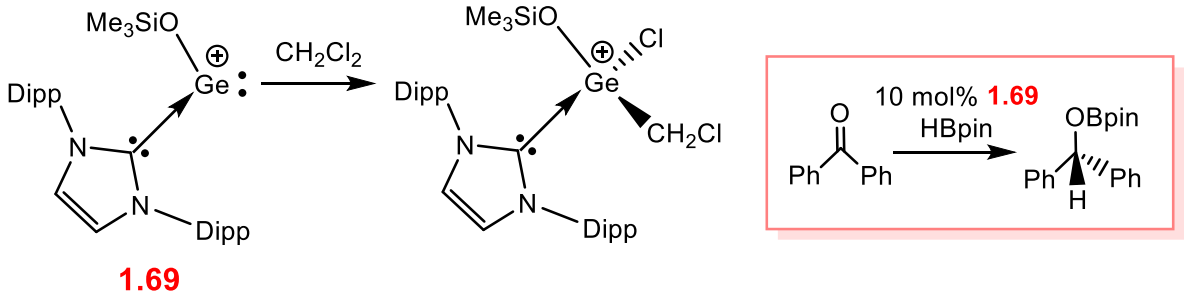
In recent work the Aldridge group have reported the acyclic, transition metal-free system **1.33**, which also possesses a small HOMO-LUMO gap (ca. 187 kJ mol^{-1}), and is capable of a number of oxidative bond activation processes.[23] Compound **1.33** oxidatively adds the C-Cl bond of dichloromethane (in which most germylenes can be handled without decomposition), as well as reacting with Me_3SiN_3 and Me_3SiCHN_2 to form relatively sterically unprotected examples of a germa-imine and germene, respectively. However, in terms of E-H bond activation chemistry, all attempts resulted in the isolation of $[IDippH]^+$-containing products, potentially suggesting insufficient stabilisation of a transient Ge^{IV} intermediate before rapid C-H elimination.



1.33

*Scheme 1.20: Oxidative reactivity of **1.33** (counteranion: $[BArF_{24}]^-$)*

A similar recent example reported by Rivard (**1.69**) was also found to be capable of the oxidative addition of dichloromethane (despite a larger HOMO-LUMO gap). This system also provided the first example of catalysis by a germanium cation (the hydroboration of hindered aryl- and alkyl-substituted ketones).[523] An aminotroponiminate-supported cation has also very recently been found to catalyse this process.[525]



*Scheme 1.21: DCM activation and catalysis by **1.69** (counteranion: $[BArF_{24}]^-$)*

Thus, a variety of intriguing examples of germylium-ylidenes have been synthesised to date. However, there are as of yet no examples of isolable transition metal-free cations that are capable of the activation of E-H bonds. Given that boryl, terphenyl and silyl ligands have proven influential in the formation of multiply-bonded species and metallylenes capable of E-H bond activation, their potential use in the stabilisation of germanium cations would represent a fascinating possibility towards reactive germylium-ylidenes. This is the focus of a significant part of this thesis.

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Chapter II

Experimental Methods

2.1 Manipulation of air- and moisture-sensitive compounds

Most of the compounds handled during the work presented in this thesis are highly sensitive to air and moisture. It was therefore necessary to use inert atmosphere techniques to manipulate these compounds.

2.1.1 Inert atmosphere techniques

The use of Schlenk lines and glove boxes allow highly air- and moisture-sensitive compounds to be stored and manipulated under an inert atmosphere of argon or nitrogen.[1–4]

Solution phase reactions were conducted using a Schlenk line, which has been shown to be an effective and efficient way of minimising exposure to oxygen and moisture. The line employed consisted of a dual Pyrex manifold: one manifold was connected to a supply of argon gas, and the other to a high vacuum pump. The argon pressure was maintained above atmospheric pressure by passing the argon stream through a mercury bubbler; the pressure within the vacuum manifold was monitored by use of a pressure gauge, and was typically maintained at ca. 10^{-2} mbar. The vacuum manifold was equipped with a liquid nitrogen trap in order to prevent solvents and other volatile substances from entering the vacuum pump.[1–4]

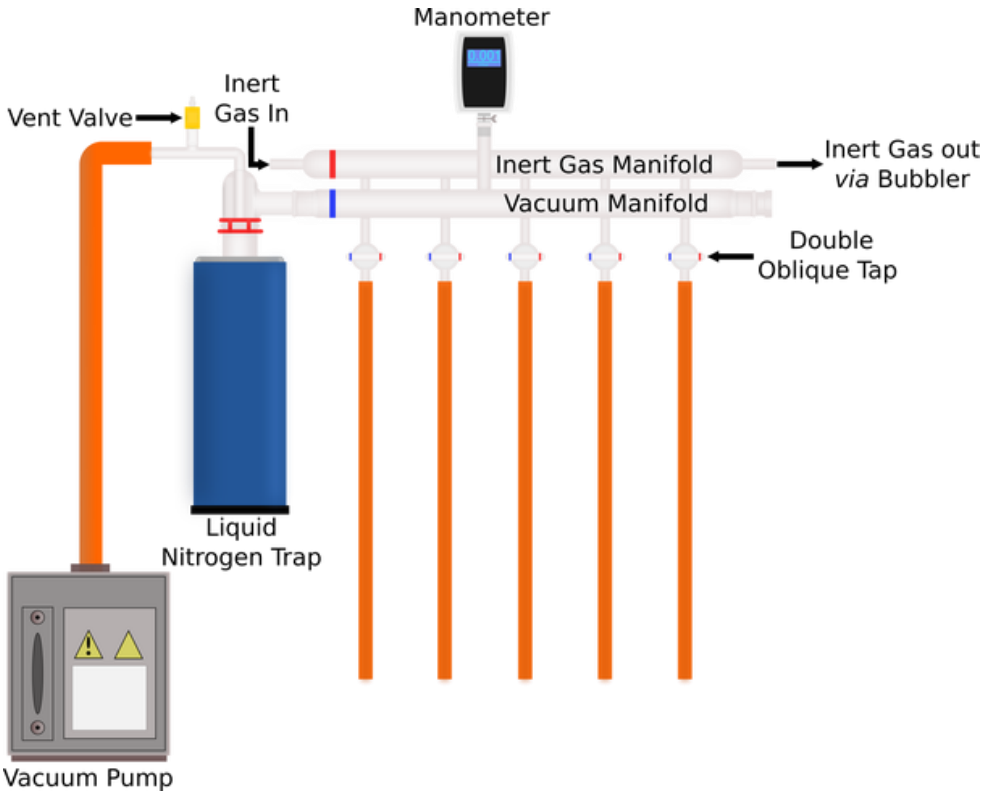


Figure 2.1: Standard set up of a Schlenk line [reproduced with permission from https://schlenklinesurvivalguide.com][4]

A series of two-way taps allowed connection of reaction vessels to both manifolds via rubber tubing, thereby allowing vessels to be evacuated and back-filled with a positive pressure of argon gas. Ground glass joints were lubricated with high vacuum grease in order to create an airtight seal. In order to ensure that the environment inside reaction vessels was as free as possible from air and moisture, a "pump and purge" cycle was applied three times, in which the vessel was evacuated to ca. 10^{-2} mbar, before being back-filled with argon gas. During the first evacuation cycle, glassware was heated strongly under vacuum using a Bunsen burner, in order to remove traces of moisture from the inside surfaces of the glass. Liquids were transferred between vessels using cannulae or syringes (purged three times with argon prior to use) to prevent exposure to air. For filtration of solutions, cannulae were fitted with glass-fibre filter paper. [1–4]

A glove box equipped with a nitrogen atmosphere was used for the manipulation and storage of air- and moisture-sensitive solids, and for the preparation of NMR samples. The atmosphere was purified by passing through activated copper metal and molecular sieves, to remove oxygen and moisture, respectively. Compounds entered the box via an antechamber, which was subject to three "pump and

purge" cycles before being opened to the atmosphere of the glove box. Neoprene gloves built into the side of the box allowed access to the sealed system.

2.2 Spectroscopic and analytical techniques

The work in this thesis involved the use of a range of characterisation techniques, the details of which are given below.

2.2.1 NMR spectroscopy

NMR spectra were measured by the author on Bruker Avance III HD Nanobay 400 MHz or Bruker Avance III 500 MHz spectrometers, or by Ms. Tina Jackson of the University of Oxford on a Bruker Avance 500 MHz spectrometer equipped with a ^{13}C detect cryoprobe. ^{1}H NMR spectra were referenced internally to residual protio-solvent, and ^{13}C NMR spectra to the deuterated solvent. ^{11}B, ^{19}F, ^{27}Al and ^{29}Si NMR spectra were referenced externally against $BF_3{\cdot}OEt_2$, $CFCl_3$, $[Al(H_2O)_6]^{3+}$ and $SiMe_4$, respectively. NMR spectra were assigned with the assistance of 2D COSY, HSQC and HMBC measurements. Air- and moisture-sensitive samples were prepared in NMR tubes equipped with a J. Young's tap, under an inert atmosphere using Schlenk line techniques or in a glove box.

2.2.2 Infrared spectroscopy

Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. Solid samples were prepared as Nujol mulls between KBr plates in a glove box, or measured using ATR; solution phase samples were prepared using a Schlenk line in a sealed cell.

2.2.3 UV-Vis spectroscopy

UV-Vis measurements were made using an Agilent Cary 4000 UV-Vis Spectrometer.

2.2.4 Mass spectrometry

ESI-MS measurements on charged compounds were carried out by Xueer Zhou of the Aldridge group using a Bruker MicroTOF ESI mass spectrometer connected to a glove box by PEEK tubing.[5]

2.2.5 Elemental analysis

Elemental analyses were carried out by Stephen Boyer, London Metropolitan University. All isolated compounds were submitted for elemental analysis, however in some cases corroboration with expected values was unsuccessful. Potential reasons for this include: the extreme moisture sensitivity of some cationic compounds, leading to both persistent contamination with small amounts of $[(NHC)H]^+$ and also potential decomposition during analysis; the known phenomenon of the formation of silicon carbide during analysis, which can lead to low carbon percentages for silicon-containing compounds;[6–10] the known phenomenon of difficulty in obtaining successful analysis for compounds with a high fluorine content.[11,12]

2.2.6 X-ray crystallography

Single crystals were mounted on MiTeGen MicroMounts using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas using an Oxford Cryosystems Cryostream unit. X-ray data were in general collected on Bruker-Nonius KappaCCD and Oxford Diffraction (Agilent) SuperNova diffractometers using Mo-K_α or Cu-K_α radiation, respectively. Data for **$[(10)_2][BArF_{24}]_2$** were collected on the I19 beamline at the Diamond Light Source synchrotron.[13] Data were reduced using Denzo/Scalepack[14] or CrysAlisPro. Structure determinations were carried out using SIR92[15,16] or SuperFlip,[17] and refined with full-matrix least-squares within CRYSTALS[18,19] or SHELX.[20,21] Data collection and structure determinations were carried out by either Dr. Christian Sindlinger or Dr. Jamie Hicks of the Aldridge group, or Dr. Amber Thompson or Dr. Kirsten Christensen of the Oxford Crystallography service. The graphics appearing in this thesis were generated using POV-Ray,[22] and are all shown with thermal ellipsoids set at the 50% probability level.

2.2.7 DFT calculations

DFT calculations were performed by Dr. Christian Sindlinger using ORCA.[23] Structures were optimised at the BP86-D3BJ/def2-SVP(TZVP on Ge) level of theory. On the BP86 optimised structures a single-point with PBE0 was performed including population analysis and natural bond orbital (NBO) calculations. NBO analysis was performed using the NBO 7.0 programme.[24]

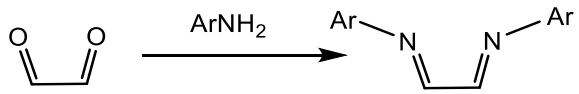
2.3 Preparation and purification of starting materials

Many commercially available compounds, solvents and gases were used in the work of this thesis. Some of these were purified prior to use. The information on the supplier, purity, and the method of further purification for these starting materials is provided as a table in Appendix 1 (see attached CD).

Known compounds which were not commercially available were synthesised according to modified literature procedures. Details of these procedures are given below.

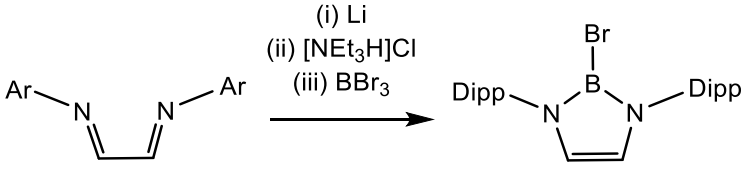
2.3.1 Preparation of boryl ligand precursors

General procedure for preparation of the diazadienes 1,4-bis(Mes)-1,4-diaza-1,3-butadiene (MesDAB), ***2.1****, and 1,4-bis(Dipp)-1,4-diaza-1,3-butadiene (DippDAB),* ***2.2***



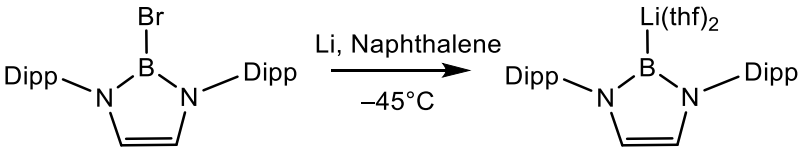
These compounds were prepared according to the procedure of Ritter,[25] which is exemplified here for the case of Ar = Dipp. A solution of $DippNH_2$ (105 mL, 557 mmol, 2.1 equiv.) and acetic acid (0.5 mL) in methanol (125 mL) was added to glyoxal (38.0 g of a 40% by weight solution in water, 262 mmol) in methanol (125 mL) at room temperature in air, and the reaction mixture stirred at 50°C for 15 min (a bright yellow precipitate appeared within minutes on heating), then at room temperature for 10 h. The solution was filtered to isolate the bright yellow precipitate, which was then washed with methanol (3 x 50 mL) and dried *in vacuo* for 2 h to yield 86 g (228 mmol, 87.2%) of a yellow solid. For the case of Ar = Mes, the use of $MesNH_2$ (140 mL, 1.00 mol) with analogous stoichiometry of other reagents gave a yield of 115 g (393 mmol, 82.8%). ^{1}H NMR data ($CDCl_3$) were consistent with literature values.[25]

Preparation of the bromoborane, 2-bromo-1,3-bis(Dipp)-1,3,2-diazaborole ({B^{Dipp}}Br), ***2.3***



(B^{Dipp})Br was prepared according to a procedure modified from that of Yamashita and Nozaki.[26] 1,4-bis(Dipp)-1,4-diaza-1,3-butadiene (17.3 g, 46 mmol) and small flattened pieces of lithium wire (0.95 g, 137 mmol, 3 equiv.) were added under argon to a large flame-dried Schlenk flask, and Et_2O (200 mL) added at room temperature. This suspension was then vigorously stirred at room temperature – the bright yellow colour changed to red within a few hours, then dark yellow by the following day, and the suspension was then stirred for a further 2 d under argon. The solution was filtered from excess lithium, $[NEt_3H]Cl$ (13.1 g, 95 mmol, 2.1 equiv.) added via a funnel, and the resulting suspension stirred for 1 h at room temperature (during which time the colour faded to a pale yellow). The solution could then be filtered from excess $[NEt_3H]Cl$, and the Et_2O and NEt_3 removed *in vacuo*. The resulting residue was dissolved in dichloromethane and cooled to 0°C; BBr_3 (4.8 mL, 51 mmol, 1.1. equiv.) was then added dropwise [Note: this was best done in a Teflon sealed ampoule, due to the tendency of BBr_3 to react with silicone grease]. After warming to room temperature, the reaction was stirred overnight. Excess BBr_3 could then be quenched with NEt^iPr_2 (19.0 mL, 109 mmol, 2.4 equiv.), and excess NEt^iPr_2 and dichloromethane then removed *in vacuo*. The resulting solid was then extracted with hot hexane (2 x 150 mL). The hexane was removed *in vacuo* until ca. 20 mL remained as part of a turbid suspension; this hexane was removed by filtration, and the resulting solid washed with cold (0°C) hexane (2 x 10 mL) and dried to yield 15.2 g (32.5 mmol, 70.7%) of a dark yellow/brown solid. ^1H and ^{11}B NMR data (C_6D_6) were consistent with literature values.[26]

Preparation of the boryllithium, (B^{Dipp})Li(thf)$_2$, ***2.4***



(B^{Dipp})Li(thf)$_2$ was prepared according to a procedure modified from that of Yamashita and Nozaki.[26] Small flattened pieces of lithium wire (0.270 g, 38.9 mmol, 10 equiv.) were added to a Schlenk flask containing naphthalene (0.050 g, 0.390 mmol, 0.1 equiv.). Alternatively, excess lithium stored from a previous preparation could be utilised, to which was added additional lithium (0.050 g) as well as the usual amount of naphthalene. The reaction mixture was cooled to −30°C in a dry-ice/acetone bath,

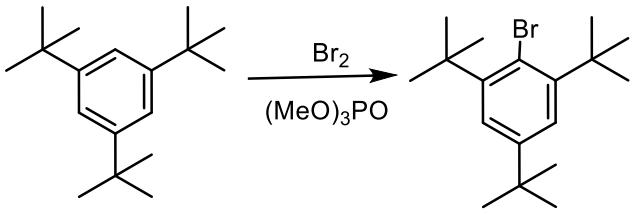
and to it was slowly added via cannula a solution of (B^{Dipp})Br (1.77 g, 3.79 mmol) in THF (30 mL). The resulting orange/brown suspension was then stirred until the colour changed to deep green (ca. 5 min if using recycled lithium, ca. 30 min if fresh), at which point the temperature was lowered to −45°C and the suspension left to stir for 3 d (cooling provided with a Huber TC45E-F-NR immersion chiller). After this time, the colour changed to dark brown. It was important for the following room temperature work-up to take place within a 2-3 h period, due to the instability of (B^{Dipp})Li(thf)$_2$ at room temperature. The solution was filtered from excess lithium into a Schlenk flask at room temperature, and the lithium washed with further THF (2 x 5 mL), which was combined with the initial filtrate. The excess lithium was then stored in a −25°C freezer for future use. The majority of THF was then removed from the filtrate *in vacuo*. The solution here was not left *in vacuo* until complete dryness (to avoid loss of the THF coordinated to lithium), but rather until a viscous brown oil was obtained (sometimes, the oil began to crystallise on the walls of the Schlenk flask as a microcrystalline solid, which was also acceptable, and this could then be dried completely). The resulting oil was then extracted with pentane (2 x 15 mL). This solution was concentrated *in vacuo*, to a volume of ca. 5-10 mL. Sometimes, significant amounts of solid appeared when there was greater than this volume of pentane remaining; this was likely either bromoborane, LiBr or lithium naphthalide impurities, and filtration was then necessary at this point before further concentration. Once the solution was concentrated, it was frozen by immersion of the Schlenk flask in liquid nitrogen; after warming and storage for ca. 2 min at room temperature, colourless rectangular seed crystals appeared on the walls of the Schlenk flask (see Figure 2.2; if they did not, further concentration and repetition of this process was necessary). Storage of the solution at −25°C overnight led to the appearance of large colourless crystals, which were isolated by filtration and washed with a small amount of cold (−25°C) pentane. The filtrate could be concentrated *in vacuo* and stored at −25°C overnight to yield a small additional crop of product, yielding in total 1.18 g (2.19 mmol, 57.7%). ^{1}H and ^{11}B NMR data (C_6D_6) were consistent with literature values[26] (though needed to be collected within 1-2 h to avoid significant decomposition being observed at room temperature).



Figure 2.2: Seed crystal formation following freezing of a solution of (B^{Dipp})Li(thf)$_2$

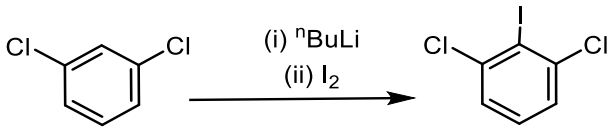
2.3.2 Preparation of aryl/terphenyl ligand precursors

Preparation of supermesityl bromide, 1-bromo-2,4,6-tritert-butylbenzene ({Mes}Br),* ***2.5***



(Mes*)Br was kindly donated by Dr. Christian Sindlinger, who prepared it according to the procedure of Knorr.[27]

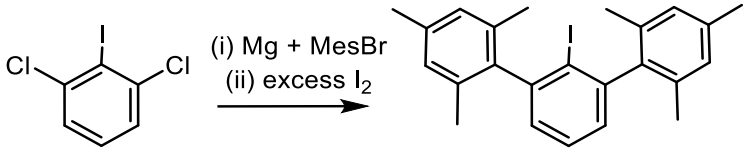
Preparation of 1,3-dichloro-2-iodobenzene, ***2.6***



1,3-dichloro-2-iodobenzene was prepared according to the procedure of Schlosser.[28] 1,3-dichlorobenzene (12.0 mL, 105 mmol) was degassed via three *freeze-pump-thaw* cycles, then cooled to −78°C and added dropwise to a solution at −78°C of ^{n}BuLi (62.5 mL of a 1.6 M solution in hexane, 100 mmol, 0.95 equiv.) in THF (140 mL). The reaction mixture was stirred for a further 2 h at this temperature, then a solution of iodine (25.4 g, 100 mmol, 0.95 equiv.) in THF (100 mL) added dropwise. The mixture was warmed to room temperature, then poured onto a saturated aqueous solution of Na_2SO_3 to quench any unreacted iodine. The aqueous phase was extracted with Et_2O (3 x 100 mL), then the dark yellow combined organic phases were dried over $MgSO_4$ and the solvent removed *in vacuo* to

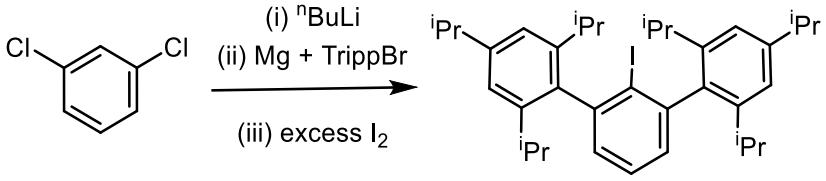
give a yellow solid. This was dissolved in minimal hot methanol, and then stored at −25°C overnight to afford a colourless crystalline solid that could be isolated by filtration for a yield of 18.1 g (66.4 mmol, 63.2%). ^{1}H NMR data ($CDCl_3$) were consistent with literature values.[28]

Preparation of 2,6-bis(Mes)-iodobenzene ({Ar^{Mes}}I), ***2.7***



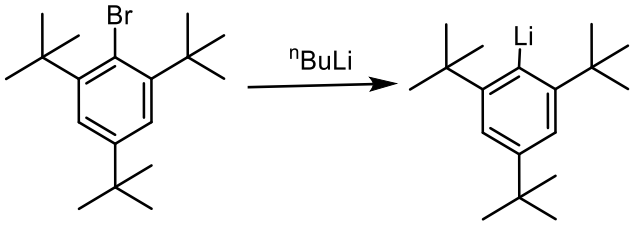
(Ar^{Mes})I was prepared according to a procedure modified from that of Toyota.[29] Freshly ground magnesium turnings (8.00 g, 329 mmol, 4.4. equiv.) were suspended in THF (70 mL) and activated with 1 or 2 drops of 1,2-dibromoethane. At 40-45°C, under vigorous stirring, a solution of MesBr (46.1 mL, 301 mmol, 4 equiv.) in THF (130 mL) was added dropwise, such that reflux was maintained. The solution was heated for a further 2 h under reflux, then cooled to room temperature and 1,3-dichloro-2-iodobenzene (20.5 g, 75 mmol) in THF (70 mL) added via cannula. The reaction was then heated under reflux overnight. After cooling to room temperature, a solution of iodine (76.4 g, 301 mmol, 4 equiv.) in THF (180 mL) was added dropwise over 3 h. The reaction was then heated under reflux for 4 h. After this period, the reaction mixture could be added to a saturated solution of Na_2SO_3 (with cooling with an ice bath), to quench any unreacted iodine. The reaction mixture was then extracted with dichloromethane (3 x 100 mL). The combined organic phases were dried over $MgSO_4$ and the solvent removed *in vacuo*. The residue was dissolved in a small amount of hexane (5 mL), and the resulting solution cooled to 3°C for 1 h to afford a white crystalline solid, which was isolated by filtration and washed with a small amount of cold hexane (2 x 5 mL) for a yield of 20.5 g (46.6 mmol, 62.1%). ^{1}H NMR data (C_6D_6) were consistent with literature values.[30]

Preparation of 2,6-bis(Tripp)-iodobenzene ({Ar^{Tripp}}I), ***2.8***



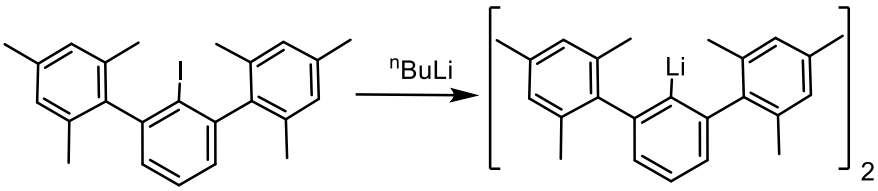
(Ar^{Tripp})I was prepared according to a procedure modified from that of Power.[31] 1,3-dichlorobenzene (11.4 mL, 100 mmol) was dissolved in THF (100 mL) and cooled to −78°C. ^{n}BuLi (62.5 mL of a 1.6 M solution in hexane, 100 mmol) was added dropwise via cannula over a period of 1.5 h. The formation of a white precipitate was observed, and stirring continued for 1 h at −78°C. Separately, a solution of TrippMgBr (235 mmol, 2.35 equiv.) in THF was freshly prepared: TrippBr (59.5 mL, 235 mmol) was added to THF (220 mL), then 50 mL of this solution was added to freshly ground magnesium turnings (5.71 g, 235 mmol) suspended in THF (80 mL) whilst heating to near reflux to ensure the reaction was initiated, then the remaining TrippBr solution was added dropwise. This solution of TrippMgBr in THF was then added to the lithiated 1,3-dichlorobenzene at −78°C over a period of 1-2 h. The reaction mixture was then warmed to room temperature and stirred overnight. The resulting brown solution was then heated under reflux for 2 h. The reaction mixture was cooled using an ice bath, iodine (34.25 g, 135 mmol) in THF (100 mL) then added, and the resulting suspension stirred vigorously overnight at room temperature. An aqueous solution of $Na_2S_2O_3$ was then added to quench any unreacted iodine. The reaction mixture was extracted with Et_2O (3 x 100 mL), the combined organic phases then dried over $MgSO_4$, and the solvent removed *in vacuo*. Washing with hexane (2 x 10 mL) yielded 40.65 g (66.8 mmol, 66.8%) of a white powder. ^{1}H NMR data ($CDCl_3$) were consistent with literature values.[32]

Preparation of supermesityl lithium ({Mes}Li),* ***2.9***



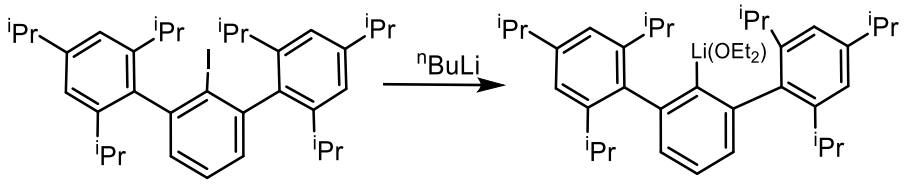
(Mes*)Li was prepared according to the procedure of Lammertsma.[30] A solution of (Mes*)Br (4.88 g, 15.0 mmol) in Et_2O (25 mL) was cooled to 0°C, and to it was added ^{n}BuLi (9.4 mL of a 1.6 M solution in hexane, 15.0 mmol) over a period of 15 min. The resulting solution was then stirred for 3 h at 0°C, then the solvent removed *in vacuo* to give a pale yellow solid. Washing with pentane (2 x 20 mL) yielded 2.82 g (11.2 mmol, 74.5%) of a white solid. ^{1}H NMR data (d_8-THF) were consistent with literature values.[30]

Preparation of (Ar^{Mes})Li, ***2.10***



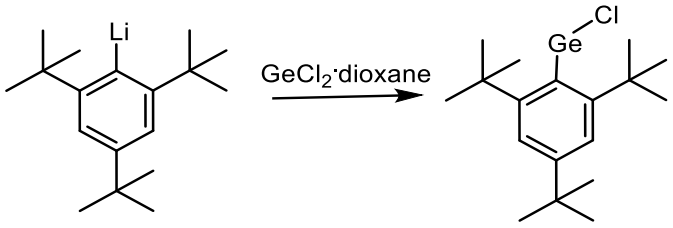
(Ar^{Mes})Li was prepared according to a procedure modified from that of Power.[33] With rapid stirring, ^{n}BuLi (6.25 mL of a 1.6 M solution in hexane, 10.0 mmol) was added to a solution of (Ar^{Mes})I (4.41 g, 10.0 mmol) in hexane (60 mL) at room temperature. The solution was stirred overnight, during which time it became cloudy. Filtration of this solution enabled the isolation of the product as a white precipitate. The filtrate was concentrated *in vacuo* to incipient crystallisation, then stored at −25°C for ca. 2 d to yield an additional crop of the product as a colourless crystalline solid, for a total yield of 2.85 g (8.90 mmol, 89.0%). ^{1}H NMR data (C_6D_6) were consistent with literature values.[30]

Preparation of (Ar^{Tripp})Li(Et_2O), ***2.11***



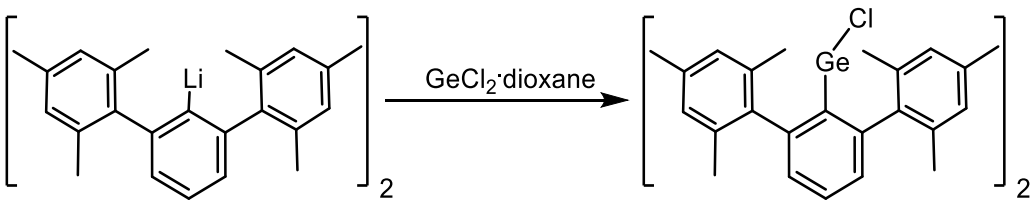
(Ar^{Tripp})Li(Et_2O) was prepared according to a procedure modified from that of Power.[32] (Ar^{Tripp})I (3.56 g, 5.85 mmol) was dissolved in a mixture of Et_2O (15 mL) and hexane (50 mL) with rapid stirring, and cooled to −78°C (at which temperature the starting material was not fully soluble). ^{n}BuLi (3.75 mL of a 1.6 M solution in hexane, 6.00 mmol) was then added dropwise to the solution, after which the reaction mixture was slowly warmed to room temperature over 6 h, and then stirred at room temperature overnight. The resulting clear solution was concentrated *in vacuo* to incipient crystallisation (ca. 25 mL), then stored at −25°C overnight to afford a colourless crystalline solid, which could be isolated by filtration for a yield of 1.80 g (3.20 mmol, 54.7%). ^{1}H NMR data (C_6D_6) were consistent with literature values.[32]

Preparation of (Mes)GeCl,* ***2.12***



(Mes*)GeCl was prepared according to the procedure of Jutzi.[34] Separate Schlenk flasks containing (Mes*)Li (1.00 g, 3.96 mmol) in THF (25 mL) and $GeCl_2$·dioxane (0.92 g, 3.97 mmol) in THF (25 mL) were cooled to −78°C, and the former added to the latter very slowly over ca. 1 h. Once addition was complete, stirring was continued at −78°C for a further 30 min, and the solution then slowly warmed to −10°C over 30 min. At this temperature, the solvent was removed *in vacuo*, and the resulting orange residue extracted with hexane (60 mL). This solution was then concentrated *in vacuo* to incipient crystallisation, and stored at −80°C overnight, to yield 0.180 g (0.509 mmol, 12.9%) of a light orange microcrystalline solid. ^{1}H NMR data (C_6D_6) were consistent with literature values.[34]

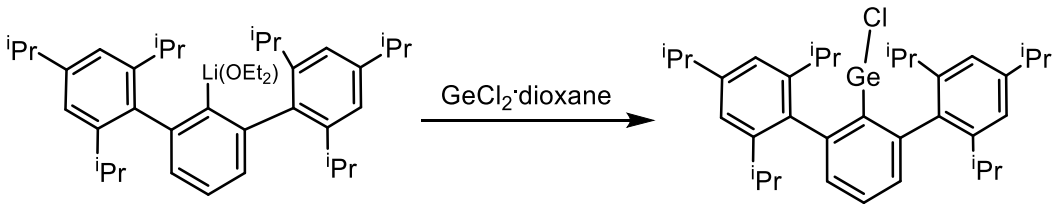
Preparation of (Ar^{Mes})GeCl, ***2.13***



(Ar^{Mes})GeCl was prepared according to the procedure of Power.[35] Separately, a solution of (Ar^{Mes})Li (0.800 g, 2.50 mmol) in THF (25 mL) and a suspension of $GeCl_2$·dioxane (0.600 g, 2.59 mmol) also in THF (25 mL) were cooled to −78°C, and the former added to the latter extremely slowly (dropwise over 1 h) with rapid stirring, to give an orange mixture (if the characteristic purple colour of (Ar^{Mes})$_2$Ge appeared, addition was halted and stirring intensified until it disappeared due to ligand redistribution). The solution was stirred for 2 h at this temperature, then warmed to room temperature and the solvent removed *in vacuo*. The orange/red residue was extracted with hexane (2 x 20 mL); this solution was concentrated *in vacuo* to incipient crystallisation, then stored at −25°C overnight to yield an orange crystalline solid, which could be isolated by filtration. The mother liquor was then concentrated *in*

vacuo and stored at −25°C to yield a further crop of orange crystals, for a total yield of 0.380 g (0.901 mmol, 36.1%). ^{1}H NMR data (C_6D_6) as reported were difficult to reproduce,[35] due to adduct formation with THF and dioxane; however, these adducts were competent for the intended onward reactions, and so the formation of useful product could be assessed by addition of excess IPrMe to an NMR sample of the product, and comparison with the signals characteristic of (IPrMe)(Ar^{Mes})GeCl (see **3.5.1**, **3**).

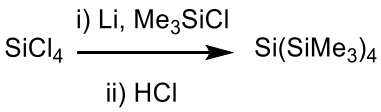
Preparation of (Ar^{Tripp})GeCl, ***2.14***



(Ar^{Tripp})GeCl was prepared according to the procedure of Power.[36] Separately, (Ar^{Tripp})Li(Et_2O) (0.99 g, 1.76 mmol) in Et_2O (25 mL) and a suspension of $GeCl_2$·dioxane (0.407 g, 1.76 mmol) also in Et_2O (25 mL) were cooled to −78°C, and the former added to the latter extremely slowly (dropwise over 1 h) with rapid stirring, to give an orange mixture. Stirring was continued as the reaction was warmed to room temperature, and then overnight at this temperature. Et_2O was removed *in vacuo*, and the orange residue extracted with hexane (2 x 20 mL). This solution was concentrated *in vacuo* to incipient crystallisation, and stored at −25°C overnight to yield an orange crystalline solid, which could be isolated by filtration. The mother liquor was then concentrated *in vacuo* and stored at −25°C to yield a further crop of orange crystals, for a total yield of 0.471 g (0.798 mmol, 45.3%). ^{1}H NMR data (C_6D_6) as reported were difficult to reproduce,[36] due to adduct formation with Et_2O and dioxane; however, these adducts were competent for the intended onward reactions, and so the formation of useful product could be assessed by addition of excess IPrMe to an NMR sample of the product, and comparison with the signals characteristic of (IPrMe)(Ar^{Tripp})GeCl (see **3.5.1**, **4**).

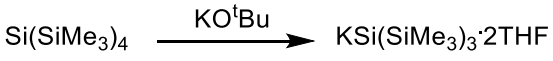
2.3.3 Preparation of silyl and amido ligand precursors

Preparation of tetrakis(trimethylsilyl)silane ($Si(SiMe_3)_4$), ***2.15***



$Si(SiMe_3)_4$ was prepared according to the procedure of Landais.[37,38] Small flattened pieces of lithium wire (7 g, 1.01 mol, 10 equiv.) were added to a flame-dried 1000 mL three-necked round bottomed flask, to which was then added THF (200 mL) followed by Me_3SiCl (56 mL, 441 mmol, 4.4 equiv., freshly distilled from magnesium). A solution of $SiCl_4$ (11.5 mL, 100 mmol, freshly distilled from CaH_2) in THF (200 mL) was prepared (this was stirred for 10 min after mixing as a uniform concentration was found to be important); 15 mL of this solution was slowly added to the suspension of Me_3SiCl and lithium in THF at room temperature, which was then stirred for 4 h at room temperature (progressively turning brown after 2-3 h). The remaining solution of $SiCl_4$ was then added over 30 min to the brown and opaque mixture. The resulting suspension was vigorously stirred at room temperature for 3 d. Under argon, the brown mixture was transferred via Teflon cannula onto celite and filtered to remove excess lithium and salts [Note: care should be taken in their quenching and disposal as these were found to be extremely pyrophoric]. To the filtrate was added an aqueous solution of HCl (50 mL of a 10% by weight solution in water), and the resulting mixture stirred for 15 min at room temperature. The organic layer was extracted with Et_2O (3 x 100 mL), and the combined organic phases then dried over $MgSO_4$. After removal of the solvent *in vacuo*, the resulting brown/orange powder was dissolved in the minimum amount of hot acetone, then stored at −25°C overnight to yield 14.0 g (43.6 mmol, 43.6%) of a white solid. ^1H and ^{29}Si NMR data (C_6D_6) were consistent with literature values.[39]

Preparation of tris(trimethylsilyl)silyl potassium ($KSi(SiMe_3)_3{\cdot}2THF$), ***2.16***



$KSi(SiMe_3)_3{\cdot}2THF$ was prepared according to the procedure of Marschner.[6,40] $Si(SiMe_3)_4$ (2.97 g, 9.26 mmol) and KO^tBu (1.09 g, 9.73 mmol, 1.05 equiv.) were dissolved in THF (60 mL), and the resulting solution stirred at room temperature overnight. The solvent was removed *in vacuo*, and the resulting

solid extracted with pentane (2 x 25 mL) [Note: the filter cannula utilised should be quenched cautiously with ^{i}PrOH as the product was found to be extremely pyrophoric]. This yellow solution was concentrated *in vacuo* to incipient crystallisation, and then stored at −80°C overnight to produce large colourless needles, which could be isolated by filtration to yield 2.64 g (6.13 mmol, 66.2%) of a yellow crystalline solid. ^{1}H and ^{29}Si NMR data (C_6D_6) were consistent with literature values.[6]

Preparation of bis(tris(trimethylsilyl)silyl) magnesium (Mg{Si(SiMe$_3$)$_3$}$_2$·2THF), ***2.17***

$$KSi(SiMe_3)_3{\cdot}2THF \xrightarrow{MgBr_2{\cdot}Et_2O} Mg\{Si(SiMe_3)_3\}_2{\cdot}2THF$$

Mg{Si(SiMe$_3$)$_3$}$_2$·2THF was prepared according to a procedure modified from that of Marschner.[41] KSi(SiMe$_3$)$_3$·2THF (3.00 g, 6.96 mmol) and MgBr$_2$·Et$_2$O (0.92 g, 3.56 mmol, 0.51 equiv.) were dissolved in toluene (30 mL), and the resulting solution stirred at room temperature for 30 min. The solution was filtered [Note: the filter cannula utilised should be quenched cautiously with ^{i}PrOH as the product was found to be extremely pyrophoric], and the filtrate concentrated *in vacuo* to incipient crystallisation. Storage at −80°C overnight resulted in the appearance of colourless needles, which could be isolated by filtration to yield 0.870 g (1.31 mmol, 36.8%) of a colourless crystalline solid. ^{1}H and ^{29}Si NMR data (C_6D_6) were consistent with literature values.[42]

Preparation of lithium diisopropylphenylamide (LiNHDipp), ***2.18***

$$NH_2Dipp \xrightarrow{^{n}BuLi} LiNHDipp$$

LiNHDipp was prepared by Matthew Usher according to the procedure of Wigley.[43]

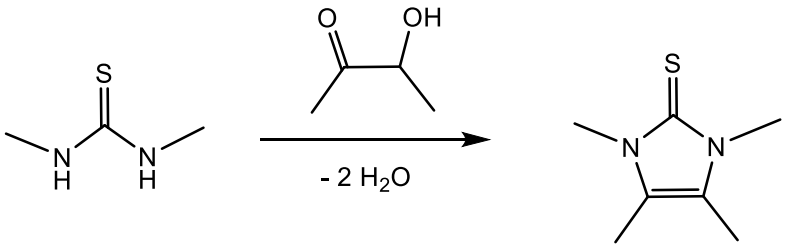
Preparation of (B^{Dipp})NHLi, ***2.19***

$$(B^{Dipp})NH_2 \xrightarrow{^{n}BuLi} (B^{Dipp})NHLi$$

(B^{Dipp})NHLi was prepared by Dr. Terrance Hadlington according to his own procedure.[10]

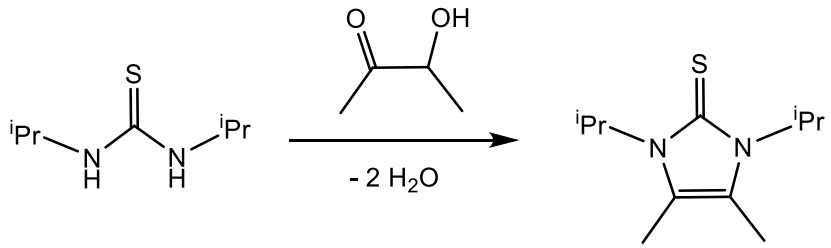
2.3.4 Preparation of N-heterocyclic carbenes

Preparation of 1,3,4,5-tetramethylimidazole-2-thione (I-Me$_4$=S), ***2.20***



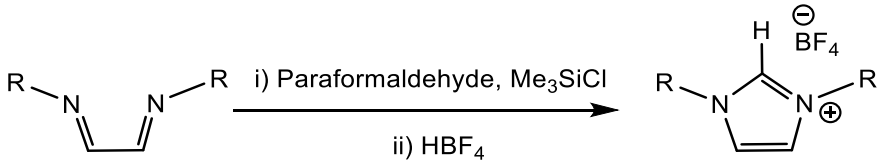
I-Me$_4$=S was prepared according to a procedure modified from that of Kuhn and Kratz.[44] 1,3-dimethylthiourea (10.42 g, 100 mmol) and acetoin (3-hydroxy-2-butanone, 8.81 g, 100 mmol) were dissolved in 1-hexanol (250 mL) in a round bottomed flask in air. A reflux condenser was fitted, and the reaction mixture heated to reflux overnight. After cooling, the solvent and evolved water were removed by vacuum distillation, and the resulting brown solid washed with cold Et_2O (2 x 5 mL) and then cold water (2 x 5 mL) to yield 13.07 g (83.7 mmol, 83.7%) of a brown/yellow solid. ^{1}H NMR data (CD_2Cl_2) were consistent with literature values.[44]

Preparation of 1,3-diisopropyl-4,5-dimethylimidazole-2-thione (IPrMe=S), ***2.21***



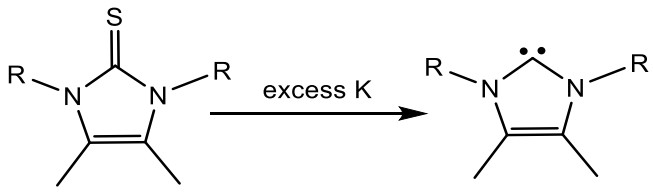
IPrMe=S was prepared according to a procedure modified from that of Sanford.[45] 1,3-diisopropylthiourea (48.1 g, 300 mmol) and acetoin (3-hydroxy-2-butanone, 29.1 g, 330 mmol, 1.1 equiv.) were dissolved in 1-hexanol (300 mL) in a round bottomed flask in air. A Dean-Stark apparatus and a reflux condenser were fitted, and the reaction mixture heated to reflux overnight. After the evolution of water had ceased (10.8 mL expected), the solution was cooled to room temperature and then stored at −25°C for 2 h. The resulting crystalline solid could be isolated by filtration and washed with cold ethanol (2 x 20 mL) to yield 44.2 g (208 mmol, 69.4%) of a white solid. ^{1}H NMR data (CD_2Cl_2) were consistent with literature values.[44]

General procedure for preparation of the imidazolium salts 1,3-bis(Mes)imidazolium tetrafluoroborate ([IMesH][BF_4]), ***2.22****, and 1,3-bis(Dipp)imidazolium tetrafluoroborate ([IDippH][BF_4]),* ***2.23***



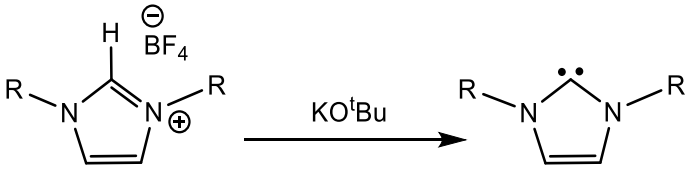
These imidazolium salts were prepared according to a common procedure, modified from those of Hintermann[46] and Nolan,[47] which is exemplified here for the case of [IDippH][BF_4]. 1,4-bis(Dipp)-1,4-diaza-1,3-butadiene (42.4 g, 112.6 mmol) and paraformaldehyde (3.48 g, 116 mmol, 1.03 equiv.) were dissolved in ethyl acetate (1000 mL) in a 2000 mL three-necked round bottomed flask in air, and the resulting suspension heated to 70°C. A solution of Me_3SiCl (14.7 mL, 116 mmol, 1.03 equiv.) in ethyl acetate (20 mL) was added dropwise over 45 min with vigorous stirring, resulting in a colour change to brown with concomitant production of a colourless precipitate. After addition was complete, the resulting suspension was stirred for a further 2 h at 70°C, then cooled to 10°C using an ice bath. The precipitate was isolated by filtration and washed with ethyl acetate (3 x 50 mL), to afford 39.5 g (93.0 mmol, 82.6%) of [IDippH]Cl as a white powder. This was dissolved in the minimum amount of water (approx. 1000 mL), and to the resulting solution was added an aqueous solution of HBF_4 (17.9 g of a 50% by weight solution in water, 102 mmol, 1.1 equiv.), with instantaneous formation of a white precipitate. The aqueous phase was extracted with dichloromethane (3 x 200 mL), the combined organic phases then dried over $MgSO_4$, and the solvent removed *in vacuo*. The resulting residue was then placed in a wide-brimmed beaker in a well-ventilated oven at 100°C overnight, to afford 37.3 g (78.3 mmol, 84.2% based on [IDippH]Cl, 69.5% based on diazadiene) of an off-white microcrystalline solid. For the case of [IMesH][BF_4], the use of 1,4-bis(Mes)-1,4-diaza-1,3-butadiene (25.3 g, 86.5 mmol) with analogous stoichiometry of other reagents gave a yield of 26.1 g (66.6 mmol, 77.0%). ^{1}H NMR data ($CDCl_3$ for [IMesH][BF_4], CD_2Cl_2 for [IDippH][BF_4]) were consistent with literature values.[47]

General procedure for preparation of the N-heterocyclic carbenes 1,3,4,5-tetramethylimidazol-2-ylidene (I-Me_4), ***2.24****, and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (IPrMe),* ***2.25***



These NHCs were prepared according to a common procedure, modified from that of Kuhn and Kratz,[44] which is exemplified here for the case of IPrMe. IPrMe=S (3.00 g, 13.1 mmol) was dissolved in THF (60 mL), the resulting solution cooled to 0°C using an ice bath, and potassium (1.76 g, 45.0 mmol, 3.4 equiv.) added. The resulting suspension was then heated under reflux for 4 h – within 30 min a vibrant baby blue colour developed and persisted. After cooling, the excess potassium was stirred a little to ensure coagulation, then left to stand overnight. The blue suspension was then removed from the excess potassium (which ideally was a singular lump at this point) via a Teflon cannula, and filtered through a pad of celite to leave a light yellow solution. The potassium and celite pad were then washed with THF (2 x 20 mL), and the washings combined with the filtrate. The solvent was removed *in vacuo*, and the resulting yellow solid purified by sublimation (60°C, $4x10^{-2}$ mbar, ca. 2 h) to afford 1.86 g (10.3 mmol, 73.2%) of a white crystalline solid. For the case of I-Me_4, the use of I-Me_4=S (3.00 g, 17.4 mmol) with analogous stoichiometry of other reagents gave a yield of 1.62 g (11.6 mmol, 66.4%). ^{1}H NMR data (C_6D_6) were consistent with literature values[44] [Note: there is an error in the shifts reported by Sanford for IPrMe].[45] Note that I-Me_4, though subliming as a white crystalline solid, quickly became red upon storage in a glove box. However, spectroscopically and from the success of onward reactions it was observed to remain pure enough for use.

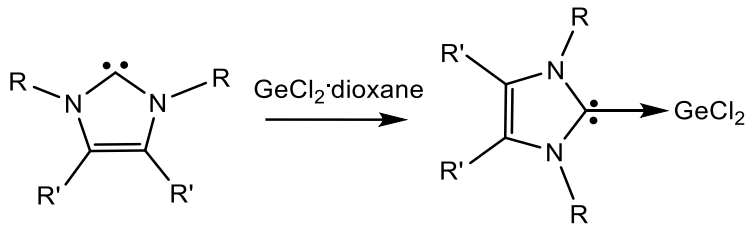
General procedure for preparation of the N-heterocyclic carbenes 1,3-bis(Mes)imidazol-2-ylidene (IMes), ***2.26****, and 1,3-bis(Dipp)imidazol-2-ylidene (IDipp),* ***2.27***



These NHCs were prepared according to a common procedure, modified from that of Nolan,[48] which is exemplified here for the case of IDipp. To a Schlenk flask containing [IDippH][BF_4] (10.0 g, 21.0 mmol) and KO^{t}Bu (2.59 g, 23.1 mmol, 1.1 equiv.) was added THF (60 mL) at room temperature. On stirring,

the colour immediately turned brown, and a white precipitate formed; stirring was then continued overnight at room temperature. The solvent was then removed *in vacuo*, and the residue extracted with hot (60°C) toluene. After removal of the toluene *in vacuo*, the residue was then washed with minimal cold (−20°C) hexane (15 mL), to yield 7.06 g (18.2 mmol, 86.5%) of a colourless powder. For the case of IMes, the use of [IMesH][BF_4] (5.00 g, 12.7 mmol) with analogous stoichiometry of other reagents gave a yield of 3.51 g (11.5 mmol, 90.5%) of a colourless powder. ^{1}H NMR data (d_8-THF for IMes, C_6D_6 for IDipp) were consistent with literature values.[47,48]

2.3.5 Preparation of NHC($GeCl_2$) adducts



Preparation of (I-Me_4)$GeCl_2$, ***2.28***

(I-Me_4)$GeCl_2$ was prepared according to the method of Filippou.[49] $GeCl_2$·dioxane (1.00 g, 4.32 mmol) was suspended in toluene (15 mL), and a solution of I-Me_4 (0.536 g, 4.32 mmol) in toluene (20 mL) was added slowly to this suspension, with rapid stirring at room temperature. Stirring was then continued for 1 h at room temperature. The resulting clear, slightly yellow solution was filtered from a small amount of an orange insoluble material. The filtrate was concentrated *in vacuo* to ca. 5 mL, leading to precipitation of a white solid; this solid was then separated from the light yellow mother liquor by filtration at −60°C, washed with pentane (2 x 5 mL) at −60°C, and dried *in vacuo* at room temperature for 2 h to afford 0.807 g (3.01 mmol, 69.8%) of a white microcrystalline solid. ^{1}H NMR data (C_6D_6) were consistent with literature values.[49]

Preparation of (IPrMe)$GeCl_2$, ***2.29***

(IPrMe)$GeCl_2$ was prepared according to a procedure modified from that of Baines.[50] To a Schlenk flask containing IPrMe (1.00 g, 5.55 mmol) and $GeCl_2$·dioxane (1.28 g, 5.53 mmol) was added benzene (5 mL). The resulting solution was stirred for 1 h at room temperature, after which time a white precipitate was observed. Hexane (10 mL) was then added to the reaction mixture, which was stirred

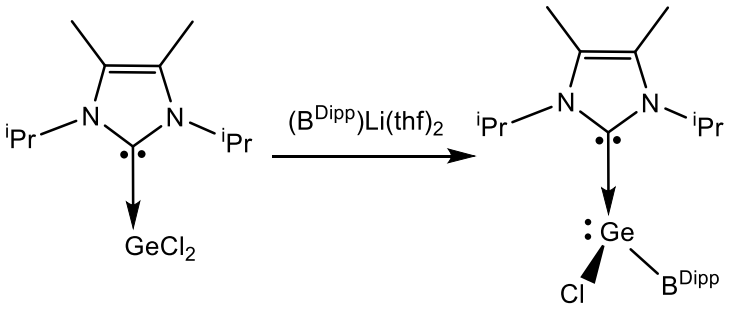
for a further 30 min at room temperature, leading to the deposition of a large amount of white precipitate; this was collected by filtration, washed with hexane (2 x 5 mL), and then dried *in vacuo* to yield 1.63 g (5.03 mmol, 91.0%) of a white solid. ^{1}H NMR data (C_6D_6) were consistent with literature values.[50]

Preparation of (IDipp)GeCl$_2$, ***2.30***

(IDipp)GeCl$_2$ was prepared according to the method of Jones.[51] To a Schlenk flask containing IDipp (1.25 g, 3.22 mmol) and GeCl$_2$·dioxane (0.750 g, 3.24 mmol) was added Et$_2$O (30 mL). The resulting suspension was stirred overnight at room temperature, and the product deposited as a colourless crystalline solid, which could be isolated by careful filtration to yield 1.20 g (2.26 mmol, 70.0%) of a crystalline solid. ^{1}H NMR data (C_6D_6) were consistent with literature values.[51]

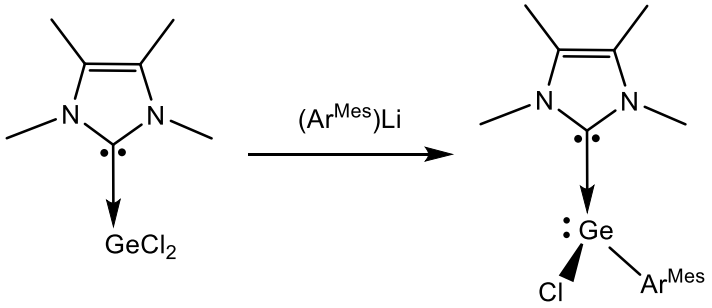
2.3.6 Preparation of NHC and anionic ligand stabilised chlorogermylenes

Preparation of (IPrMe)(B^{Dipp})GeCl, ***2.31***



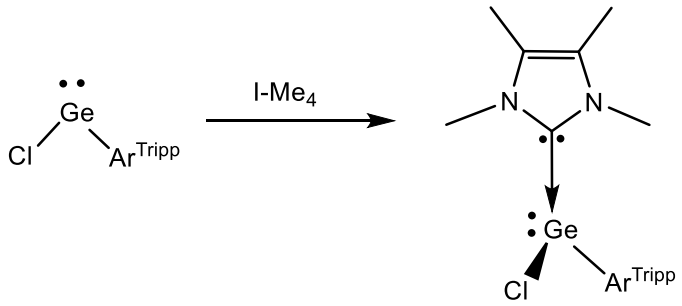
(IPrMe)(B^{Dipp})GeCl was prepared according to the procedure of Aldridge.[52] To a solution of (IPrMe)GeCl$_2$ (0.648 g, 2.00 mmol) in Et$_2$O (10 mL) at −35°C was slowly added a pre-cooled (−35°C) solution of (B^{Dipp})Li(thf)$_2$ (1.185 g, 2.20 mmol, 1.1 equiv.) in Et$_2$O (15 mL). After stirring for 30 min at this temperature, the reaction mixture was gradually warmed to room temperature and stirred for 2.5 h. The solvent was then removed *in vacuo* to give an orange residue, which was extracted with toluene (2 x 20 mL) [Note: it is inadvisable to place a stirrer bar in the Schlenk flask of the filtrate, as it will inevitably become irreconcilably stuck to the oily product]. The toluene was removed *in vacuo*, to yield an orange oil; this was triturated with hexane (2 x 5 mL), and stored at −25°C overnight to yield 1.21 g (1.79 mmol, 89.5%) of a pale yellow solid that could be isolated by filtration. ^{1}H NMR data (C_6D_6) were consistent with literature values.[52]

Preparation of (I-Me$_4$)(Ar^{Mes})GeCl, ***2.32***



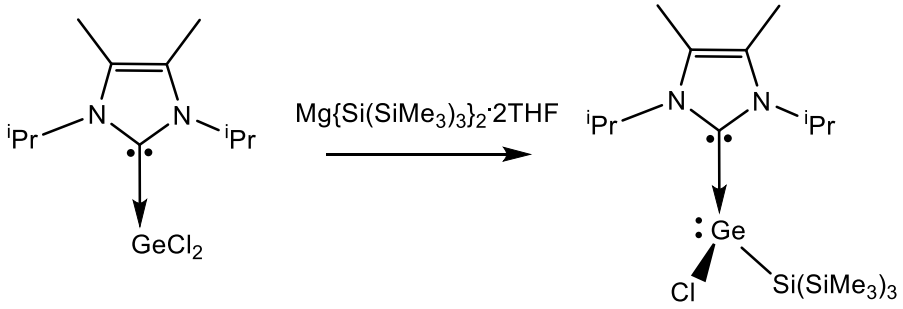
(I-Me$_4$)(Ar^{Mes})GeCl was prepared according to a procedure modified from that of Filippou.[49] Separately, a suspension of (I-Me$_4$)GeCl$_2$ (0.536 g, 2.00 mmol) in toluene (20 mL) and a solution of (Ar^{Mes})Li (0.642 g, 2.00 mmol) in toluene (20 mL) were cooled to −78°C, and the latter was added to the former quickly with rapid stirring. The reaction mixture was stirred for 1 h at −78°C, leading to an almost colourless solution and a white insoluble solid. The reaction mixture was warmed to −20°C and stirred for a further 1 h, during which time the colour changed to light blue; the reaction mixture was then warmed to 0°C, and stirred for a further 2 h, to afford a dark blue solution with a white precipitate; finally, the reaction mixture was warmed to room temperature, and stirred overnight, resulting in an orange solution and a white precipitate. Pentane (15 mL) was added, and the suspension filtered via cannula at room temperature; the residue was then washed with a toluene:pentane mixture (2:1, 2 x 10 mL), and these washings were combined with the filtrate. The resulting clear orange filtrate was concentrated *in vacuo* to about 2 mL, then cooled to 0°C. Pre-cooled (0°C) pentane (5 mL) was added, and a light yellow solid precipitated, which was isolated by filtration at 0°C, washed with pre-cooled (0°C) pentane (2 x 10 mL) at 0°C, and dried *in vacuo* to yield 0.759 g (1.39 mmol, 69.5%) of a white powder. ^{1}H NMR data (C_6D_6) were consistent with literature values.[49]

Preparation of (I-Me$_4$)(Ar^{Tripp})GeCl, ***2.33***



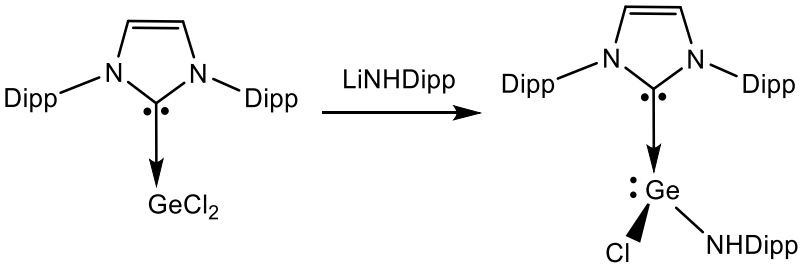
(I-Me_4)(Ar^{Tripp})GeCl was prepared according to the procedure of Filippou.[49] A solution of I-Me_4 (0.093 g, 0.749 mmol, 1.1 equiv.) in toluene (10 mL) was added to an orange solution of (Ar^{Tripp})GeCl (0.400 g, 0.678 mmol) also in toluene (10 mL) with rapid stirring at room temperature, resulting in an immediate colour change to a light yellow. The solution was stirred for a further 30 min, and then the toluene removed *in vacuo*. The light yellow residue was washed with hexane (2 x 5 mL) and dried to yield 0.374 g (0.524 mmol, 77.3%) of a white solid. ^{1}H NMR data (C_6D_6) were consistent with literature values.[49]

Preparation of (IPrMe){(Me_3Si)$_3$Si}GeCl, ***2.34***



(IPrMe){(Me_3Si)$_3$Si}GeCl was prepared according to a procedure modified from that of Escudié and Castel.[53] Separately, a solution of Mg{Si($SiMe_3$)$_3$}$_2$·2THF (0.282 g, 0.425 mmol, 0.55 equiv.) in THF (10 mL) and a solution of (IPrMe)$GeCl_2$ (0.250 g, 0.772 mmol) also in THF (10 mL) were cooled to −35°C, and the former added dropwise to the latter. The reaction mixture was stirred for 30 min at this temperature, then slowly warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the orange residue extracted with toluene (2 x 20 mL). After removal of the solvent *in vacuo*, the oily residue was triturated with pentane (2 x 5 mL) and stored at −25°C overnight, to yield 0.204 g (0.381 mmol, 49.3%) of a pale yellow solid that could be isolated by filtration. ^{1}H NMR data (C_6D_6) were consistent with literature values.[53]

Preparation of (IDipp)(DippNH)GeCl, ***2.35***



(IDipp)(DippNH)GeCl was prepared according to a procedure modified from that of Rivard.[54] Separately, a solution of LiNHDipp (0.172 g, 0.939 mmol) in Et_2O (10 mL) and a solution of (IDipp)$GeCl_2$ (0.500 g, 0.940 mmol) also in Et_2O (10 mL) were cooled to −35°C, and the former added dropwise to the latter. The reaction mixture was stirred for 30 min at this temperature, then slowly warmed to room temperature and stirring was then continued overnight. The solvent was removed *in vacuo*, and the resulting residue extracted with toluene (2 x 20 mL); this could then be removed *in vacuo*, and the crude product washed with hexane (2 x 10 mL) to yield 0.580 g (0.862 mmol, 91.7%) of an off-white solid. ^{1}H NMR data (C_6D_6) were consistent with literature values.[54]

2.3.7 Preparation of WCA precursors

*Preparation of Li[Al(OR^F)$_4$], **2.36***

$$Li[AlH_4] \xrightarrow{HOC(CF_3)_3} Li[Al(OC(CF_3)_3)_4]$$

Li[Al(OR^F)$_4$] was prepared according to a procedure modified from that of Krossing.[55] Purified $Li[AlH_4]$ (0.265 g, 6.98 mmol) was slurried in toluene (30 mL) at 0°C, and $HOC(CF_3)_3$ (4.00 mL, 28.7 mmol, 4.1 equiv.) was added via syringe over 5 min; the reaction mixture was then stirred for 1 h at 0°C, then heated under reflux overnight. A light orange solution was formed, accompanied by some grey precipitate. The suspension was cooled to −30°C for 1 h, causing the precipitation of more solid, and this precipitate was then isolated by filtration. This crude material was purified by sublimation (130°C, $4x10^{-2}$ mbar, ca. 2 h) to yield 4.99 g (5.12 mmol, 73.4%) of a white powder. ^{19}F, ^{27}Al and ^{13}C NMR data ($CDCl_3$) were consistent with literature values[55] (though in our hands the compound was insoluble in $CDCl_3$, and addition of a drop of THF was necessary to achieve solubility).

*Preparation of Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (Na[BArF$_{24}$]), **2.37***

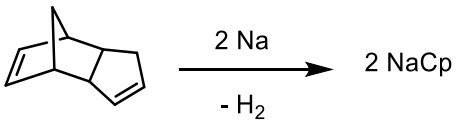
$$Na[BF_4] \xrightarrow{Mg,\ 3,5\text{-}(CF_3)_2C_6H_3Br} Na[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$$

$Na[BArF_{24}]$ was prepared according to the procedure of Reger.[56] A 1000 mL three-necked round bottomed flask fitted with a reflux condenser and an addition funnel was charged with magnesium turnings (2.02 g, 83.1 mmol, 6.5 equiv.), $Na[BF_4]$ (1.40 g, 12.8 mmol) and Et_2O (300 mL). 1,2-

dibromoethane (1.0 ml, 11.6 mmol, 0.9 equiv.) was added, and the flask heated for several minutes with a heat gun to initiate the reaction. After the heat was removed, 3,5-bis(trifluoromethyl)bromobenzene (12.4 ml, 71.9 mmol, 5.6 equiv.) diluted with Et_2O (100 mL) was added dropwise over 30 min, such that a gentle reflux was maintained. After the addition was complete, the reaction mixture was heated with an oil bath to continue the reflux for a further 30 min. The heat was then removed, and the reaction mixture left to stir overnight at room temperature. It was then opened to air and added to Na_2CO_3 (32 g) in water (400 mL), stirred for 30 min, and filtered. The aqueous phase was then extracted with Et_2O (3 x 50 mL), and the combined organic phases dried over $MgSO_4$ and treated with decolourising charcoal. The suspension was then filtered, and the solvent removed *in vacuo* to yield an oily solid. This was dissolved in benzene (400 mL), and water was removed using a Dean-Stark trap by azeotropic distillation for 2 h. The orange supernatant could then be removed by cannula-filtration at room temperature, and the remaining solid dried overnight *in vacuo* to yield 7.40 g (8.35 mmol, 65.2%) of a white solid. ^{1}H, ^{11}B and ^{19}F NMR data (d_6-acetone) were consistent with literature values.[56,57] Note that a superior work-up and drying procedure, utilising a double recrystallisation step followed by drying at high temperature *in vacuo* (rather than the tedious azeotropic distillation deployed here), has very recently been published.[58]

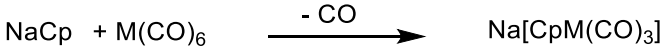
2.3.8 Preparation of transition metal precursors

Preparation of sodium cyclopentadienide (NaCp), ***2.38***



NaCp was prepared by Dr. René Frank according to the procedure of Roesky.[59]

*General procedure for preparation of the metal salts Na[CpM(CO)$_3$] (M = Mo {**2.39**}, W {**2.40**})*



The carbonylate species Na[CpM(CO)$_3$] (M = Mo, W) were prepared according to a common procedure, modified from that of Wilkinson,[60] which is exemplified here for the case of M = Mo. To a Schlenk flask containing NaCp (0.668 g, 7.58 mmol) and $Mo(CO)_6$ (2.00 g, 7.58 mmol) was added THF (100 mL). The

reaction mixture was then heated under reflux overnight. After cooling to room temperature, the resulting orange solution was filtered from a small amount of insoluble brown material, and the THF then removed *in vacuo*. The crude product was then washed with hexane (2 x 20 mL) to yield 1.62 g (6.04 mmol, 79.7%) of a light yellow powder. For the case of $Na[CpW(CO)_3]$, the use of $W(CO)_6$ (2.00 g, 5.68 mmol) with analogous stoichiometry of other reagents gave a yield of 1.29 g (3.62 mmol, 63.8%) of a light yellow powder. ^1H and ^{13}C NMR (CD_3CN for M = Mo, d_6-acetone for M = W), and IR data were consistent with literature values.[61,62]

Preparation of Li[CpMo(CO)$_3$], ***2.41***

$$Na[CpMo(CO)_3] \xrightarrow{HCl} CpMo(CO)_3H \xrightarrow{^nBuLi} Li[CpMo(CO)_3]$$

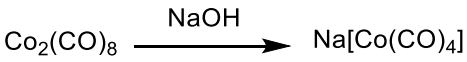
$Li[CpMo(CO)_3]$ was prepared according to a procedure modified from that of Filippou.[63–66] An orange solution of $Na[CpMo(CO)_3]$ in THF was freshly prepared as above (from 2 g [22.7 mmol] of NaCp and 6 g [22.7 mmol] of $Mo(CO)_6$). To this was added at room temperature an excess of aqueous HCl (4 mL of a 37% by weight solution in water), leading to the appearance of a white precipitate. Excess HCl was quenched by the addition of degassed NEt^iPr_2 (5 mL), leading to further white precipitate, and the orange solution was filtered from the precipitated NaCl and $[NEt^iPr_2]Cl$. The solvent was removed *in vacuo* to give a yellow residue, which was purified by sublimation (50°C, $4x10^{-2}$ mbar, ca. 2 h) to afford $CpMo(CO)_3H$ as a yellow crystalline solid (4.12 g, 16.7 mmol, 73.8%). This was dissolved in pentane (60 mL), and ^{n}BuLi (11.6 mL of a 1.6 M solution in hexane, 18.6 mmol, 1.1 equiv.) added dropwise at −40°C, resulting in an immediately cloudy solution. The reaction mixture was warmed to room temperature and then stirred for a further 1 h. The precipitate was isolated by filtration, washed with pentane (2 x 10 mL) and dried *in vacuo* to yield 3.96 g (15.7 mmol, 94.1% based on $CpMo(CO)_3H$, 69.2% based on $Mo(CO)_6$) of a cream solid. ^1H and ^{13}C NMR (CD_3CN), and IR data were consistent with literature values.[66]

Preparation of Na[CpFe(CO)$_2$], ***2.42***

$$\{CpFe(CO)_2\}_2 \xrightarrow{Na/Hg} Na[CpFe(CO)_2]$$

$Na[CpFe(CO)_2]$ was prepared by Dr. René Frank according to the procedure of Hartwig.[67]

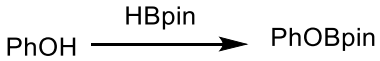
Preparation of $Na[Co(CO)_4]$, ***2.43***



$Na[Co(CO)_4]$ was prepared by James Howell according to the procedure of Horváth.[68]

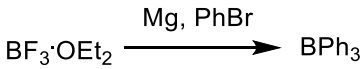
2.3.9 Preparation of miscellaneous compounds

Preparation of PhOBpin, ***2.44***



PhOBpin was prepared according to a procedure modified from that of Bertrand.[69] In a Schlenk flask, PhOH (0.100 g, 1.06 mmol) was dissolved in acetonitrile (10 mL), and to this solution was added HBpin (0.30 mL, 2.07 mmol, 2 equiv.). The solution was then stirred for 1 h. After this period, the volatiles were removed *in vacuo*, to yield 0.202 g (0.918 mmol, 86.6%) of a white crystalline solid. ^{1}H and ^{11}B NMR data ($CDCl_3$) were consistent with literature values.[54] NMR data were also recorded in C_6D_5Br and d_8-THF, for comparison with reaction mixtures in Chapter 4 [^{1}H NMR (400.2 MHz, C_6D_5Br [d_8-THF], 298 K): 1.29 [1.28] (s, 12H, C4/C5-C**H**$_3$), 7.07-7.34 [6.96-7.23] (m, 5H, Ph); $^{11}B\{^{1}H\}$ NMR (128.4 MHz, C_6D_5Br [d_8-THF], 298K): 22.1 [21.8] (**B**pin) ppm].

Preparation of triphenyl borane (BPh_3), ***2.45***



BPh_3 was prepared by Lu Ying according to the procedure of Brown.[70]

2.4 References

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Chapter III

Synthesis and Structure of Low-Valent Germanium Cations

3.1 Introduction

3.1.1 Strongly donating ligands in low-valent germanium chemistry

Synthetic and reactivity studies of digermenes,[1] digermynes,[1] germylenes,[2] germylynes[3] and related low-valent germanium compounds have been an area of considerable interest over recent decades. Some of the landmark and most reactive examples of these compounds have featured strongly σ-donating ligands such as boryl,[4,5] terphenyl[6–13] and silyl[4] ligands.

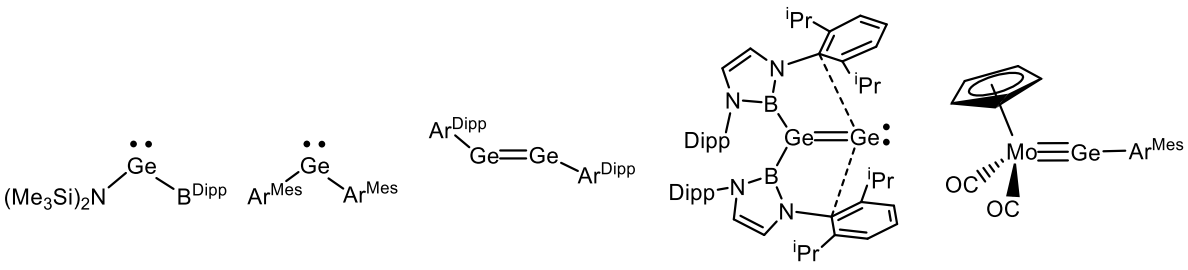


Figure 3.1: Landmark germanium compounds featuring boryl and terphenyl ligands

Cationic germylium-ylidenes have, by contrast, been considerably less explored than these neutral systems,[14–16] and there are no isolable examples of germylium-ylidenes featuring boryl, terphenyl,[17] silyl and related strong σ-donor ligands. The synthesis of such cations would be expected to be of considerable interest in terms of their structure and bonding, as well as in engendering reactive germanium centres capable of small molecule activation.

3.1.2 Structural features of low-valent group 14 compounds

Subtle steric and electronic effects influence the structure of low-valent germanium species.[18] Thus, for example, $(Ph_2Ge)_n$ exists as polymers[19] or cyclic oligomers (n = 4, 5, 6),[20–24] $Mes_2Ge{=}GeMes_2$ is dimeric in the solid state and solution,[25] (Tbt)(Mes)Ge=Ge(Mes)(Tbt) is dimeric in the solid state and exists in equilibrium with the corresponding germylene in solution,[26,27] and (Tbt)(Tripp)Ge is a monomeric germylene both in the solid state and solution.[28] Regarding cationic systems (where there

is an additional electrostatic disincentive to aggregation), [(NHC){Cp*W(CO)$_3$}Ge]^+_n (**1.67**) is dimeric when NHC = I-Me$_4$ or IPrMe, but monomeric when NHC = IDipp.[29]

Considerations other than simple steric bulk/ligand donor strength also apply. Secondary interactions with the backbone/periphery of the ligands (e.g. through dispersion forces) may help to stabilise a monomeric germanium species (Figure 3.2). Complexation between arenes and low-valent main group elements has long been known[30] (though with relatively few examples for germanium),[31,32] and hence flanking aryl interactions between ligand peripheries and low-valent centres is a possible means of stabilisation. Such interactions have been identified in a diarsagermylene prepared by Izod (where the inability of As to planarise prevents As-Ge π-donation),[33] in a boryl-substituted digermavinylidene,[5] in quasi-one-coordinate amido-substituted germylium-ylidenes synthesised by Jones[34] and Hinz,[35] and recently in [(Ar^{Tripp})GeH$_2$]$^+$.[17] Regarding the other members of group 14, Wesemann has studied flanking aryl interactions of terphenyl ligands in stannylium-ylidenes,[17,36,37] interactions which have also been observed in silylium cations.[38,39] Interactions with aromatic solvents are also a possibility, with Power's quasi-one-coordinate lead cation exhibiting a weak interaction with a toluene molecule,[40] and Wesemann's recent analogous tin compound being stabilised by benzene coordination.[17] That (Ar^{Tripp})E group 13 species do not engage[41–43] in aryl interactions but isoelectronic [L$_n$(Ar^{Tripp})E]$^+$ group 14 cations do[17] is telling of the considerable electrophilicity engendered by cationisation.

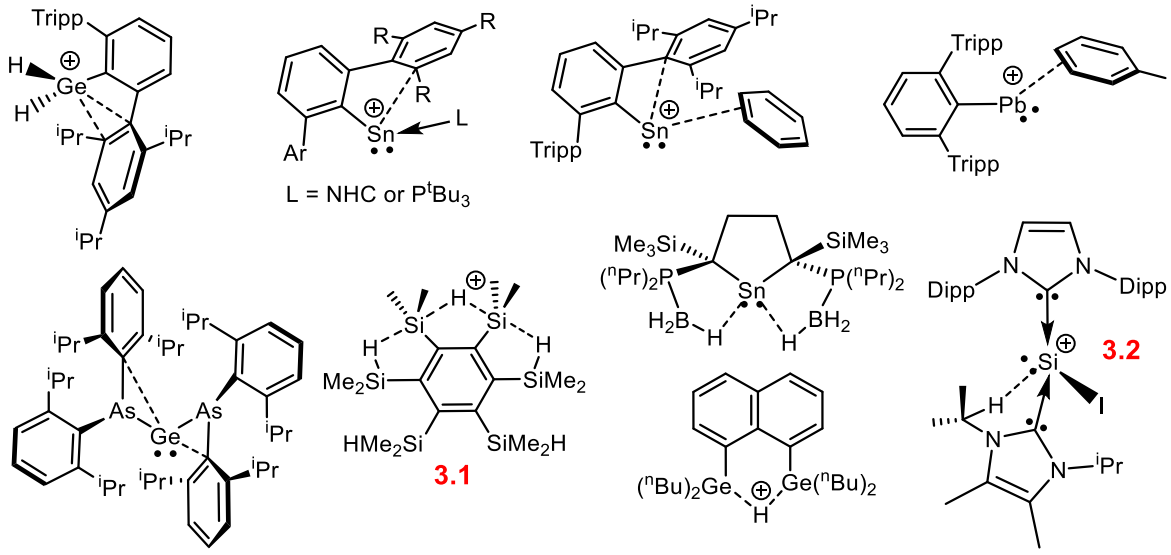
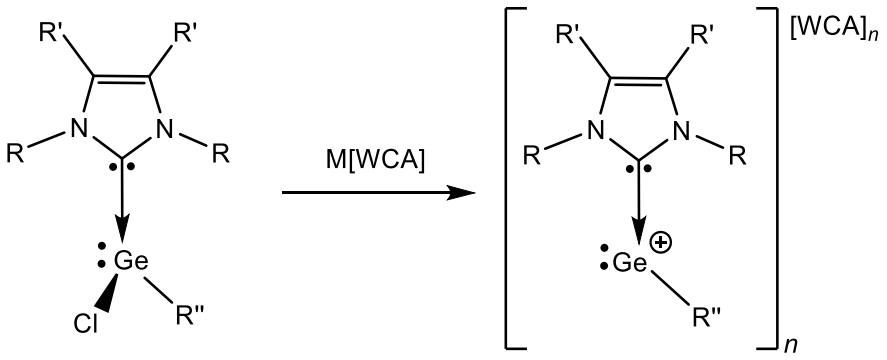


Figure 3.2: Novel interactions involving low-valent group 14 species (counteranions: (top row) [Al(OR^F)$_4$]$^-$, [HB(C$_6$F$_5$)$_3$]$^-$, [Al(OR^F)$_4$]$^-$, [MeB(C$_6$F$_5$)$_3$]$^-$, (bottom row) N/A, [BArF$_{20}$]$^-$, N/A, [BArF$_{20}$]$^-$, I$^-$)

Bridging Si-H-Si interactions have been observed in many silylium cations,[44–48] as have agostic interactions[49] (involving either Si-H or C-H[50,51] bonds). **3.1** is a beautiful example illustrating both of these types of interaction.[52,53] These features have also been seen in germylium cations, though much more rarely.[51,54,55] Furthermore, Izod has demonstrated various examples of B-H···Sn/Pb agostic interactions in stannylenes and plumbylenes.[56–62] A more obscure interaction was observed by Filippou in the silylium-ylidene $[(IDipp)(IPrMe)SiI]^+$ (**3.2**).[63] The shortness of a C-H···Si interaction involving the $CH(CH_3)_2$ group of the IPrMe ligand (2.57(1) Å), as well as the presence of a doublet (J = 10.4 Hz) in the ^{29}Si NMR spectrum (that could be confirmed by 2D techniques as being due to coupling to an IPrMe C**H**$(CH_3)_2$ proton), led to a description of this cation as featuring an anagostic interaction involving silicon. Such an interaction, between the silicon lone pair and the C-H bond, is interesting as a potential intermediate towards C-H activation.[63]

3.2 Project aims

In this chapter, efforts towards the synthesis and characterisation of low-valent germylium-ylidenes will be described. Primarily, this will involve the use of boryl, silyl and terphenyl ligands, with the aim of generating reactive cations capable of E-H bond activation. Amido-substituted cations will provide comparison. Given the lack of any examples of isolable truly one-coordinate tetrylium-ylidenes, even with the use of extremely bulky ligands,[34] and the extreme reactivity displayed by one-cooordinate terphenyl-substituted silylium-ylidenes[39] and germylium-ylidenes[17] upon *in situ*-generation, the possibility of isolating one-coordinate germylium-ylidenes substituted solely by strong donors seems slim. Hence, pairing with an additional neutral donor is appropriate, with the criteria of being small (so as not to sterically prejudice further oxidative reactivity), featuring relatively inert peripheral moieties, and being readily synthetically accessible in good yield. The I-Me_4 and IPrMe (and IMes and IDipp to a lesser extent) NHCs are thus ideal for this purpose, with the choice providing room for variation in steric bulk and donor strength.



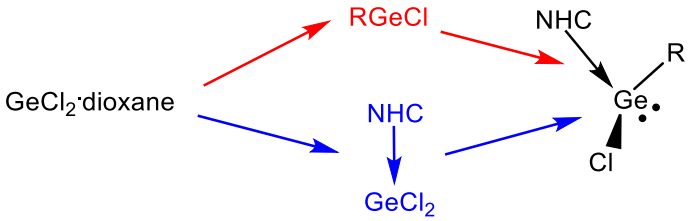
Scheme 3.1: Target synthetic route to novel germylium-ylidenes

Given the established synthetic viability of NHC-coordinated boryl-, silyl-, terphenyl- and amido-substituted chlorogermylenes,[5,64–66] these provide an ideal library of starting materials for the synthesis of germylium-ylidenes by chloride abstraction. Efforts towards the syntheses of known and novel NHC-coordinated chlorogermylenes will be described. Weakly coordinating anions can then be introduced via chloride abstraction with their alkali metal salts, to hopefully generate low-valent germylium-ylidenes.

3.3 Results and discussion

3.3.1 Chlorogermylene synthesis and structure

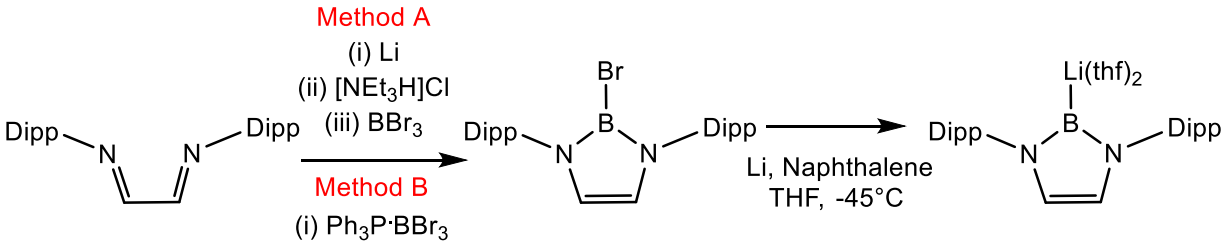
The synthesis of NHC-coordinated chlorogermylenes of the type (NHC)(R)GeCl can be envisaged via two routes starting from commercially available $GeCl_2$·dioxane: either initial salt metathesis with an alkali metal salt of the anionic ligand to form donor-free chlorogermylenes, $(RGeCl)_n$, followed by coordination of an NHC; or initial synthesis of NHC($GeCl_2$) adduct, followed by salt metathesis. Both of these routes for different ligand combinations will be explored in this section.



Scheme 3.2: Possible syntheses of chlorogermylenes

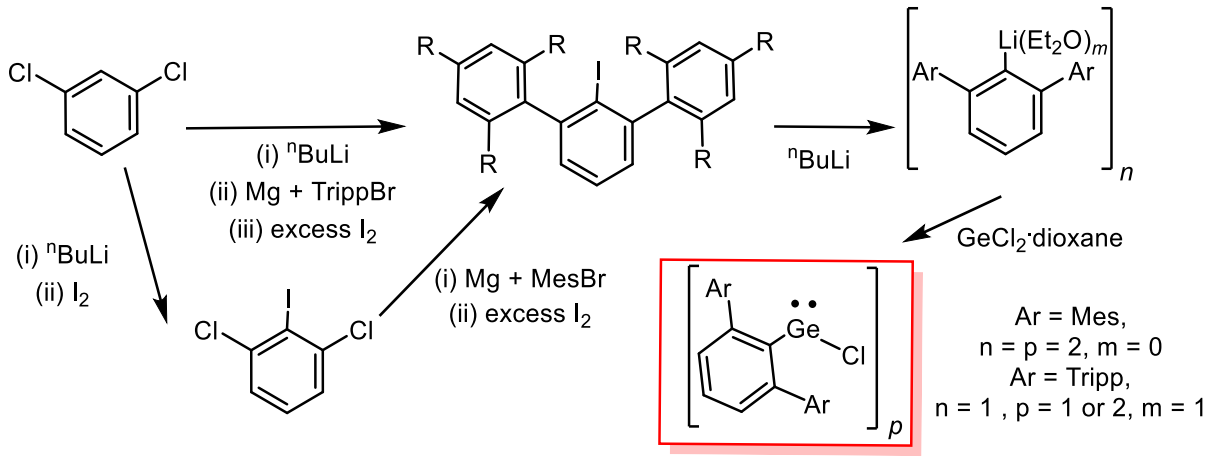
The boryllithium reagent $(B^{Dipp})Li(thf)_2$ is the variant that has been by far the most widely deployed,[67] particularly within main group chemistry and especially within the Aldridge group;[4,68–71] hence this boryl system has been exclusively utilised in this work, given the group's synthetic expertise and

experience. It can be prepared in a notoriously frustrating procedure by reduction of the bromoborane precursor (B^{Dipp})Br.[72] This bromoborane was prepared via the "traditional" procedure originally deployed by Yamashita and Nozaki, of reduction of the diazabutadiene precursor with lithium followed by treatment with BBr_3.[72] Although a quicker method, via direct reaction of the diazabutadiene with $Ph_3P{\cdot}BBr_3$,[73] has been more recently reported, this was found to give a product of insufficient purity for subsequent reduction to the boryllithium.



*Scheme 3.3: Syntheses of the bromoborane, (B^{Dipp})Br (**2.3**), and its reduction to boryllithium (**2.4**)*

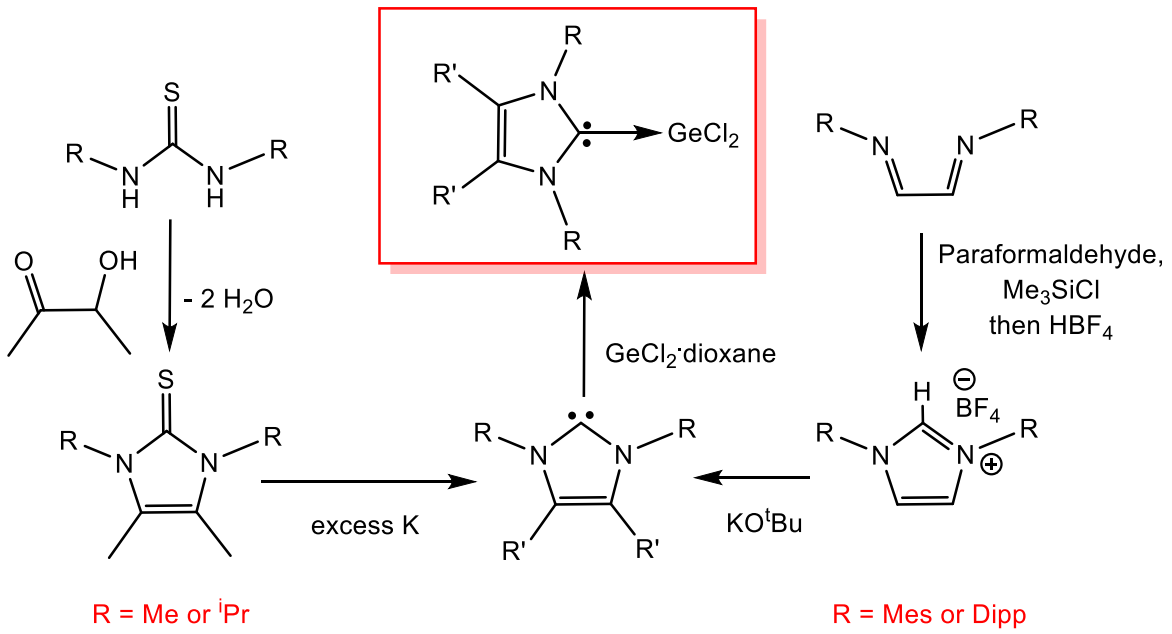
The Ar^{Mes} and Ar^{Tripp} terphenyl ligands have also been utilised in this work, due to a desire for contrasting steric bulk combined with their relative synthetic ease; though the Ar^{Dipp} ligand has been widely deployed by the Power group,[11,12,74,75] the steric contrast to Ar^{Mes} or Ar^{Tripp} was not enough to motivate its lengthier synthesis (as DippBr is, unlike MesBr and TrippBr, commercially unavailable/unreasonably expensive). The terphenyl iodide precursors (Ar^{Mes})I and (Ar^{Tripp})I were prepared on a large scale (ca. 40 g) via established Hart coupling methodologies.[75–77] In the case of (Ar^{Tripp})I, this was done in a one-step procedure;[78] however, in synthesising (Ar^{Mes})I, the intermediate dichloroiodobenzene was isolated due to private communications suggesting this was a higher yielding route to a cleaner product.[79–81] These iodide precursors could then be lithiated using ^{n}BuLi according to modified literature procedures.[82,83] (Mes*)Br was synthesised via the reaction of Mes*H with Br_2,[84] and could also be readily lithiated with ^{n}BuLi.[85]



*Scheme 3.4: Syntheses of iodo-terphenyl precursors (**2.7**, **2.8**), subsequent lithiation (**2.10**, **2.11**), and synthesis of terphenyl-substituted chlorogermylenes (**2.13**, **2.14**)*

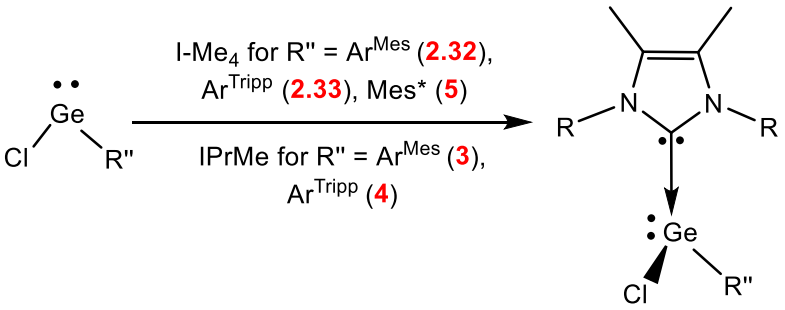
(Ar^{Tripp})Li(Et_2O), (Ar^{Mes})Li and (Mes*)Li could all be combined with $GeCl_2$·dioxane to furnish previously reported chlorogermylenes of the form $(ArGeCl)_n$.[7,86,87] For all of these reactions care has to be taken with regards to stoichiometry and rate of addition, as the corresponding diaryl germylenes can be formed (e.g. if one adds (Ar^{Mes})Li to $GeCl_2$·dioxane too quickly, the characteristic bright purple colour of (Ar^{Mes})$_2$Ge appears, rather than the desired orange). No species of the type $(ArGeCl)_n$ are known for less bulky aryl groups, and despite attempts these could not be obtained in this work. Furthermore, (B^{Dipp})GeCl (as well as the bis(boryl) germylene) has proven inaccessible despite numerous synthetic attempts by myself and others within the Aldridge group, primarily due to the tendency for formation of the chloroborane (B^{Dipp})Cl. Similarly, the unreported hypersilyl system {(Me_3Si)$_3$Si}GeCl could not be accessed. Presumably, as occurs in attempts to synthesise {(Me_3Si)$_3$Si}$_2$Ge, there is migration of $SiMe_3$ groups to the germanium centre (indeed, {(Me_3Si)$_3$Si}$_2$Ge has only been synthesised when stabilised by an additional phosphine or NHC donor).[88,89]

Within this work, (NHC)$GeCl_2$ compounds have been synthesised reproducibly in good yield according to literature procedures for NHC = I-Me_4,[64] IPrMe,[90] IDipp,[91] as well as for (previously unreported) IMes (**1**), by the combination of the free NHC and $GeCl_2$·dioxane. These NHCs themselves can readily be accessed from air-stable precursors, either via reduction of thiones with potassium,[92] or deprotonation of imidazolium salts with KO^{t}Bu.[93] The novel diiodo complex (IDipp)GeI_2 (**2**) was also made, given the incompatibility of some potential onward reagents with chloride and the greater leaving group ability of iodide.[63,90]



*Scheme 3.5: Syntheses of NHC precursors (**2.20**-**2.23**), NHCs (**2.24**-**2.27**) and (NHC)$GeCl_2$ adducts (**2.28**-**2.30**, **1**)*

Addition of either I-Me_4 or IPrMe to orange solutions of (Ar^{Mes})GeCl or (Ar^{Tripp})GeCl in toluene at room temperature led to immediate decolourisation; following washing with hexane to remove any of the readily soluble starting materials, the hexane-insoluble chlorogermylenes (I-Me_4)(Ar^{Mes})GeCl (**2.32**), (I-Me_4)(Ar^{Tripp})GeCl (**2.33**), (IPrMe)(Ar^{Mes})GeCl (**3**) and (IPrMe)(Ar^{Tripp})GeCl (**4**) could be isolated in good yield. The I-Me_4-coordinated species have been previously reported by Filippou,[64] although only **2.33** was crystallographically characterised. While further crystallographic characterisation proved elusive in this study, the ^{1}H NMR spectra are informative concerning the relative degrees of steric crowding about the germanium centres. Thus, (IPrMe)(Ar^{Tripp})GeCl features two well-resolved ^{1}H NMR signals ($v_{1/2}$ = 31.0 Hz and 31.1 Hz) corresponding to the two NHC C**H**(CH_3)$_2$ protons, while (IPrMe)(Ar^{Mes})GeCl features two extremely broad signals ($v_{1/2}$ = 121.5 Hz and 111.3 Hz) characteristic of intermediate exchange, and the even less sterically encumbered (IPrMe)(B^{Dipp})GeCl (**2.31**, *vide infra*) features a single signal ($v_{1/2}$ = 31.6 Hz) corresponding to two protons in the fast exchange regime. With a view to targeting a germanium analogue of Wesemann's [(^{t}Bu$_3$P)(Ar^{Tripp})Sn]$^+$,[36] the coordination of P^{t}Bu$_3$ was attempted with (Ar^{Mes})GeCl and (Ar^{Tripp})GeCl; however, no reaction was observed in either case, potentially reflecting the smaller size of germanium as compared to tin (though, in Wesemann's case, it should be noted that the cation was not accessed via the corresponding chlorostannylene).



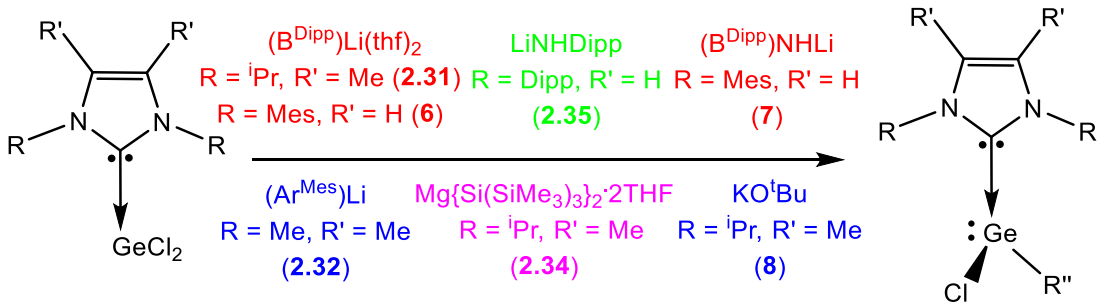
*Scheme 3.6: Synthesis of chlorogermylenes (**2.32**, **2.33**, **3**, **4** and **5**) via NHC addition to species of the type $(RGeCl)_n$*

Combination of I-Me_4 and (Mes*)GeCl in C_6D_6 in a J. Young's NMR tube led initially to the clean formation of a single new species observable by ^{1}H NMR spectroscopy, proposed to be (I-Me_4)(Mes*)GeCl (**5**). However, rapidly (within 1 h), a multitude of new resonances appeared in the ^{1}H NMR spectrum, accompanied by the formation of precipitate that could be isolated and identified by ^{1}H NMR spectroscopy as featuring the $[I\text{-}Me_4H]^+$ cation, suggesting that the steric encumbrance of the ligands in this case is excessive, and leads to the chlorogermylene being unstable at room temperature. This is consistent with the unavoidable steric crowding provided in the locality of element centres by Mes* ligands, as opposed to more flexible terphenyl ligands. Formation of the chlorogermylene *in situ* followed by immediate reaction with a chloride abstraction agent at low temperature was attempted to see if this could alleviate the steric pressure and enable the isolation of a stable cation, however this proved unsuccessful.

Metathesis of an alkali metal salt of a ligand with an NHC adduct of $GeCl_2$ has been utilised for the boryl and silyl cases where RGeCl is inaccessible. (IPrMe)(B^{Dipp})GeCl[5] (**2.31**) and (IMes)(B^{Dipp})GeCl (**6**) were obtained in good yield from the addition of (B^{Dipp})Li(thf)$_2$ to the corresponding adducts (NHC)$GeCl_2$ at −35°C in Et_2O. Interestingly, all additions of (B^{Dipp})Li(thf)$_2$ to (I-Me_4)$GeCl_2$ (either at −35°C or −78°C in Et_2O) only resulted in the isolation of decomposition products, primarily $B^{Dipp}H$. Potentially, I-Me_4 may provide too little steric bulk to stabilise the (B^{Dipp})GeCl moiety. However, it seems peculiar that such a small change may produce such a drastic effect; an alternative explanation could be that the more acidic NCH_3 protons are more liable to deprotonation by the highly reactive boryllithium. Towards the other extreme, a boryl analogue of (IDipp){$(Me_3Si)_2HC$}GeCl was sought featuring the

IDipp carbene, however this appears to be too bulky (%V_{bur}: 36.5% (IMes) and 45.4% (IDipp)),[94] and again only decomposition products were observed.

In a modified literature procedure, the combination of Mg{Si(SiMe$_3$)$_3$}$_2$·2THF with (IPrMe)GeCl$_2$ enabled the synthesis of (IPrMe){(Me$_3$Si)$_3$Si}GeCl (**2.34**).[65] As reported in the literature, attempted reactions between KSi(SiMe$_3$)$_3$·2THF and (IPrMe)GeCl$_2$ were unsuccessful, with the only identifiable product in the ^{29}Si NMR spectrum being small amounts of the disilagermirane (Me$_3$Si)$_2$Si{Ge(SiMe$_3$)$_2$}Si(SiMe$_3$)$_2$.[95] Hence, the milder magnesium reagent (synthesised in turn from the potassium species) was utilised.



*Scheme 3.7: Synthesis of chlorogermylenes (**2.31**, **2.32**, **2.34**, **2.35**, **6**, **7**, **8**) via salt metathesis with (NHC)GeCl$_2$*

For terphenyl ligands, the yields of (ArGeCl)$_n$ for Ar^{Mes} and Ar^{Tripp} have been found to be poor, hence the synthesis of chlorogermylenes via (NHC)GeCl$_2$ was viewed as a preferable route. In practice this has only been achieved for the least sterically crowded system, **2.32**,[64] with no chlorogermylene isolable from the reaction of (Ar^{Mes})Li and (IPrMe)GeCl$_2$.

Amido-substituted chlorogermylenes were also sought, as π-donating, σ-withdrawing comparisons to the above cases. Thus, (IDipp)(DippNH)GeCl (**2.35**) could be obtained following the procedure of Rivard, via the combination of LiNHDipp and (IDipp)GeCl$_2$ in Et$_2$O,[66] while (IMes){(B^{Dipp})NH}GeCl (**7**) was synthesised from the combination of (B^{Dipp})NHLi and (IMes)GeCl$_2$ in a new procedure. Single crystals of **7** suitable for X-ray diffraction were obtained by layering a concentrated toluene solution with hexane, and the resulting structure is shown in Figure 3.3. The alkoxide-substituted (IPrMe)(O^{t}Bu)GeCl (**8**) was also synthesised analogously from KO^{t}Bu and (IPrMe)GeCl$_2$; given that (IPrMe)Ge(O^{t}Bu)$_2$ is accessible,[96] slow addition of one equivalent of KO^{t}Bu at low temperature was necessary to ensure monosubstitution.

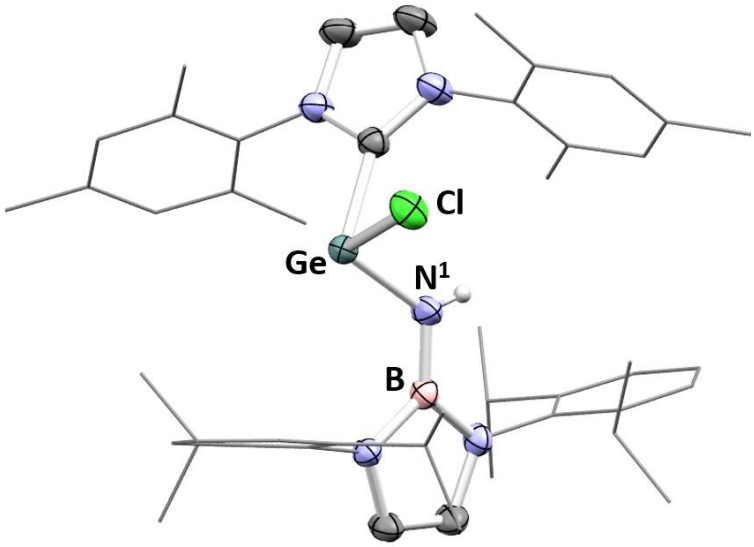


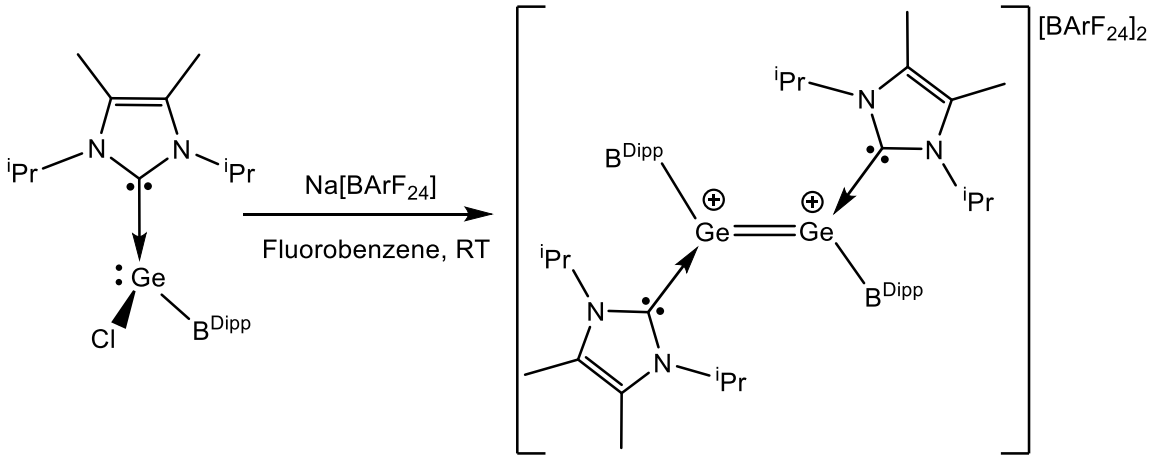
*Figure 3.3: Structure of **7**. For clarity, hydrogen atoms (other than GeN**H**) omitted, and NHC Mes and B^{Dipp} Dipp groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-N^1: 1.877(2), Ge-C_{NHC}: 2.114(2), Ge-Cl: 2.3095(7), N^1-Ge-C_{NHC}: 95.85(9)*

While terphenyl- and boryl-substituted germylenes have a storied history in small molecule activation, this is less the case for chlorogermylenes due to the electron-withdrawing nature of the chloride substituent (with no reported examples of E-H bond activation for $(ArGeCl)_n$ species). Furthermore, the donation of an NHC into the empty orbital of a germylene would be further expected to quench its possible reactivity.[97] Thus, for example, the addition of the "germylene trap" Et_3SiH to $(IPrMe)(B^{Dipp})GeCl$ yielded no reaction, even after prolonged heating at elevated temperature.

3.3.2 Synthesis and structure of boryl-substituted germanium cations

Following synthesis of NHC-coordinated chlorogermylenes, chloride abstraction with alkali metal salts of weakly coordinating anions could be attempted towards the synthesis of germylium-ylidenes. $Li[Al(OR^F)_4]$ and $Na[BArF_{24}]$ were chosen for this purpose, as both of these can be accessed in reliable literature procedures,[98,99] and have been extensively applied for the isolation of germylium-ylidenes.[17,29,34,35,100–102] The availability of a choice of weakly coordinating anion is desirable, as, although both of these reagents would be expected to abstract a chloride, there are potential differences in solubility and crystallinity between complexes of the two anions. With regards to other potential options, salts of the $[BArF_{20}]^-$ anion are made via LiC_6F_5, which is potentially explosive,[103]

while carboranes have lengthy syntheses,[104] and hence the use of either of these was considered undesirable.



Scheme 3.8: Synthesis of ***[(9)$_2$][BArF$_{24}$]$_2$***

Combination of (IPrMe)(B^{Dipp})GeCl (**2.31**) and Na[BArF$_{24}$] in fluorobenzene at room temperature led to a rapid colour change to red and concomitant precipitate formation; following filtration, concentration, layering with hexane and storage at −25°C, deep red crystals could be isolated. These were revealed by X-ray diffraction analysis to contain the dicationic dimer, [(IPrMe)(B^{Dipp})Ge=Ge(B^{Dipp})(IPrMe)][BArF$_{24}$]$_2$, **[(9)$_2$][BArF$_{24}$]$_2$**. The contrast with the (monomeric) structure determined for [(IDipp){(Me$_3$Si)$_2$HC}Ge][BArF$_{24}$] (**1.33**) presumably reflects the lower cumulative steric demands of the B^{Dipp} and IPrMe fragments compared to CH(SiMe$_3$)$_2$ and IDipp, as well as the smaller HOMO-LUMO gap, which promotes dimerisation through the formation of donor/acceptor interactions. The electrostatic disincentive to dimerisation is presumably mitigated by delocalisation of the positive charge associated with each germanium centre into the carbene heterocycle.

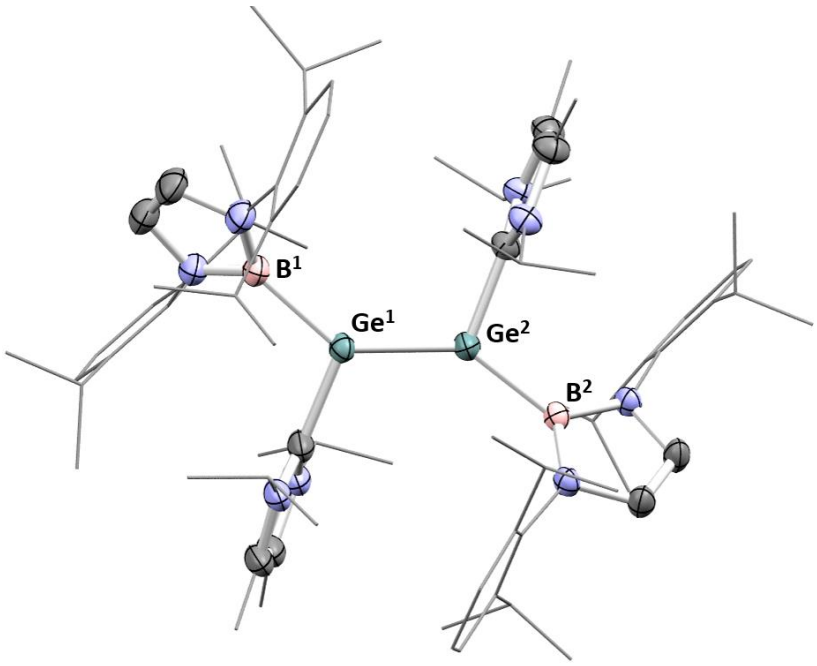


Figure 3.4: Structure of ***[(9)$_2$][BArF$_{24}$]$_2$****. For clarity, [BArF$_{24}$]$^-$ counteranions and hydrogen atoms omitted, and B^{Dipp} Dipp and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge^1-B^1: 2.081(3), Ge^2-B^2: 2.100(4), Ge^1-C$_{NHC}$^{1}: 2.002(3), Ge^2-C$_{NHC}$^{2}: 2.016(4), Ge^1-Ge^2: 2.300(2), B^1-Ge^1-C$_{NHC}$^{1}: 105.3(1), B^2-Ge^2-C$_{NHC}$^{2}: 107.4(2), B^1-Ge^1-Ge^2: 139.0(1), B^2-Ge^2-Ge^1: 136.1(1), C$_{NHC}$^{1}-Ge^1-Ge^2: 109.3(1), C$_{NHC}$^{2}-Ge^2-Ge^1: 109.6(1)*

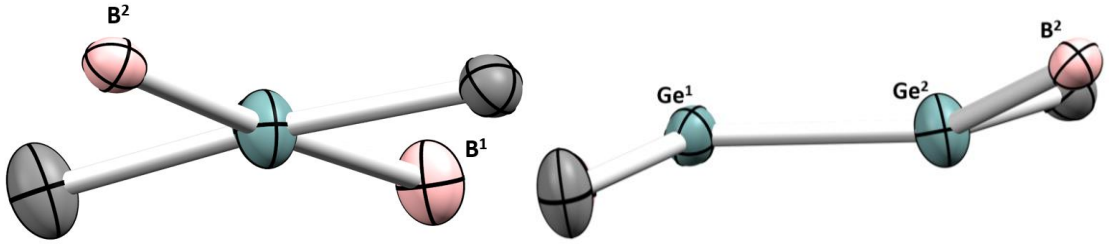


Figure 3.5: Newman projection along the Ge-Ge bond of ***[(9)$_2$][BArF$_{24}$]$_2$*** *(illustrating E geometry) (L), and a perpendicular view of the Ge-Ge bond (illustrating trans-bending and slight twist) (R)*

Concerning the structure of **[(9)$_2$][BArF$_{24}$]$_2$**, the Ge-Ge bond length of 2.300(2) Å is considerably shorter than twice the covalent radius of germanium (2.42 Å),[105] and consistent with digermenes of the form $R_2Ge=GeR_2$ (Table 3.1). Comparison of other structural metrics of **[(9)$_2$][BArF$_{24}$]$_2$** with these digermenes is also provided in Table 3.1; the trans-bent disposition of the ligands, *E* geometry (see Newman projection), and unspectacular slight twist about the Ge-Ge bond are all as expected for a digermene.[1] As such, **[(9)$_2$][BArF$_{24}$]$_2$** can be considered as a digermene featuring pendant (cationic) imidazolium units.

	[(9)$_2$][BArF$_{24}$]$_2$	**R$_2$GeGeR$_2$**	
		R = CH(SiMe$_3$)$_2$[106]	**R = Mes**[25]
Ge-Ge (Å)	2.300(2)	2.347(2)	2.286(1)
Trans-bent (fold) angle (°)	25.7 (Ge^1) and 26.0 (Ge^2)	32.0	33.4
Sum of angles at germanium (°)	353.6 (Ge^1) and 353.1 (Ge^2)	348.5	348.2
Twist angle (°)	4.2	0	2.9

*Table 3.1: Comparison of the structural metrics of **[(9)$_2$][BArF$_{24}$]$_2$** with those of charge-neutral digermenes, R$_2$GeGeR$_2$. Trans-bent angle found from C$_{NHC}$/B centroid-Ge-Ge angle. Twist angle is the angle between the two BGeC$_{NHC}$ planes.*

The Ge-Ge bond length is similar to the neutral boryl-substituted Ge^I compound (IPrMe)(B^{Dipp})Ge=Ge(B^{Dipp}) (2.279(1) Å).[5] It can also be compared to Tobita's cationic systems [(NHC){Cp*W(CO)$_3$}Ge=Ge{Cp*W(CO)$_3$}(NHC)]$^{2+}$ (bond lengths: 2.429(1) Å (NHC = IPrMe) and 2.345(2) Å (NHC = I-Me$_4$)),[29] suggesting that the steric bulk of the boryl ligand is smaller than this tungsten carbonyl fragment. The structure of **[(9)$_2$][BArF$_{24}$]$_2$** can also be compared to doubly-bonded digermynes such as Power's (Ar^{Dipp})GeGe(Ar^{Dipp}), which features a similar bond length (2.2850(4) Å) but a planar RGeGeR array. In **[(9)$_2$][BArF$_{24}$]$_2$** the central boryl rings are twisted from the central bond (dihedral angles between the planes defined by the central boryl ring and the BGeGeB array of 21.2° (Ge^1) and 73.5° (Ge^1)), as would be expected given the presence of the NHCs. Predictably, the central boryl and NHC rings are orientated approximately orthogonal to one another. This can be quantified by the dihedral angle between the least squares planes defined by the central rings of the boryl and NHC ligands, of 83.7° (Ge^1) and 82.5° (Ge^2) at each germanium centre (in subsequent discussion, these planes will be referred to as B^{plane} and NHC^{plane}, respectively).

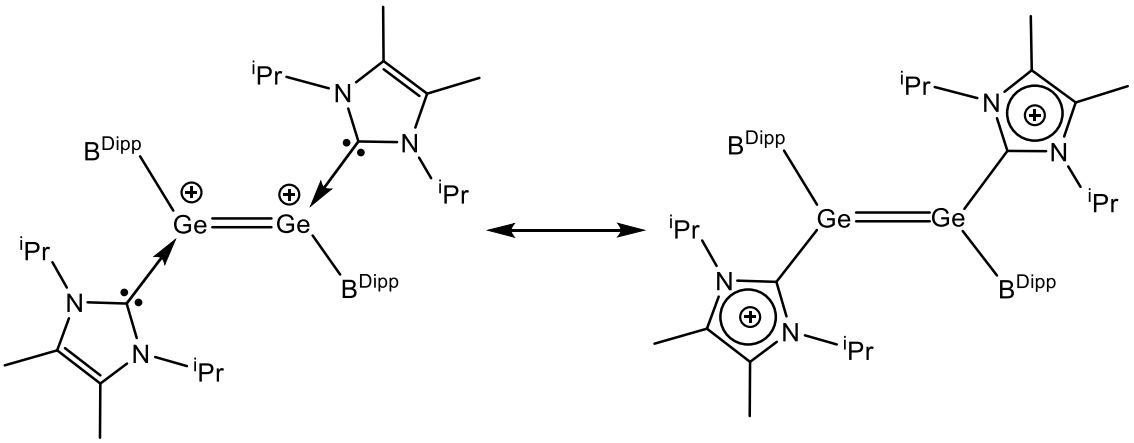
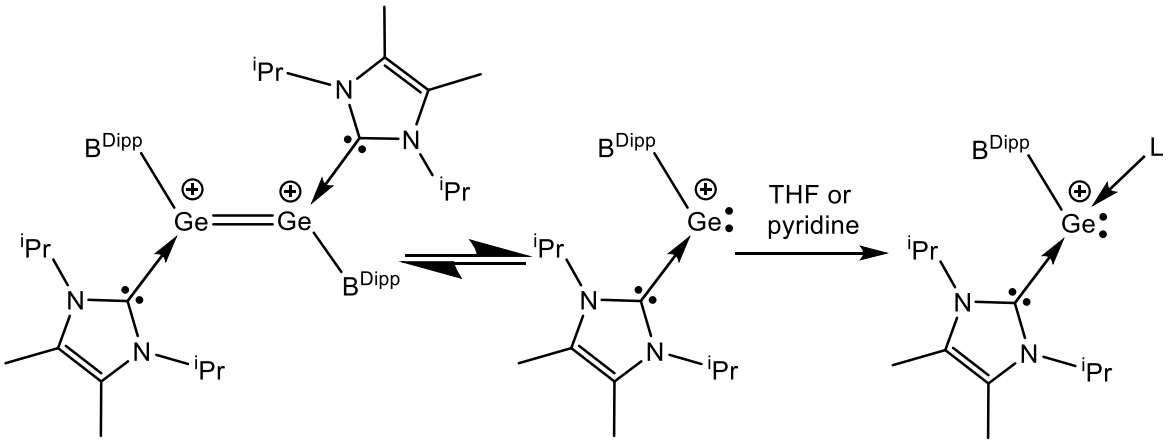


Figure 3.6: Delocalisation of cationic charge into the carbene heterocyclic ring in ***[(9)$_2$][BArF$_{24}$]$_2$*** *(counteranion omitted)*

The Ge-B (2.081(3)/2.100(4) Å) and Ge-C_{NHC} (2.002(3)/2.016(4) Å) distances can be compared to those in the precursor **2.31** (2.111(3) Å and 2.084(2) Å, respectively), with predictable bond-shortening observed upon chloride abstraction.[100,102] Finally, the shortest distance between a fluorine atom of a $[BArF_{24}]^-$ unit and germanium is over 6 Å, illustrating a lack of interaction and thus the weakly coordinating nature of this anion. It is also the case for all other cations subsequently discussed within this chapter that the shortest distance between a fluorine of the $[BArF_{24}]^-$ or $[Al(OR^F)_4]^-$ counteranion and germanium is greater than the sum of the van der Waals radii (3.58 Å).[107]

Unfortunately the relative insolubility of **[(9)$_2$][BArF$_{24}$]$_2$** in non-donor deuterated solvents has hindered the study of its structure in solution (while the lack of convenient NMR-active heteronuclei minimises the interpretability of NMR spectra in non-deuterated solvents). However, UV-Vis measurements in fluorobenzene (specifically a peak at 462 nm) provide some evidence for the presence of a Ge=Ge bonded species in this solvent (cf. 455 nm for (IDipp)Ge=Ge(IDipp),[91] 434 nm for (IPrMe)(B^{Dipp})Ge=Ge(B^{Dipp}), 460 nm for (B^{Dipp})$_2$Ge=Ge,[5] 439 nm for (Tbt)(Mes)Ge=Ge(Mes)(Tbt))[27], while reactivity studies suggest the existence of an equilibrium and some dissociation to a monomeric form (*vide infra*).[27,108] Moreover, whereas previously synthesised digermenes that do not dissociate in solution (e.g. $Mes_2Ge=GeMes_2$) have only been shown to form monomeric adducts with stronger donors such as NHCs,[109,110] in this case the monomeric form can be trapped out by the use of a weaker donor (e.g. by simply dissolving in THF), further suggesting some degree of dissociation in solution.



*Scheme 3.9: Potential equilibrium between dimeric and monomeric forms of **[9][BArF$_{24}$]**, and trapping with donor solvents (counteranion omitted)*

Thus, the adducts [(IPrMe)(B^{Dipp})Ge(d$_8$-THF)][BArF$_{24}$] (**[9(d$_8$-THF)][BArF$_{24}$]**) and [(IPrMe)(B^{Dipp})Ge(d$_5$-pyridine)][BArF$_{24}$] (**[9(d$_5$-pyridine)][BArF$_{24}$]**) can be accessed by dissolution of **[(9)$_2$][BArF$_{24}$]$_2$** in d$_8$-THF or d$_5$-pyridine, respectively. To confirm the expected monomeric structures, single crystals suitable for X-ray diffraction were obtained by layering concentrated protio-THF or pyridine solutions of **[(9)$_2$][BArF$_{24}$]$_2$** with hexane, followed by storage at −25°C. In both of these monomeric monocations, greater pyramidalisation is seen at germanium than in the dicationic dimer (sum of angles at germanium: 353.6°/353.1° (**[(9)$_2$][BArF$_{24}$]$_2$**), 298.6° (**[9(pyridine)][BArF$_{24}$]**) and 293.6° (**[9(THF)][BArF$_{24}$]**)). In both, the angle subtended at germanium by the bonds to the neutral donors is close to 90° (87.5(2)° and 90.2(1)° for **[9(THF)][BArF$_{24}$]** and **[9(pyridine)][BArF$_{24}$]**, respectively, as opposed to C$_{NHC}$-Ge-Ge angles of 109.3(1)° and 109.6(1)° in **[(9)$_2$][BArF$_{24}$]$_2$**), reflecting the concentration of p-orbital character in these bonds, while those involving the boryl substituent are markedly wider (100.9(2)°-105.5(1)°), reflecting the greater steric demands of the boryl ligand as well as electronic effects. The Ge-B and Ge-C$_{NHC}$ distances can be observed to become progressively longer as the donor strength increases (2.091 (mean)/2.009 Å (mean), 2.127(5)/2.074(5) Å and 2.114(4)/2.083(4) Å for **[(9)$_2$][BArF$_{24}$]$_2$**, **[9(THF)][BArF$_{24}$]** and **[9(pyridine)][BArF$_{24}$]**, respectively).

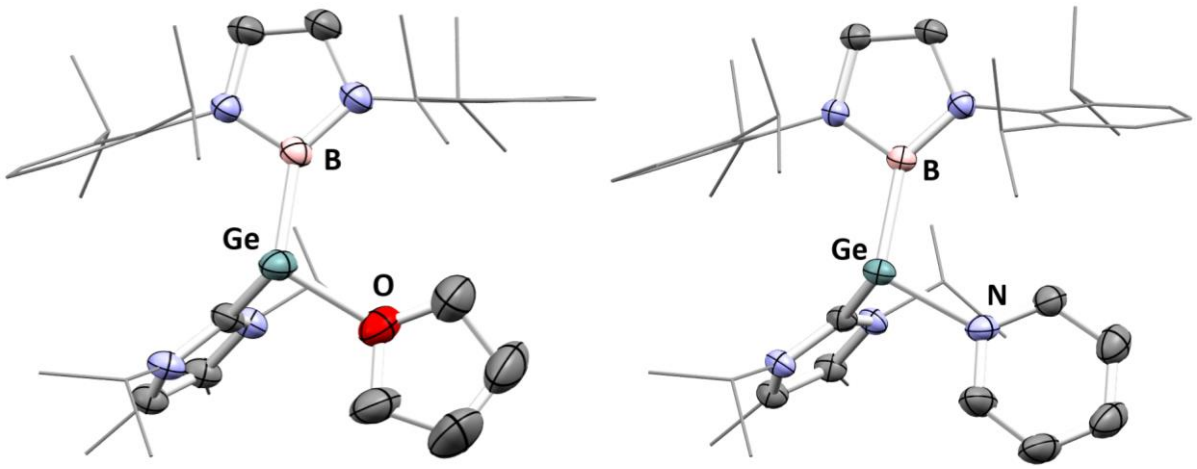


Figure 3.7: Structures of ***[9(THF)][BArF$_{24}$]*** *(L) and* ***[9(pyridine)][BArF$_{24}$]*** *(R). For clarity, [BArF$_{24}$]$^-$ counteranion and hydrogen atoms omitted, and B^{Dipp} Dipp and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): (for* ***[9(THF)][BArF$_{24}$]****) Ge-B: 2.127(5), Ge-C$_{NHC}$: 2.074(5), Ge-O: 2.120(4), B-Ge-C$_{NHC}$: 100.9(2), B-Ge-O: 105.2(2), C$_{NHC}$-Ge-O: 87.5(2); (for* ***[9(pyridine)][BArF$_{24}$]****) Ge-B: 2.114(4), Ge-C$_{NHC}$: 2.083(4), Ge-N: 2.095(3), B-Ge-C$_{NHC}$: 102.9(1), B-Ge-N: 105.5(1), C$_{NHC}$-Ge-N: 90.2(1)*

The NHC and THF/pyridine rings are approximately orthogonal (dihedral angles between the planes defined by their central rings of 84.0° and 78.0°, respectively). Because of its relatively small alkyl substituents, there is only minor structural distortion of the NHC ligand (with respect to the germanium centre) needed to avoid steric clash in these more sterically crowded monomeric structures. The data in Table 3.2 (rows 1-3) illustrate the similarity between various structural metrics of the NHC in **[(9)$_2$][BArF$_{24}$]$_2$** and in the adducts, **[9(THF)][BArF$_{24}$]** and **[9(pyridine)][BArF$_{24}$]**. Given the boryl ligand features bulky 2,6-substituted aryl rings, its opportunities to avoid steric clash with the other ligands through variation in mutual orientation are more limited, and hence the structure of the boryl rings in the monomeric complexes are considerably more distorted (with respect to the germanium centre) as compared to the dimer, with far greater change than the NHC. This is illustrated by the data in rows 4-6 in Table 3.2.

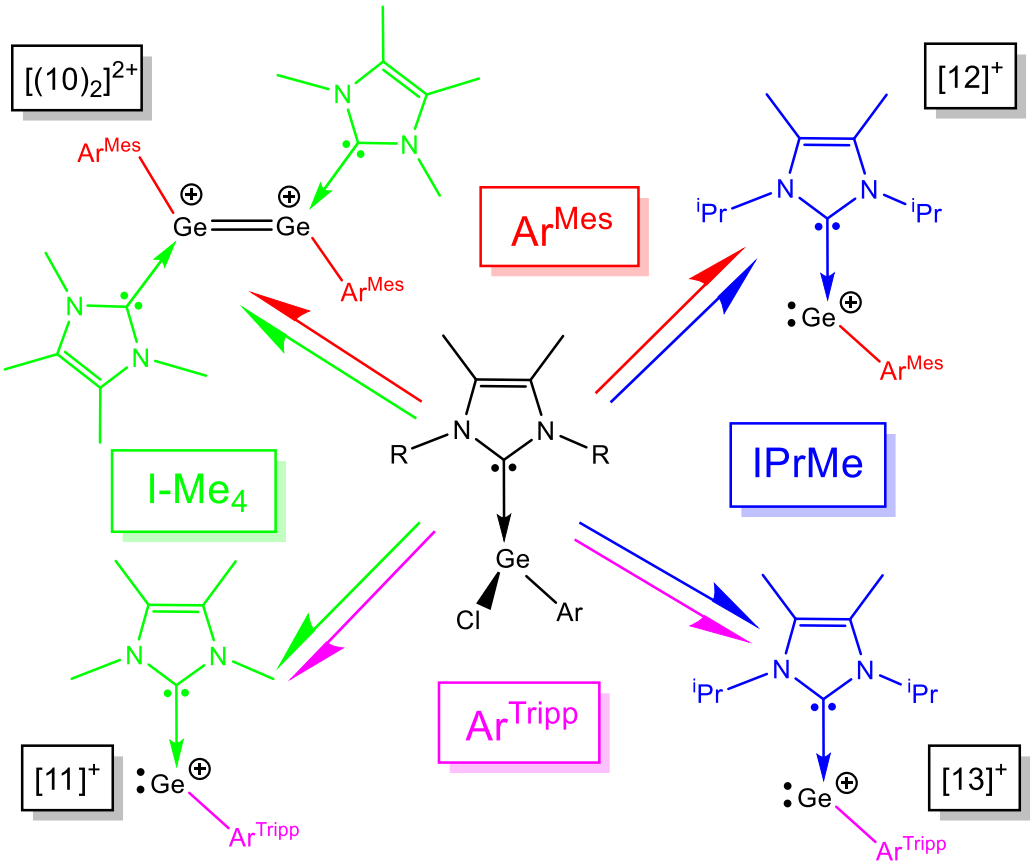
	$[(9)_2][BArF_{24}]_2$ (Ge^1 and Ge^2)	**$[9(THF)][BArF_{24}]$**	**$[9(pyridine)][BArF_{24}]$**
Ge-C_{NHC}-N_{NHC} (°)	126.0(2)/126.9(2) and 120.4(3)/131.9(3)	122.0(3)/131.8(3)	121.9(2)/132.4(3)
C4/5 centroid-C_{NHC}-Ge (°)	178.6 and 172.4	172.5	172.2
Ge-NHC^{plane} (Å)	0.041 and 0.185	0.202	0.207
Ge-B-N_{Boryl} (°)	123.6(2)/131.0(2) and 124.4(2)/129.1(2)	113.3(3)/140.0(4)	114.6(2)/138.4(3)
C4/5 centroid-B-Ge (°)	172.4 and 170.2	161.9	159.8
Ge-B^{plane} (Å)	0.259 and 0.348	0.426	0.572

Table 3.2: Comparison of structural metrics for boryl-substituted cations. C4/5 refer to the backbone carbon atoms of the boryl and NHC heterocyclic cores. Ge-B^{plane}/Ge-NHC^{plane} refer to the perpendicular distances between the germanium atom and the least squares planes defined by the central rings of the boryl and NHC ligands, respectively.

Combination of (IMes)(B^{Dipp})GeCl (**6**) with $Na[BArF_{24}]$, $Li[Al(OR^F)_4]$ or $Na[B(3,5\text{-}Cl_2C_6H_3)_4]$ in fluorobenzene led immediately to a colour change to a distinctive violet colour, however unfortunately, despite repeated attempts, no single crystals suitable for X-ray crystallography could be obtained (with oily phases always resulting).

3.3.3 Synthesis and structure of terphenyl-substituted germanium cations

Combination of the terphenyl-substituted chlorogermylenes **2.32**, **2.33**, **3** and **4** with $Na[BArF_{24}]$ or $Li[Al(OR^F)_4]$ in fluorobenzene led immediately to a colour change to deep red. Following filtration, concentration, layering with hexane and storage at −25°C, from these reactions, crystals could be isolated, which were orange for the I-Me_4 cases, and red for those cations containing IPrMe. Generally, use of the $[BArF_{24}]^-$ counteranion resulted in higher quality single crystals for X-ray diffraction.



Scheme 3.10: Syntheses of terphenyl-substituted germylium-ylidenes, ***[(10)$_2$][WCA]$_2$, [11][WCA], [12][WCA],*** *and* ***[13][WCA]****. General conditions: Na[BArF$_{24}$] or Li[Al(OR^F)$_4$], fluorobenzene, room temperature. Counteranions omitted.*

Due to the small size of the crystals obtained from the reaction of **2.32** and Na[BArF$_{24}$], X-ray diffraction analysis at the Diamond Light Source synchroton was necessary to reveal the product structure as the dicationic dimer, [(I-Me$_4$)(Ar^{Mes})Ge=Ge(Ar^{Mes})(I-Me$_4$)][BArF$_{24}$]$_2$, **[(10)$_2$][BArF$_{24}$]$_2$**. In general, preparative-scale synthesis of this cation proved challenging; hence, its behaviour in solution, as well as its reactivity, were primarily investigated using *in situ*-generated solutions of **[(10)$_2$][Al(OR^F)$_4$]$_2$** in C_6D_5Br (as the crystallinity of Li[Al(OR^F)$_4$] resulted in greater convenience for small-scale reactions).

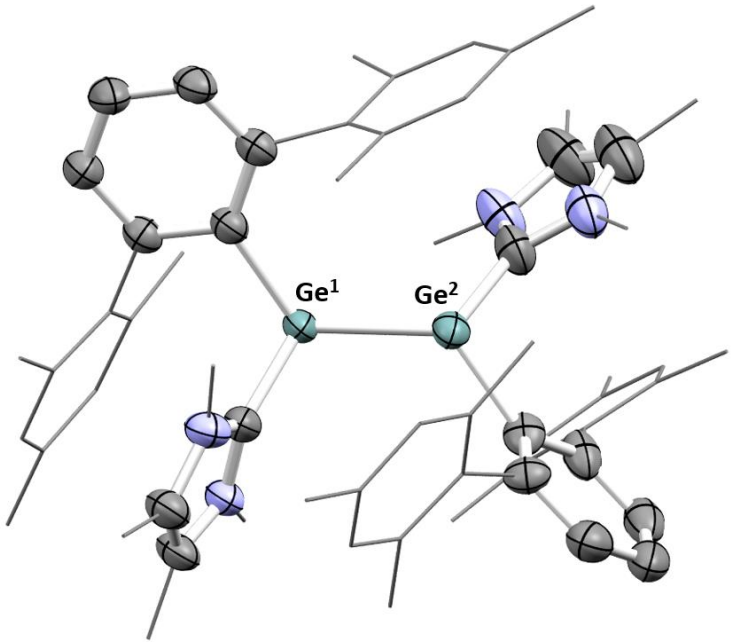


Figure 3.8: Structure of ***[(10)$_2$][BArF$_{24}$]$_2$****. For clarity, [BArF$_{24}$]$^-$ counteranions and hydrogen atoms omitted, and Ar^{Mes} Mes and NHC Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge^1-C$_{Ar}$^{1}: 1.963(4), Ge^2-C$_{Ar}$^{2}: 1.990(3), Ge^1-C$_{NHC}$^{1}: 2.038(4), Ge^2-C$_{NHC}$^{2}: 1.993(4), Ge^1-Ge^2: 2.3801(8), C$_{Ar}$^{1}-Ge^1-C$_{NHC}$^{1}: 103.95(15), C$_{Ar}$^{2}-Ge^2-C$_{NHC}$^{2}: 105.98(16), C$_{Ar}$^{1}-Ge^1-Ge^2: 122.93(11), C$_{Ar}$^{2}-Ge^2-Ge^1: 127.00(11), C$_{NHC}$^{1}-Ge^1-Ge^2: 110.12(11), C$_{NHC}$^{2}-Ge^2-Ge^1: 112.89(14)*

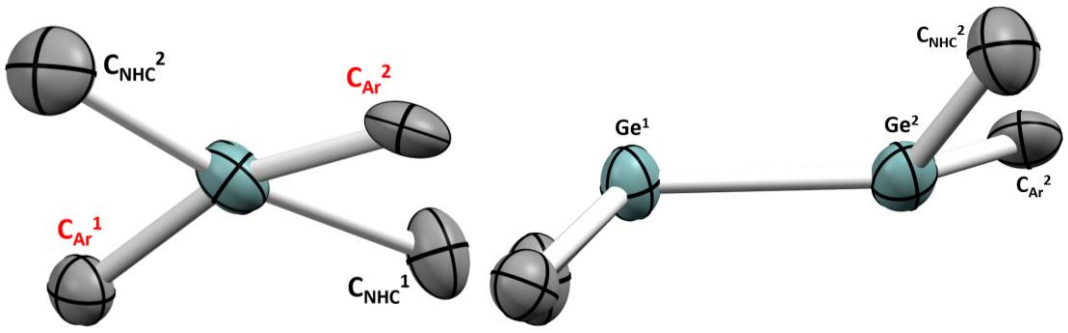


Figure 3.9: Newman projection along the Ge-Ge bond of ***[(10)$_2$][BArF$_{24}$]$_2$*** *(illustrating E geometry) (L), and a perpendicular view of the Ge-Ge bond (illustrating trans-bending and twist) (R)*

The structure of **[(10)$_2$][BArF$_{24}$]$_2$** is analogous to that of **[(9)$_2$][BArF$_{24}$]$_2$**, with a trans-bent disposition of the ligands and an *E* geometry. Relative to the boryl system, the greater steric demand of the terphenyl ligand (6-membered vs. 5-membered central ring, and shorter Ge-C vs. Ge-B bond), as well as its weaker donor strength, result in a longer Ge-Ge bond length (2.3801(8) Å vs. 2.300(2) Å), and increased degree of trans-bending: trans-bent angles, 44.2° (Ge^1) and 34.6° (Ge^2), vs. 25.7°/26.0°; sum of angles at germanium, 337.0° (Ge^1) and 345.9° (Ge^2), vs. 353.6°/353.1°. Furthermore, there is a more pronounced twist (twist angle: 14.5°, vs. 4.2°) between the C$_{Ar}$GeC$_{NHC}$ planes.

The ^{1}H NMR spectrum of **[(10)$_2$][Al(OR^F)$_4$]$_2$** in C_6D_5Br features extremely broad signals corresponding to the terphenyl and NHC methyl groups, possibly due to, for example, an equilibrium between dimeric and monomeric forms and/or fluxional flanking interactions (*vide infra*). Unfortunately, variable temperature NMR studies were uninformative, due to the insolubility of the compound at lower temperatures and its tendency to decompose at higher ones. However, upon addition of excess THF, the ^{1}H NMR spectrum in C_6D_5Br features (i) considerably sharpened resonances (for instance, the NHC NC**H**$_3$ signal at ca. 3 ppm reduces in width from $v_{1/2}$ = 68.4 Hz to 15.1 Hz), and (ii) changes in the chemical shift, most noticeably for the *o*-C**H**$_3$ resonances of the Ar^{Mes} mesityl ring (from 1.99 and 2.17 ppm to 2.16 and 2.51 ppm). These observations are consistent with the trapping out of a monomeric adduct, **[10(THF)][Al(OR^F)$_4$]**, and the fact that the presence of an additional ligand considerably reduces flanking aryl interactions. Furthermore, UV-Vis studies in fluorobenzene (specifically a peak at 441 nm) are indicative of the presence of a Ge=Ge doubly-bonded species in this solvent (*vide supra*). Thus, an analogous situation to **[(9)$_2$][BArF$_{24}$]$_2$** can be proposed, i.e. an equilibrium between dimer and monomer in non-donor solvents, which can be trapped out as an adduct in donor solvents.

[(I-Me$_4$)(Ar^{Tripp})Ge][BArF$_{24}$] (**[11][BArF$_{24}$]**), by contrast, exhibits a monomeric structure in the solid state. This can be compared with (Ph)(Ar^{Tripp})Ge=Ge(Ar^{Tripp})(Ph), a neutral digermene featuring ligands of similar steric bulk but with a Ge=Ge double bond in the solid state and solution.[111] A crude comparison thus suggests that the electrostatic disincentive to dimerisation proves to be significant in this case. As compared to **[(10)$_2$][BArF$_{24}$]$_2$**, the Ar^{Tripp} ligand (as opposed to Ar^{Mes}) presumably provides greater steric and electronic stabilisation of the monomeric form. However, an investigation of the solid state structure is nevertheless intriguing to assess whether there are other factors at play.

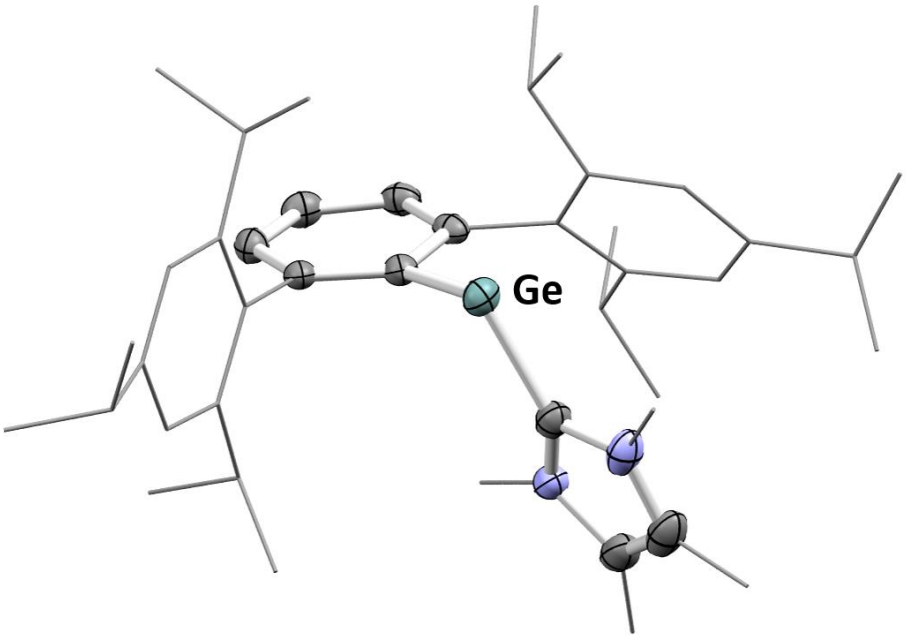


*Figure 3.10: Structure of **[11][BArF$_{24}$]**. For clarity, [BArF$_{24}$]$^-$ counteranion, fluorobenzene molecule and hydrogen atoms omitted, and Ar^{Tripp} Tripp and NHC Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-C$_{Ar}$: 1.991(3), Ge-C$_{NHC}$: 2.067(3), C$_{Ar}$-Ge-C$_{NHC}$: 101.7(1)*

The unit cell of **[11][BArF$_{24}$]** contains a molecule of fluorobenzene (disordered over two positions), though structural parameters imply a lack of significant interaction with the cationic germanium centre. The shortest distance between a fluorobenzene carbon atom and the germanium centre is 3.51(2) Å (next shortest: 3.99(2) Å) in one of the disordered positions and 3.57(2) Å (next shortest: 3.98(1) Å) in the other. The distances of the germanium atom from the centroid of the fluorobenzene rings are 4.275 Å and 4.283 Å, respectively. These shortest C-Ge distances are only slightly shorter than the sum of the van der Waals radii (3.81 Å).[107] Furthermore, they are also signficantly longer than the closest contacts for *bona fide* interactions of low-valent group 14 centres with aromatic solvent molecules (cf. [(Ar^{Tripp})Sn···(benzene)]$^+$, shortest contact: 2.893(7) Å;[17] [(Ar^{Tripp})Pb···(toluene)]$^+$, shortest contact: 2.832(10) Å;[40] [Et$_3$Si···(toluene)]$^+$, shortest contact: 2.18 Å),[112] as well as those in [Cp*Ge]$^+$ (mean C-Ge distance: 2.255(2) Å)[113] and [(*p*-C$_6$H$_4$CH$_2$CH$_2$)$_3$GeCl]$^+$ (arene centroid-Ge distances: 2.797, 2.722, 2.715 Å).[31]

Moreover, the fact that both **[(10)$_2$][BArF$_{24}$]$_2$** and **[11][BArF$_{24}$]** were obtained via reactions in fluorobenzene, and that thus fluorobenzene coordination is available as a stabilising mechanism for the monomeric form of **[(10)$_2$][BArF$_{24}$]$_2$**, suggests that any minor solvent coordination is not the decisive factor in favouring a monomeric structure for **[11][BArF$_{24}$]**. A potentially more significant

influence appears to be a flanking aryl interaction from the more electron-rich terphenyl ligand, as evidenced by a considerable distortion of one of the aryl rings in the terphenyl ligand (see Figure 3.11). Thus, the shortest C_{ortho}-Ge distance is 2.589(4) Å (shortest distances: C_{ipso}-Ge, 2.846(4) Å; Tripp centroid-Ge, 3.271 Å), which is considerably shorter than in the precursor **2.33** (shortest distances: C_{ortho}-Ge, 3.481(3) Å; C_{ipso}-Ge, 3.140(3) Å; Tripp centroid-Ge, 4.028 Å),[64] and in the undistorted aryl ring (shortest distances: C_{ortho}-Ge, 3.776(4) Å; C_{ipso}-Ge, 3.311(4) Å; Tripp centroid-Ge, 4.108 Å), as well as in other terphenyl-substituted cations synthesised in this study (*vide infra*). This shortest C_{aryl}-Ge distance is even shorter than those observed in, for example, Wesemann's recent terphenyl-substituted stannylium-ylidene (2.659(6) Å),[17] Izod's diarsagermylene (2.666(3) Å),[33] Jones' quasi-one-coordinate amidogermylium-ylidene (2.642(2) Å),[34] and a boryl-subsituted digermavinylidene (2.904(2) Å),[5] though longer than in $[(Ar^{Tripp})GeH_2]^+$, where the smaller size and greater electrophilicity of the Ge^{IV} cation (and the absence of other strong donor ligands) leads to an even closer approach (shortest C_{aryl}-Ge distance: 2.251(3) Å).[17]

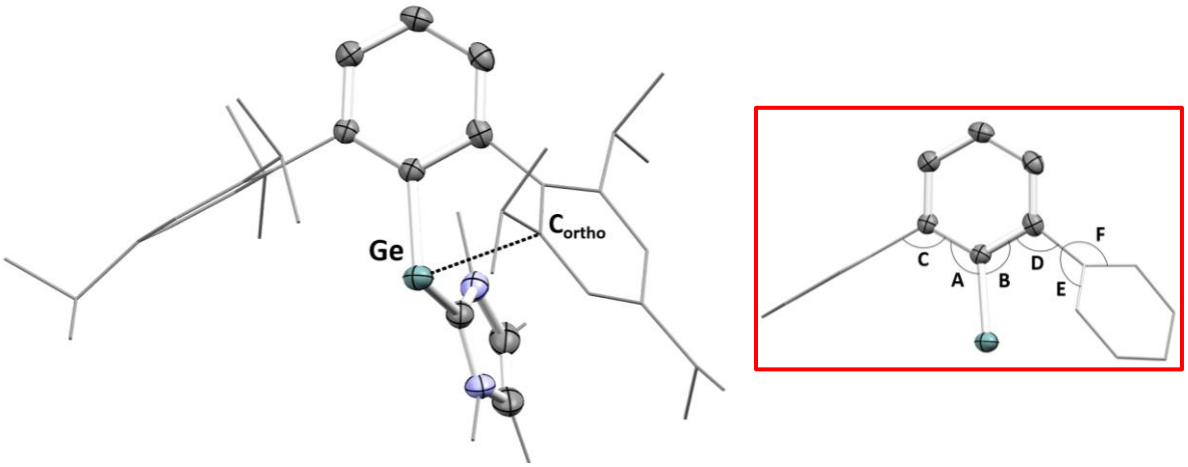


Figure 3.11: Illustration of the flanking aryl interaction in ***[11][BArF$_{24}$]***

Furthermore, various angles associated with the germanium-bound terphenyl ligand are also consistent with coordination of the flanking aryl ring (see labelling scheme in Figure 3.11). The precursor chlorogermylene **2.33** features disparate A and B angles due to the steric effects of the chloride ligand (A = 114.0(2)° and B = 126.7(2)°, difference = 12.7°). Upon abstraction of the chloride the ordering of these angles is reversed due to the aryl interaction (A = 124.4(2)°, B = 114.1(2)°, difference = 10.3°). Furthermore, the C and D angles are very similar in **2.33** (C = 123.5(2)°, D =

124.9(2)°, difference = 1.4°), while there is a marked distortion in **[11][BArF$_{24}$]** (C = 120.6(3)°, D = 113.0(3)°, difference = 7.6°), due to the "leaning in" of the Tripp ring. This also leads to a difference between the E and F angles (E = 117.4(3)°, F = 122.9(3)°, difference = 5.5°), which is not observed in the undistorted Tripp ring of **[11][BArF$_{24}$]** (difference = 1.2°), nor in **2.33** (differences = 2.5° and 0.2°). Whereas in **2.33** and the undistorted ring of **[11][BArF$_{24}$]** the Tripp ring(s) are orientated approximately perpendicular to the central terphenyl ring (dihedral angles between the planes defined by the aromatic rings: 81.6°/74.3° and 87.1°, respectively), there is a considerable move away from orthogonality for the distorted ring (dihedral angle between planes: 56.8°). In solution in C_6D_5Br, the ^{1}H NMR spectrum of **[11][BArF$_{24}$]** features extremely broad resonances, suggesting that the flanking aryl interaction is maintained.

Some further comparisons are also possible between **[11][BArF$_{24}$]** and its chlorogermylene precursor **2.33**. There is an expected shortening of the bonds to the ligands upon chloride abstraction (**2.33**, Ge-C_{Ar}: 2.035(3) Å, and Ge-C_{NHC}: 2.071(3) Å; **[11][BArF$_{24}$]**, Ge-C_{Ar}: 1.991(3) Å, and Ge-C_{NHC}: 2.067(3) Å). Whereas in **2.33** the germanium centre is displaced from the planes defined by the central terphenyl and NHC rings (Ar^{plane} and NHC^{plane}) to alleviate steric crowding (C_{para}-C_{ipso}-Ge angle: 167.9(1)°, Ge-Ar^{plane}: 0.327 Å, Ge-NHC^{plane}: 0.489 Å), structural metrics indicate this is not the case upon halide abstraction (C_{para}-C_{ipso}-Ge angle: 172.2(2)°, Ge-Ar^{plane}: 0.152 Å, Ge-NHC^{plane}: 0.036 Å). Instead, in the cation, steric clash between the NHC and Tripp rings can be minimised by the alignment of the NHC ring essentially coplanar with the C_{NHC}-Ge-C_{Ar} plane (dihedral angle between this and NHC^{plane}: 7.9°, vs. 80.3° in **2.33**).

[(IPrMe)(Ar^{Mes})Ge][BArF$_{24}$], **[12][BArF$_{24}$]** (which co-crystallised with 47% [(IPrMe)(Ar^{Mes})GeH(OH)][BArF$_{24}$]), and **[12][Al(OR^F)$_4$]** (which features two independent molecules in the unit cell) could both be identified as monomeric in the solid state by X-ray crystallography, suggesting minimal effects from the counteranion on the extent of aggregation. Given both (i) the higher quality of the data for the structure featuring [BArF$_{24}$]$^-$ (R-factor of 7.87% vs. 12.53%, due to characteristic disorder in the [Al(OR^F)$_4$]$^-$ anion), and (ii) the greater ease of comparison with the other

terphenyl-substituted cations reported in this study (all of which were crystallised with $[BArF_{24}]^-$), solid state discussion henceforth will focus on the structural metrics of **[12][BArF$_{24}$]**. The corresponding values of all metrics for **[12][Al(OR^F)$_4$]** can be found in Table 3.3, and illustrate that the same trends still hold regardless of counteranion. Discussions regarding behaviour in solution will focus on the more cleanly prepared **[12][Al(OR^F)$_4$]**.

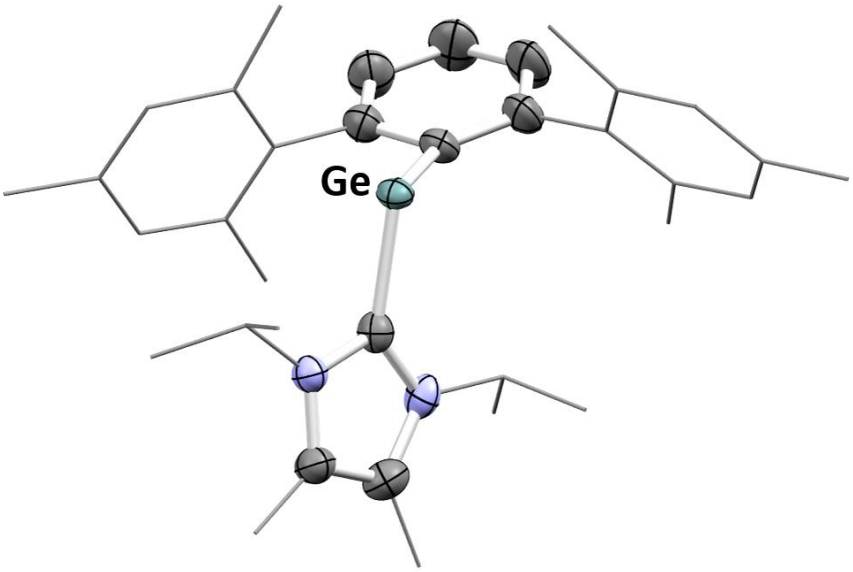


*Figure 3.12: Structure of **[12][BArF$_{24}$]**. For clarity, $[BArF_{24}]^-$ counteranion and hydrogen atoms omitted, and Ar^{Mes} Mes and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°) [metrics for $[Al(OR^F)_4]^-$ analogue in parentheses]: Ge-C_{Ar}: 2.004(4) [1.969(5)/1.994(5)], Ge-C_{NHC}: 2.139(3) [2.070(6)/2.051(4)], C_{Ar}-Ge-C_{NHC}: 102.9(1) [105.0(2)/108.6(2)]*

As compared to **[(10)$_2$][BArF$_{24}$]$_2$**, the higher donor strength and greater steric bulk of the IPrMe NHC (%V_{bur}: 26.2% (I-Me$_4$) and 38.5% (IPrMe))[94] would be expected to favour the monomeric form. Structurally, there is considerable displacement of the germanium atom to one side of the terphenyl ligand (A = 105.7(3)°, B = 132.0(3)°, difference = 26.3°; shortest C_{ipso}-Ge distance: 2.761(4) Å). While this could be an indication of a significant flanking aryl interaction, the structural parameters of the adjacent Mes group are minimally distorted (C = 119.7(3)°, D = 122.7(3)°, difference = 3.0°; E-F difference = 2.3°). Hence, this displacement appears more likely to be due to minimisation of the steric congestion arising from the bulkier NHC isopropyl substituents. This also leads to a marked displacement of the germanium atom from the planes defined by the central terphenyl and NHC rings (C_{para}-C_{ipso}-Ge angle: 161.7(2)°; Ge-Ar^{plane}: 0.383 Å; Ge-NHC^{plane}: 0.346 Å), and a twisting of the NHC (N_{NHC}-C_{NHC}-Ge-C_{Ar} torsion: 44.7(4)°). The lack of any significant aryl π-interaction is also suggested by

the ^{1}H NMR spectrum of **[12][Al(OR^{F})$_4$]** in C_6D_5Br, which features considerably narrower resonances as compared to **[(10)$_2$][Al(OR^{F})$_4$]$_2$** and **[11][BArF$_{24}$]**.

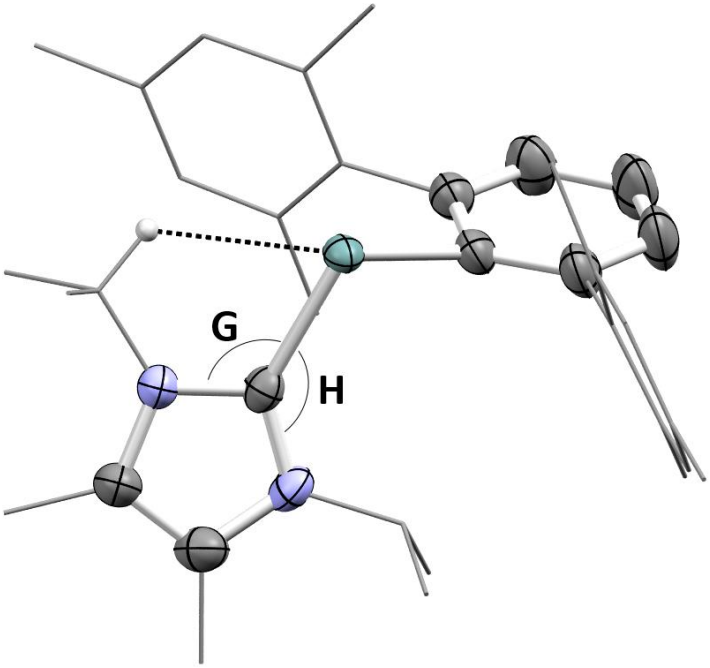


*Figure 3.13: Canting of the NHC towards the germanium centre in **[12][BArF$_{24}$]***

A further structural feature apparent in **[12][BArF$_{24}$]** is the considerable canting of the NHC towards the germanium centre, as reflected in the large difference in the G and H angles (Figure 3.13, G = 117.3(2)°, H = 135.5(2)°, difference = 18.2°), and a remarkable closeness of a C**H**$(CH_3)_2$ isopropyl proton to the germanium centre (2.575 Å). This distance is essentially the same as that observed by Filippou in the silylium-ylidene [(IDipp)(IPrMe)SiI]$^{+}$ (**3.2**; 2.57(1) Å), a compound for which ^{29}Si NMR and computational data suggest the presence of an anagostic interaction between silicon and this C-H bond.[63] There are no reported examples of such interactions involving low-valent germanium centres. Returning to the structure of **[11][BArF$_{24}$]**, it can be seen that there is a similar discrepancy in the G and H angles (G = 117.7(3)°, H = 137.4(3)°, difference = 19.7°), although the closest approach of a C**H**$(CH_3)_2$ proton to the germanium centre is slightly less pronounced (shortest C-H···Ge distance: 2.622 Å). Of course, such comparisons of C-H···Ge distances are made with the usual caveats concerning the ability of X-ray diffraction to yield reliable H-atom positions.

		[11][BArF$_{24}$]	[12][BArF$_{24}$]	[12][Al(OR^F)$_4$]	[13][BArF$_{24}$]
ANGLES (°)	**A**	124.4(2)	105.7(3)	111.1(4)/129.9(4)	125.7(2)
	B	114.1(2)	132.0(3)	127.6(4)/106.9(3)	110.0(2)
	|A-B|	10.3	26.3	16.5/23.0	15.7
	C	120.6(3)	119.7(3)	118.8(5)/122.2(4)	119.6(2)
	D	113.0(3)	122.7(3)	119.8(5)/118.5(4)	118.5(2)
	|C-D|	7.6	3.0	1.0/3.7	1.1
	|E-F|	5.5	2.3	2.7/0.1	3.0
	G	117.7(3)	117.3(2)	119.5(4)/118.8(3)	120.2(2)
	H	137.4(3)	135.5(2)	132.1(4)/132.2(3)	131.2(2)
	|G-H|	19.7	18.2	12.6/13.4	11.0
C_{para}-C_{ipso}-Ge		172.2(2)	161.7(2)	166.2(3)/160.2(3)	158.8(1)
N_{NHC}-C_{NHC}-Ge-C_{Ar} torsion		7.3(4)	44.7(4)	48.6(6)/51.5(5)	58.3(3)
DISTANCES (Å)	**C_{ortho}-Ge**	2.589(4)	3.055(4)	3.250(5)/3.133(5)	3.226(3)
	C_{ipso}-Ge	2.846(4)	2.761(4)	2.882(5)/2.781(5)	2.867(3)
	$Ar_{centroid}$-Ge	3.271	3.518	3.655/3.535	3.642
	C-H···Ge	2.622	2.575	2.610/2.614	2.669
	Ge-Ar^{plane}	0.152	0.383	0.321/0.516	0.633
	Ge-NHC^{plane}	0.036	0.346	0.334/0.510	0.471

Table 3.3: Comparison of structural metrics for terphenyl-substituted monomeric cations. Distances given are the shortest if there is more than one possibility. For definitions of metrics, see Figures 3.11 and 3.13 and surrounding discussions.

The ^{1}H NMR spectrum of **[12][Al(OR^F)$_4$]** contains only one resonance corresponding to each of the NHC C**H**(CH$_3$)$_2$ and CH(C**H**$_3$)$_2$ environments. Unfortunately, due to poor solubility at lower temperatures and the relatively high freezing point of bromobenzene (ca. −30°C), NMR studies at low temperature did

not permit the observation of desymmetrisation of these signals that might provide evidence for an anagostic interaction in solution. Small impurities in the ^{1}H NMR spectrum could be shown by DOSY studies not to correspond to a dimeric form of this species, and more likely arise from the activation of, for example, solvent, flanking ligand moieties[17] or adventitious moisture.

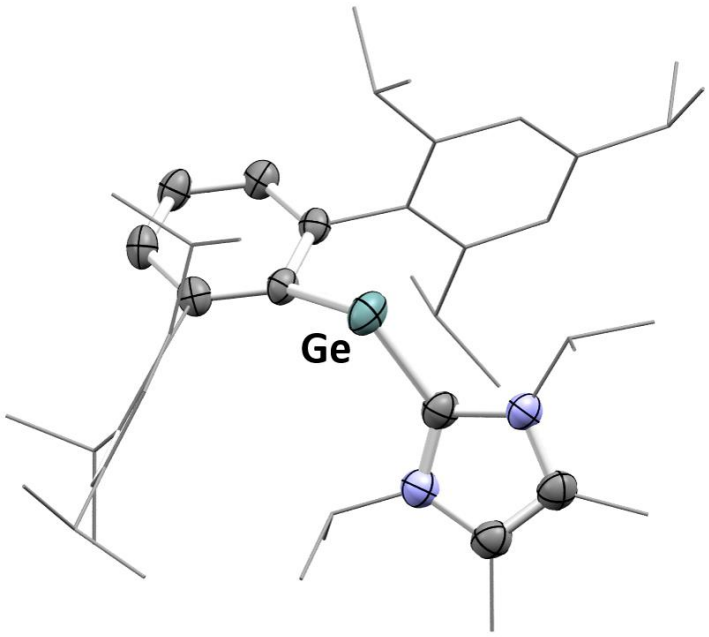


*Figure 3.14: Structure of **[13][BArF$_{24}$]**. For clarity, [BArF$_{24}$]$^{-}$ counteranion and hydrogen atoms omitted, and Ar^{Tripp} Tripp and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-C$_{Ar}$: 1.980(2), Ge-C$_{NHC}$: 2.059(3), C$_{Ar}$-Ge-C$_{NHC}$: 107.2(1)*

Finally, as would be expected due to the presence of the most strongly donating and bulky NHC and terphenyl ligands, [(IPrMe)(Ar^{Tripp})Ge][BArF$_{24}$] (**[13][BArF$_{24}$]**) features a monomeric structure in the solid state. Structural metrics imply that the use of these ligands alone is sufficient to stabilise the monomeric form, with minimal distortions that would suggest the presence of significant flanking aryl or anagostic interactions. As for the case of **[12][BArF$_{24}$]**, the displacement of germanium to one side of the terphenyl ligand (A-B difference = 15.7°, leading to a short C$_{ipso}$-Ge distance: 2.867(3) Å) appears most likely to be due to alleviation of steric pressure (as there is minimal further alteration to the adjacent Tripp ring; angle differences: C-D = 1.1°, E-F = 3.0°). Furthermore, there is considerably less canting of the NHC as compared to **[11][BArF$_{24}$]** and **[12][BArF$_{24}$]** (G-H difference = 11.0°, shortest C-H···Ge distance: 2.669 Å), suggesting a potential anagostic interaction is less significant for this cation.

The sharpness of the resonances in the ^{1}H NMR spectrum in C_6D_5Br suggest the lack of fluxional interactions in solution.

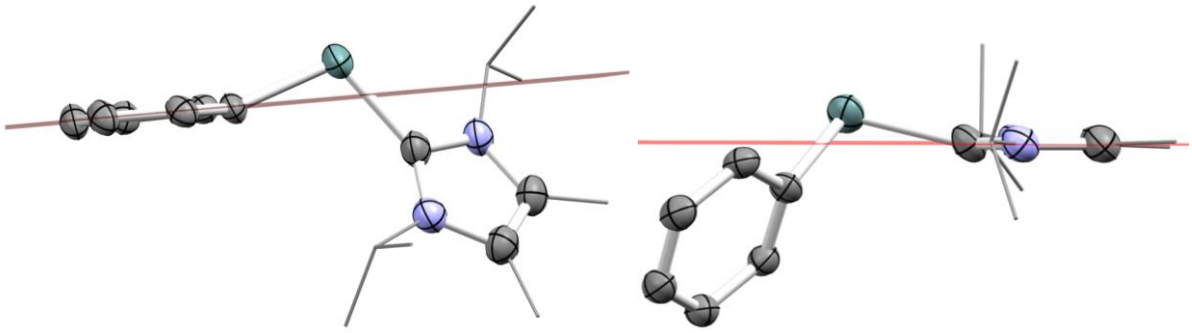


*Figure 3.15: Deviation of germanium from Ar^{plane} (L) and NHC^{plane} (R) in **[13][BArF$_{24}$]** (Tripp groups of Ar^{Tripp} omitted)*

As well as deviating from the centre of the terphenyl ligand, the germanium centre in **[13][BArF$_{24}$]** also undergoes the most pronounced "popping out" of the planes Ar^{plane} and NHC^{plane} to reduce steric crowding. For example, the C_{para}-C_{ipso}-Ge angle is 158.8(1)°, the distances Ge-Ar^{plane}/Ge-NHC^{plane} are 0.633/0.471 Å, respectively, and there is an N_{NHC}-C_{NHC}-Ge-C_{Ar} torsion of 58.3(3)°, values which represent considerably greater deviations than those seen for **[11][BArF$_{24}$]** and **[12][BArF$_{24}$]** (see Table 3.3). **[13][BArF$_{24}$]** also features the widest C_{NHC}-Ge-C_{Ar} angle, 107.2(1)°, while the Ge-C_{Ar} (1.980(2) Å) and Ge-C_{NHC} (2.059(3) Å) distances are shorter than those in the other monomeric cations.

The colour of the terphenyl-substituted cations is potentially informative of their electronic structure. Thus, as the combined donor strength of the NHC and terphenyl ligands increases, then the colour changes progressively from orange through to red. This is consistent with an elevation of the energy of the HOMO, leading to a smaller HOMO-LUMO gap, so a smaller energy absorption in the visible region and a lengthening of the wavelength of the colour that is observed. Unfortunately, however, attempts to quantify this trend through UV-Vis spectroscopy were thwarted by the extreme moisture sensitivity of the cations, which led to a difficulty in obtaining reproducible spectra.

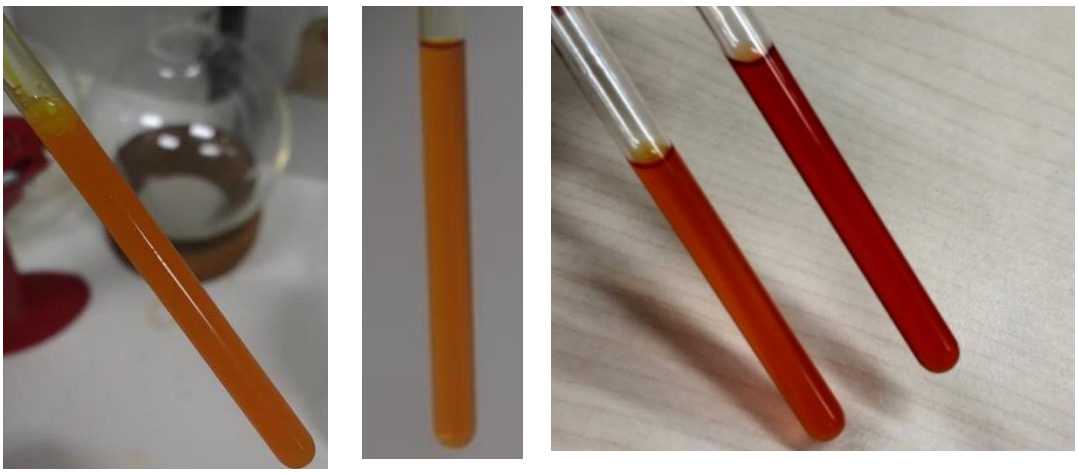


Figure 3.16: ***[(10)$_2$][Al(OR^F)$_4$]$_2$, [11][BArF$_{24}$], [12][Al(OR^F)$_4$],*** *and* ***[13][BArF$_{24}$]*** *in C_6D_5Br*

DFT calculations were performed to investigate the bonding in the monomeric cations **[11][BArF$_{24}$]**, **[12][BArF$_{24}$]** and **[13][BArF$_{24}$]**. The optimised structure agreed best with that from crystallography in the case of **[13][BArF$_{24}$]**; the HOMO and LUMO are depicted in Figure 3.17, and are predictably centred on the germanium lone pair and p-orbital, respectively. Natural bond orbital (NBO) analysis reveals that the lone pair of **[13][BArF$_{24}$]** has 83% s-character. NBO analysis also provides insight into potential flanking aryl interactions in each of these cations. The second order perturbation energies for the interaction between an aryl π-bond of the adjacent aryl ring and a vacant p-orbital at germanium are respectively 8.2, 6.1 and 6.3 kcal mol^{-1} for **[11][BArF$_{24}$]**, **[12][BArF$_{24}$]** and **[13][BArF$_{24}$]**, agreeing with the conclusions made from crystallographic data that **[11][BArF$_{24}$]** features the most significant aryl interaction. In this case, the "vacant" orbital at germanium is found to have an occupancy of 0.187 electrons, in line with the value found, for example, in Izod's diarsagermylene.[33] The interaction between the two relevant NBO orbitals in the case of **[11][BArF$_{24}$]** is depicted in Figure 3.18 (L). Anagostic interactions could also be investigated. In the cases of **[11][BArF$_{24}$]** and **[13][BArF$_{24}$]**, second order perturbation analysis suggests interactions between the germanium lone pair and the NHC $(CH_3)_2$C-H σ*-orbital, with energies of 2.0 kcal mol^{-1} and 0.87 kcal mol^{-1}, respectively. The interaction between the two relevant NBO orbitals in the case of **[11][BArF$_{24}$]** is depicted in Figure 3.18 (R). Though the smaller energy for **[13][BArF$_{24}$]** as compared to **[11][BArF$_{24}$]** is consistent with the conclusions about the relative size of a potential anagostic interaction made from crystallographic data, it is surprising, given the short C-H···Ge distance, that no such interaction was identified by NBO analysis

in the case of **[12][BArF$_{24}$]**. In the case of Filippou's silylium-ylidene **3.2**, a slightly larger stabilisation energy of 3.3 kcal mol^{-1} was found from NBO second order perturbation analysis for the analagous orbital interaction.[63]

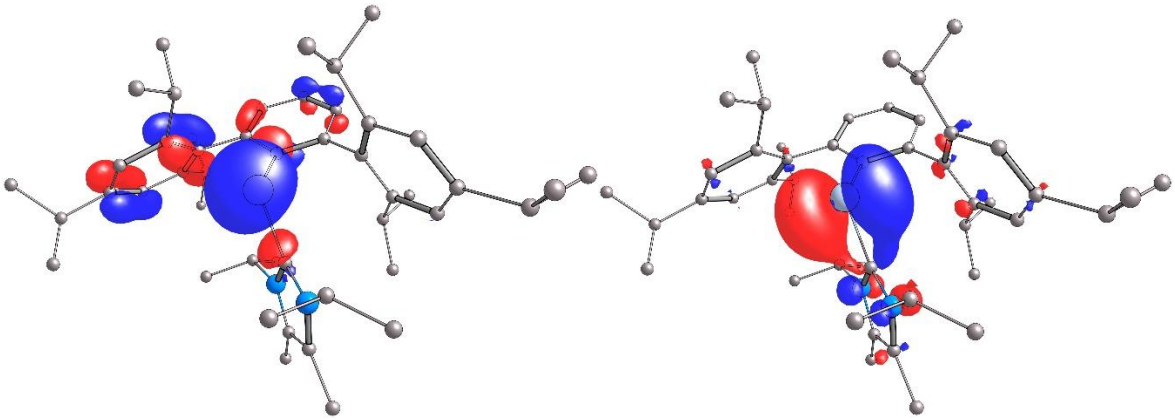


*Figure 3.17: HOMO (L) and LUMO (R) of **[13][BArF$_{24}$]***

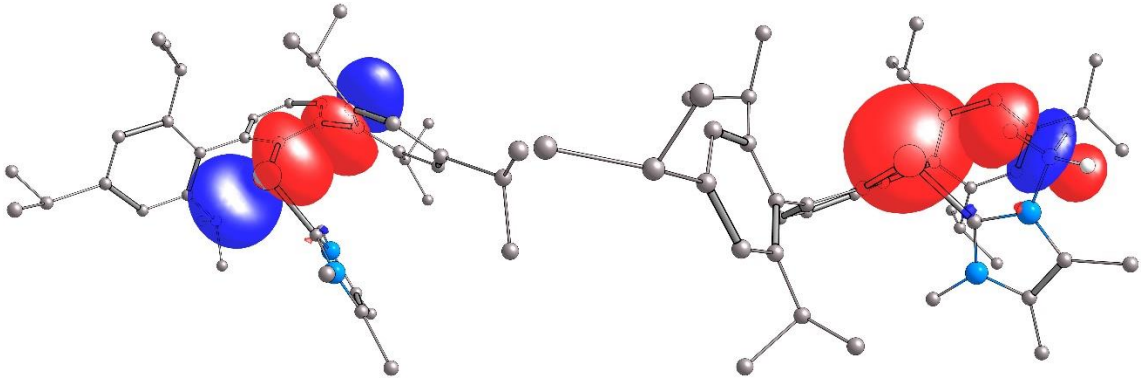


*Figure 3.18: NBO orbitals involved in aryl (L) and anagostic (R) interactions in **[11][BArF$_{24}$]***

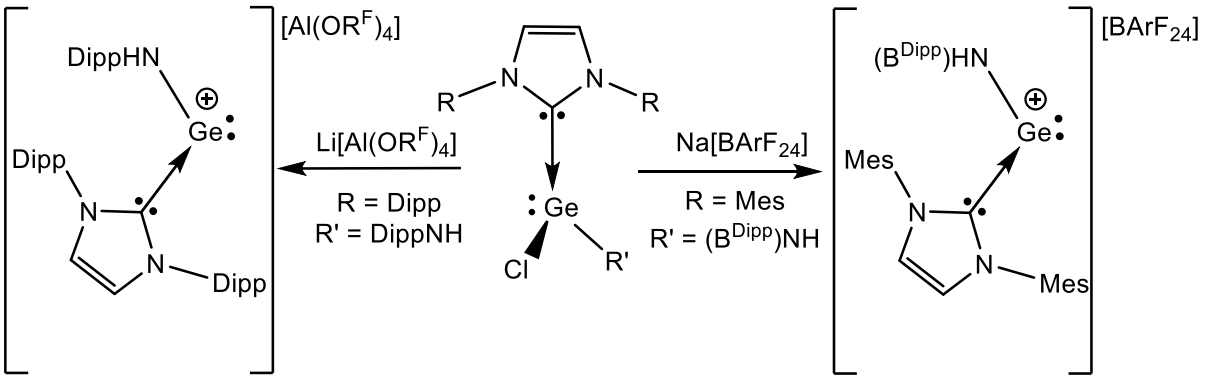
3.3.4 Attempted synthesis of a silyl-substituted germanium cation

Upon combination of (IPrMe){(Me$_3$Si)$_3$Si}GeCl (**2.34**) and either Li[Al(OR^F)$_4$] or Na[BArF$_{24}$] in fluorobenzene, an immediate colour change to deep red could be observed. However, within minutes, the colour darkened from red to brown; attempts to grow single crystals from this reaction mixture yielded only [IPrMeH][WCA] salts. When the same reaction was performed *in situ* in C$_6$D$_5$Br, the ^{1}H NMR spectrum was messy and difficult to reproduce, and was unchanged upon addition of a "germylene trap" such as Et$_3$SiH. Presumably, a cation is initially formed, but rapid migration of an SiMe$_3$ group to germanium, for example, could then initiate decomposition reactions. Such migration has precedent in attempts to form silyl-substituted germylenes;[88,89,95,114,115] in those cases, the germylene could be trapped by coordination of a phosphine or NHC donor. However, in this case,

performing the chloride abstraction reaction in the presence of an NHC (I-Me_4 or IPrMe) still resulted in the formation of an intractable mess. In hindsight, an alkyl-substituted silyl group (e.g. Si^tBu_3) would have been more appropriate due to the lower likelihood of the substituents migrating.[116] (NHC)(R_3Si)GeCl chlorogermylenes featuring such substituents have been accessed in unpublished work by Filippou.[117]

3.3.5 Synthesis and structure of amido- and borylamido-substituted germanium cations

For comparison with the above strongly σ-donating ligands, the synthesis of cations substituted by π-donating, σ-withdrawing amido ligands was sought. Thus, the combinations of (IDipp)(DippNH)GeCl (**2.35**) with Li[Al(OR^F)$_4$], and (IMes){(B^{Dipp})NH}GeCl (**7**) with Na[$BArF_{24}$], in fluorobenzene led immediately to colour changes to orange and red, respectively. Subsequent filtration, concentration and layering with hexane enabled the isolation of orange and red crystals respectively, identifiable by X-ray diffraction as the monomeric cations [(IDipp)(DippNH)Ge][Al(OR^F)$_4$] (**[14][Al(OR^F)$_4$]**) and [(IMes){(B^{Dipp})NH}Ge][$BArF_{24}$] (**[15][$BArF_{24}$]**).



*Scheme 3.11: Syntheses of **[14][Al(OR^F)$_4$]** and **[15][$BArF_{24}$]** (both reactions in fluorobenzene at room temperature)*

The structure of **[14][Al(OR^F)$_4$]** can be compared with that of the precursor **2.35** (which features two independent molecules in the unit cell).[66] Thus, following chloride abstraction there is a shortening of the Ge-C_{NHC} bond from 2.093(3)/2.103(3) Å to 2.079(2) Å, as well as a more substantial reduction of the Ge-N^1 bond length from 1.897(2)/1.903(2) Å to 1.811(2) Å. Insofar as X-ray diffraction can yield reliable H-atom positions, N^1 appears to be planar (sum of angles = 359.9°), and this fact, in

combination with the large reduction in the Ge-N^1 bond length as compared to **2.35**, suggests significant N to Ge π-donation and partial Ge-N double bond character in **[14][Al(OR^F)$_4$]**.

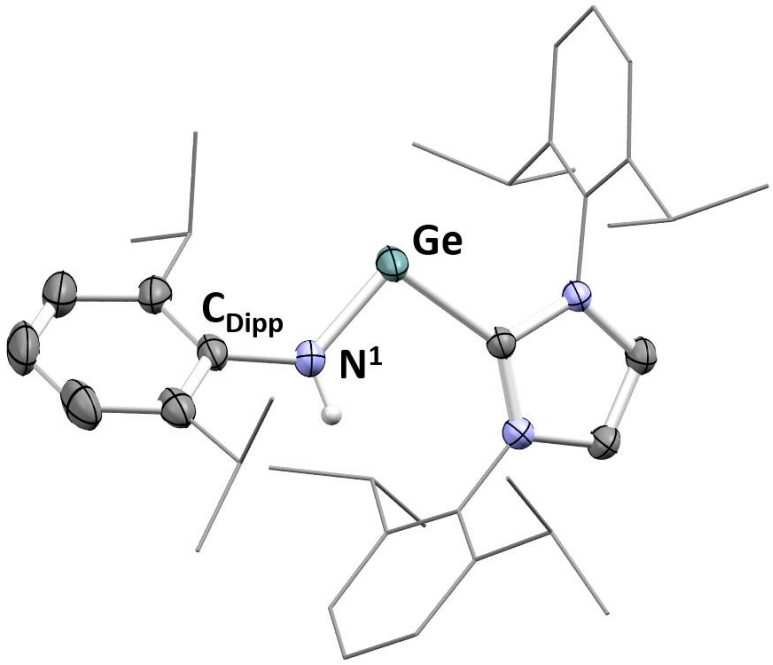


*Figure 3.19: Structure of **[14][Al(OR^F)$_4$]**. For clarity, [Al(OR^F)$_4$]$^-$ counteranion and hydrogen atoms (other than GeN**H**) omitted, and NHC Dipp and NHDipp ^{i}Pr groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-N^1: 1.811(2), Ge-C$_{NHC}$: 2.079(2), N^1-Ge-C$_{NHC}$: 95.75(8)*

Though uncommented on by Rivard, a potential feature of note in the structure of **2.35** is the small C_{Dipp}-N^1-Ge angle of 113.6(2)/117.9(2)°, resulting in a short C_{Dipp}-Ge distance of 2.788(3)/2.857(3) Å. This could result from the avoidance of steric hindrance with the bulky Dipp groups of the NHC, as well as a potential flanking donation from the aryl group to the germanium centre, rendered electron-deficient due to the presence of electronegative amido and chloride substituents, and potentially from partial double bond character of the N^1-C_{Dipp} bond. In the structure of the cation, this angle (127.1(2)°) and distance (2.906(2) Å) are greater, presumably because of lessened steric effects as a result of the removal of one of the substituents, the satiation of the electron deficiency by π-donation from nitrogen, and the lesser extent of N^1 to C_{Dipp} π-delocalisation.

Compound **[14][Al(OR^F)$_4$]** is the first example of a germylium-ylidene substituted by a primary amido group, which are rare ligands in germylenes[4,118–120] (and indeed metallylenes)[121] more generally. The Ge-N^1 distance (1.811(2) Å) is predictably shorter than the majority of acyclic amido-substituted germylenes (featuring secondary amido substituents),[122–125] but similar to the primary

amido/terphenyl-substituted germylenes (Ar^{Dipp})Ge(NHDipp) (1.815(2) Å) and (Ar^{Mes})Ge(NHDipp) (1.808(2) Å),[4] and Jones' super bulky amido-substituted cation (1.8153(18) Å),[34] with the shorter length as compared to $(Ar^{Mes}NH)_2Ge$ (1.896(2) Å)[119] reflecting the competition between two donors in that case.

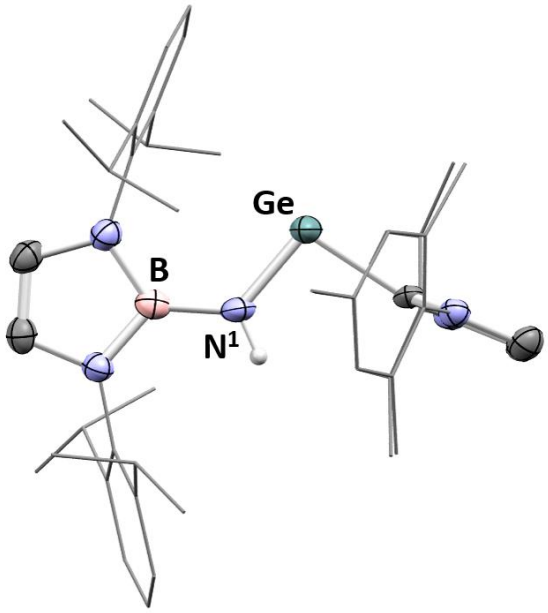


*Figure 3.20: Structure of **[15][BArF$_{24}$]**. For clarity, [BArF$_{24}$]$^-$ counteranion and hydrogen atoms (other than GeN**H**) omitted, and NHC Mes and B^{Dipp} Dipp groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-N^1: 1.814(6), Ge-C$_{NHC}$: 2.096(5), N^1-Ge-C$_{NHC}$: 96.2(2)*

Notable in the structure of **[15][BArF$_{24}$]** are (i) the orthogonality of the two ligands (dihedral angle between NHC^{plane} and B^{plane}: 80.7°), presumably to prevent steric clash of the bulky aryl groups, and (ii) the coplanarity of the central boryl ring and the BNHGe core (dihedral angle between B^{plane} and that defined by the BNHGe array: 4.9°; $N_{Boryl}BN^1Ge$ torsion: 5(1)°). These metrics are more towards orthogonality and coplanarity respectively than in the chlorogermylene precursor **7** (angles: dihedral B^{plane}/NHC^{plane}, 70.5°; dihedral B^{plane}/BNHGe, 15.8°; $N_{Boryl}BN^1Ge$ torsion, 14.8(3)°). The coplanarity in **[15][BArF$_{24}$]** suggests that there is both N^1 to Ge and N^1 to B π-donation, with comparison of bond lengths to **7** suggesting an increase in the former and a decrease in the latter upon chloride abstraction: the Ge-N^1 bond shortens from 1.877(2) Å to 1.814(6) Å, while the N^1-B bond lengthens from 1.407(3) Å to 1.445(8) Å. That the N^1-B bond length is only slightly longer than the endocyclic B-N_{Boryl} distances (1.427(9)/1.432(8) Å) is consistent with still considerable N^1 to B π-donation in **[15][BArF$_{24}$]**, however.

Borylamido ligands of the form (B^{Dipp})(R_3Si)N (R = Me, Ph) have been recently applied in low-valent germanium (and other group 14 element) chemistry,[126–128] though **[15][BArF$_{24}$]** represents the first structurally characterised example featuring the (B^{Dipp})NH ligand, as well as the first example of a borylamido-substituted germanium cation. This structure contrasts with previously reported borylamido-substituted metallylenes, where the bulky SiR_3 moieties preclude the coplanarity of the boryl ring and the central BSiN(E) plane. As such, this illustrates the advantage of deploying the svelte (B^{Dipp})NH ligand, which enables coplanarity and so facilitates N^1 to B π-donation, reducing π-donation to germanium and so potentially engendering higher reactivity at the germanium centre (through a reduced elevation of the LUMO energy).[129] Consistent with this is the red colour of **[15][BArF$_{24}$]**, as compared to the orange **[14][Al(OR^F)$_4$]**, indicating a smaller HOMO-LUMO gap.

3.4 Conclusions

In this chapter, the syntheses of several known and novel NHC-coordinated chlorogermylenes were described. Chloride abstraction from these precursors utilising sources of weakly coordinating anions enabled the synthesis of a series of germylium-ylidenes. A boryl-substituted example, **[9][BArF$_{24}$]**, dimeric in the solid state, was found to form monomeric adducts with THF and pyridine. These represent the first examples of boryl-substituted germanium cations. Variation of terphenyl and NHC ligands enabled the syntheses of the first four examples of isolable terphenyl-substituted germylium-ylidenes; use of the smallest substituents resulted in a cation which is dimeric in the solid state, however increasing the steric bulk of either the NHC or terphenyl ligand led to the isolation of monomeric cations. Novel structural features could be identified in these, primarily, evidence for flanking aryl interactions, especially in **[11][BArF$_{24}$]**, and for potential anagostic interactions. These interactions were also investigated computationally. The first examples of primary amido- and borylamido-substituted germylium-ylidenes could also be synthesised. Given the strong donor ligands utilised, the boryl- and terphenyl-substituted cations would be expected to have interesting reactivity towards small molecules, which will be explored in the following chapter.

3.5 Synthesis and characterisation of novel compounds

3.5.1 Synthesis of novel chlorogermylenes and precursors

Synthesis of (IMes)$GeCl_2$, 1

To a Schlenk flask containing IMes (1.25 g, 4.11 mmol) and $GeCl_2$·dioxane (0.951 g, 4.11 mmol) was added Et_2O (30 mL). The resulting suspension was stirred overnight at room temperature, and the product deposited as a colourless crystalline solid, which could be isolated by careful filtration to yield 1.62 g (3.62 mmol, 88.0%) of a crystalline solid.

Spectroscopic data for 1:

^{1}H NMR (400.2 MHz, C_6D_6, 298 K): 2.05 (s, 6H, *p*-C**H**$_3$, NHC), 2.07 (s, 12H, *o*-C**H**$_3$, NHC), 5.87 (s, 2H, C4/C5-**H**, NHC), 6.69 (s, 4H, *m*-Ph, NHC) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): 18.3 (*o*-**C**H$_3$, NHC), 21.4 (*p*-**C**H$_3$, NHC), 123.4 (C4/C5-**C**, NHC), 129.9 (*m*-Ph, NHC), 133.8 (*i*-Ph, NHC), 135.6 (*o*-Ph, NHC), 140.5 (*p*-Ph, NHC), 172.8 (**C**$_{NHC}$) ppm.

Synthesis of (IDipp)GeI_2, 2

To a solution of (IDipp)$GeCl_2$ (0.500 g, 0.940 mmol) in benzene (5 mL) was added Me_3SiI (0.150 mL, 1.05 mmol, 1.1 equiv) at room temperature. The solution turned yellow immediately, and was stirred for 1 h at room temperature, during which time a yellow precipitate deposited. Hexane (5 mL) was then added, increasing the amount of precipitate, which could be isolated by filtration to yield 0.632 g (0.884 mmol, 94.0%) of a yellow solid.

Spectroscopic data for 2:

^{1}H NMR (400.2 MHz, CD_2Cl_2, 298 K): 1.24 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, NHC), 1.38 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, NHC), 2.36 (sept, 4H, $^3J_{HH}$ = 6.7 Hz, C**H**(CH$_3$)$_2$, NHC), 7.46 (d, 4H, $^3J_{HH}$ = 7.8 Hz, *m*-Ph, NHC), 7.69 (t, 2H, $^3J_{HH}$ = 7.8 Hz, *p*-Ph, NHC), 7.74 (s, 2H, C4/C5-**H**, NHC) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 298 K): 22.5, 26.7 (CH(**C**H$_3$)$_2$, NHC), 29.9 (**C**H(CH$_3$)$_2$, NHC), 125.6 (*m*-Ph, NHC), 129.1 (C4/C5-**C**, NHC), 132.1 (*i*-Ph, NHC), 133.4 (*p*-Ph, NHC), 145.7 (*o*-Ph, NHC), 153.5 (**C**$_{NHC}$) ppm.

Syntheses of (I-Me$_4$)(Ar^{Mes})GeCl, 2.32, (IPrMe)(Ar^{Mes})GeCl, 3, and (IPrMe)(Ar^{Tripp})GeCl, 4

These compounds were prepared by a common procedure, which is exemplified here for the case of (IPrMe)(Ar^{Mes})GeCl (**3**). A solution of IPrMe (0.188 g, 1.04 mmol, 1.1 equiv.) in toluene (10 mL) was added to an orange solution of (Ar^{Mes})GeCl (0.400 g, 0.949 mmol) also in toluene (10 mL) with rapid stirring at room temperature, resulting in an immediate colour change to light yellow. The solution was stirred for a further 30 min at room temperature, and the toluene then removed *in vacuo*. The resulting light yellow solid was washed with hexane (2 x 10 mL) and dried *in vacuo* to yield 0.420 g (0.698 mmol, 73.5%) of a white solid.

Spectroscopic data for 3:

^{1}H NMR (499.9 MHz, C_6D_6, 298 K): 0.94 (overlapping br. m, 9H, CH(C**H**$_3$)$_2$, NHC), 1.26 (br. d, 3H, CH(C**H**$_3$)$_2$, NHC), 1.50 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.18 (s, 6H, *o*-C**H**$_3$, Mes), 2.25 (s, 6H, *p*-C**H**$_3$, Mes), 2.49 (s, 6H, *o*-C**H**$_3$, Mes), 4.76 (br. m, 1H, C**H**(CH$_3$)$_2$, NHC), 5.40 (br. m, 1H, C**H**(CH$_3$)$_2$, NHC), 6.81 (s, 2H, *m*-Ph, Mes), 6.96 (overlapping s, 2H, *m*-Ph, Mes), 6.98 (overlapping d, 2H, $^3J_{HH}$ = 7.8 Hz, *m*-Ph, C_6H_3), 7.22 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph, C_6H_3) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): 10.5 (C4/C5-**C**H$_3$, NHC), 21.7 (*p*-**C**H$_3$, Mes), 22.0, 22.4 (*o*-**C**H$_3$, Mes), 22.9 (CH(**C**H$_3$)$_2$, NHC), 52.8 (**C**H(CH$_3$)$_2$, NHC), 125.8 (C4/C5-**C**, NHC), 127.0 (*p*-Ph, C_6H_3), 128.8, 129.4 (*m*-Ph, Mes), 129.9 (*m*-Ph, C_6H_3), 136.2 (*p*-Ph, Mes), 137.07, 137.12 (*o*-Ph, Mes), 140.9 (*i*-Ph, Mes), 147.5 (*o*-Ph, C_6H_3), 157.1 (*i*-Ph, C_6H_3), 173.6 (**C**$_{NHC}$) ppm.

Elemental microanalysis: found (calc. for $C_{35}H_{45}ClGeN_2$): C 69.32 (69.85)%, H 7.12 (7.54)%, N 4.56 (4.65)%

For the case of (IPrMe)(Ar^{Tripp})GeCl (**4**), (Ar^{Tripp})GeCl (0.400 g, 0.678 mmol) and IPrMe (0.134 g, 0.743 mmol, 1.1 equiv.) were combined to yield 0.432 g (0.561 mmol, 82.7%) of a white solid.

Spectroscopic data for 4:

^{1}H NMR (500.3 MHz, C_6D_6, 298 K): 0.59 (br., 3H, CH(C**H**$_3$)$_2$, NHC), 0.87 (br., 3H, CH(C**H**$_3$)$_2$, NHC), 1.16 (br., 3H, CH(C**H**$_3$)$_2$, NHC), 1.21 (d, 9H, $^3J_{HH}$ = 6.6 Hz, *o*-CH(C**H**$_3$)$_2$, Tripp), 1.33 (br. d, 18H, *o*-, *p*-CH(C**H**$_3$)$_2$, Tripp), 1.40 (overlapping br., 3H, CH(C**H**$_3$)$_2$, NHC), 1.40 (overlapping br., 3H, *o*-CH(C**H**$_3$)$_2$, Tripp), 1.40 (overlapping br. s, 3H, C4/C5-C**H**$_3$, NHC), 1.60 (br. s, 3H, C4/C5-C**H**$_3$, NHC), 1.68 (d, 6H, $^3J_{HH}$ = 6.8 Hz, *o*-

CH(C**H**$_3$)$_2$, Tripp), 2.92 (br. m, 2H, *p*-C**H**(CH$_3$)$_2$, Tripp), 3.26 (v. br. m, 2H, *o*-C**H**(CH$_3$)$_2$, Tripp), 3.42 (sept, 2H, $^3J_{HH}$ = 6.6 Hz, *o*-C**H**(CH$_3$)$_2$, Tripp), 4.95 (br. m, 1H, C**H**(CH$_3$)$_2$, NHC), 5.65 (br. m, 1H, C**H**(CH$_3$)$_2$, NHC), 7.06 (m, 2H, *m*-Ph, C$_6$H$_3$), 7.16 (overlapping s [with C$_6$D$_6$], 2H, *m*-Ph, Tripp), 7.27 (s, 2H, *m*-Ph, Tripp), 7.30 (overlapping m, 1H, *p*-Ph, C$_6$H$_3$) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 298 K): 10.5 (C4/C5-**C**H$_3$, NHC), 21.0, 22.0, 22.9, 23.7 (CH(**C**H$_3$)$_2$, NHC), 24.7, 24.8 (CH(**C**H$_3$)$_2$, Tripp), 26.8 (*o*-CH(**C**H$_3$)$_2$, Tripp), 31.6, 31.9 (*o*-**C**H(CH$_3$)$_2$, Tripp), 35.0 (*p*-**C**H(CH$_3$)$_2$, Tripp), 52.5, 53.1 (**C**H(CH$_3$)$_2$, NHC), 121.3, 121.4 (*m*-Ph, Tripp), 125.4 (*p*-Ph, C$_6$H$_3$), 126.0, 126.6 (C4/C5-**C**, NHC), 132.1 (*m*-Ph, C$_6$H$_3$), 140.4 (*i*-Ph, Tripp), 147.5 (*o*-Ph, Tripp), 147.9 (*p*-Ph, Tripp), 148.5 (*o*-Ph, C$_6$H$_3$), 157.3 (*i*-Ph, C$_6$H$_3$), 172.7 (**C**$_{NHC}$) ppm.

For the case of (I-Me$_4$)(Ar^{Mes})GeCl (**2.32**), (Ar^{Mes})GeCl (0.200 g, 0.474 mmol) and I-Me$_4$ (0.065 g, 0.523 mmol, 1.1 equiv.) were combined to yield 0.163 g (0.299 mmol, 63.0%) of a white solid. ^{1}H NMR data (C$_6$D$_6$) were consistent with literature values.[64] However, the best overall route to this compound was found to be via salt metathesis of (I-Me$_4$)GeCl$_2$ and (Ar^{Mes})Li (see **2.3.6**).

Generation of (I-Me$_4$)(Mes*)GeCl, 5

(Mes*)GeCl (0.020 g, 0.0566 mmol) and I-Me$_4$ (0.008 g, 0.0644 mmol, 1.1 equiv.) were combined at room temperature in C$_6$D$_6$ (0.5 mL) in a J. Young's NMR tube, with an immediate loss of the orange colour of (Mes*)GeCl to give a colourless solution. Monitoring via ^{1}H NMR spectroscopy confirmed complete conversion to product after ca. 5 min at room temperature. Full characterising data could not be obtained due to the short-lived nature of this species.

Spectroscopic data for 5:

^{1}H NMR (400.2 MHz, C$_6$D$_6$, 298 K): 1.17 (s, 6H, C4/C5-C**H**$_3$, NHC), 1.40 (s, 9H, *p*-C(C**H**$_3$)$_3$, Mes*), 1.56 (br. s, 18H, *o*-C(C**H**$_3$)$_3$, Mes*), 2.89 (br. s, 6H, NC**H**$_3$, NHC), 7.38 (br. s, 2H, *m*-Ph, C$_6$H$_3$) ppm.

Synthesis of (IMes)(B^{Dipp})GeCl, 6

To a solution of (IMes)GeCl$_2$ (0.416 g, 0.929 mmol) in Et$_2$O (10 mL) at −35°C was slowly added a pre-cooled (−35°C) solution of (B^{Dipp})Li(thf)$_2$ (0.550 g, 1.02 mmol, 1.1 equiv.) in Et$_2$O (15 mL). After stirring for 30 min at this temperature, the reaction mixture was gradually warmed to room temperature and

stirred for 2.5 h. The solvent was then removed *in vacuo*, and the residue extracted with toluene (2 x 10 mL). The toluene was removed *in vacuo*, to yield an orange solid; this was triturated with hexane (2 x 5 mL), and stored at −25°C overnight to yield 0.620 g (0.775 mmol, 83.4%) of a pale yellow solid that could be isolated by filtration.

Spectroscopic data for 6:

^{1}H NMR (400.2 MHz, C_6D_6, 298 K): 1.01 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.22 (overlapping d, 6H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.23 (overlapping d, 6H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.30 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.56 (s, 6H, *o*-C**H**$_3$, NHC), 2.18 (s, 6H, C**H**$_3$, NHC), 2.20 (s, 6H, C**H**$_3$, NHC), 3.34 (sept, 2H, $^{3}J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.45 (sept, 2H, $^{3}J_{HH}$ = 6.6 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 5.82 (s, 2H, C4/C5-**H**, NHC), 6.21 (s, 2H, C4/C5-**H**, B^{Dipp}), 6.61 (s, 2H, *m*-Ph, NHC), 6.71 (s, 2H, *m*-Ph, NHC), 7.08-7.24 (m, 6H, Ph, B^{Dipp}) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6, 298 K): 34 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): 18.2 (*o*-**C**H$_3$, NHC), 19.4, 21.5 (**C**H$_3$, NHC), 23.9, 24.3, 24.9, 25.3, 26.9 (CH(**C**H$_3$)$_2$, B^{Dipp}), 28.7, 29.3 (**C**H(CH$_3$)$_2$, B^{Dipp}), 123.2 (C4/C5-**C**, B^{Dipp}), 124.0, 124.1 (*m*-Ph, B^{Dipp}), 124.3 (C4/C5-**C**, NHC), [signal for *p*-Ph, B^{Dipp} obscured by that for C_6D_6], 129.86, 129.91 (*m*-Ph, NHC), 134.9 (*i*-Ph, NHC), 136.0, 136.1 (*o*-Ph, NHC), 139.0 (*p*-Ph, NHC), 142.8 (*i*-Ph, B^{Dipp}), 146.5, 146.8 (*o*-Ph, B^{Dipp}), 177.6 (**C**$_{NHC}$) ppm.

Synthesis of (IMes){(B^{Dipp})NH}GeCl, 7

To a solution of (IMes)$GeCl_2$ (0.200 g, 0.446 mmol) in Et_2O (10 mL) at −35°C was slowly added a pre-cooled (−35°C) solution of (B^{Dipp})NHLi (0.183 g, 0.447 mmol) in Et_2O (15 mL). After stirring for 30 min at this temperature, the reaction mixture was gradually warmed to room temperature and stirred for 2.5 h. The solvent was then removed *in vacuo*, and the residue extracted with toluene (2 x 10 mL). The toluene was removed *in vacuo*, to yield a pale yellow solid; this was triturated with hexane (2 x 5 mL), and stored at −25°C overnight to yield 0.317 g (0.389 mmol, 87.2%) of an off-white solid that could be isolated by filtration. Single crystals suitable for X-ray diffraction were grown by layering a concentrated toluene solution with hexane, followed by storage at −25°C for 2 d.

Spectroscopic data for 7:

^{1}H NMR (400.2 MHz, C_6D_6, 298 K): 1.26 (overlapping d, 18H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.38 (d, 6H, $^{3}J_{HH}$ = 6.6 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.84 (s, 6H, *o*-C**H**$_3$, NHC), 1.98 (s, 6H, *o*-C**H**$_3$, NHC), 2.15 (s, 6H, *p*-C**H**$_3$, NHC), 2.82 (s, 1H, GeN**H**), 3.52 (sept, 4H, $^{3}J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 5.75 (s, 2H, C4/C5-**H**, NHC), 5.99 (s, 2H, C4/C5-**H**, B^{Dipp}), 6.46 (s, 2H, *m*-Ph, NHC), 6.67 (s, 2H, *m*-Ph, NHC), 7.15 (overlapping d [with C_6D_6], 4H, *m*-Ph, B^{Dipp}), 7.22 (br. t, 2H, *p*-Ph, B^{Dipp}) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6, 298 K): 24 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): 18.2, 18.7 (*o*-**C**H$_3$, NHC), 21.7 (*p*-**C**H$_3$, NHC), 24.1, 24.2, 25.7, 25.8 (CH(**C**H$_3$)$_2$, B^{Dipp}), 28.8, 29.0 (**C**H(CH$_3$)$_2$, B^{Dipp}), 118.1 (C4/C5-**C**, B^{Dipp}), 122.7 (C4/C5-**C**, NHC), 123.6, 123.9 (*m*-Ph, B^{Dipp}), 127.2 (*p*-Ph, B^{Dipp}), 129.7, 129.8 (*m*-Ph, NHC), 134.1 (*i*-Ph, NHC), 135.1, 135.6 (*o*-Ph, NHC), 139.6 (*p*-Ph, NHC), 141.1 (*i*-Ph, B^{Dipp}), 147.7, 148.1 (*o*-Ph, B^{Dipp}), 176.1 (**C**$_{NHC}$) ppm.

Crystallographic data for 7:

$C_{47}H_{61}BClGeN_5$, M_r = 814.85, monoclinic, $P2_1/n$, a = 11.4237(2) Å, b = 15.7658(3) Å, c = 25.3662(5) Å, α = 90°, β = 100.294(2)°, γ = 90°, V = 4495.01(15) Å^3, Z = 4, R_1 = 0.0418 (7201, I>2σ{I}), wR_2 = 0.1110 (all 9474 unique reflections).

Synthesis of (IPrMe)(O^{t}Bu)GeCl, 8

To a solution of (IPrMe)$GeCl_2$ (0.400 g, 1.24 mmol) in THF (10 mL) at −35°C was added dropwise over 30 min a pre-cooled (−35°C) solution of KO^{t}Bu (0.139 g, 1.24 mmol) in THF (10 mL). After stirring for a further 30 min at this temperature, the reaction mixture was gradually warmed to room temperature and stirred overnight. The solvent was then removed *in vacuo*, and the residue extracted with toluene (2 x 10 mL). The toluene was removed *in vacuo*, to yield a colourless oil; this was triturated with hexane (2 x 5 mL), and stored at −25°C overnight to yield 0.362 g (1.00 mmol, 80.6%) of a white solid that could be isolated by filtration.

Spectroscopic data for 8:

^{1}H NMR (400.2 MHz, C_6D_6, 298 K): 1.22 (d, 12H, $^{3}J_{HH}$ = 7.1 Hz, CH(C**H**$_3$)$_2$, NHC), 1.49 (s, 6H, C4/C5-C**H**$_3$, NHC), 1.69 (s, 9H, C(C**H**$_3$)$_3$, O^{t}Bu), 5.89 (br. m, 2H, C**H**(CH$_3$)$_2$, NHC) ppm.

$^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 298 K): 10.0 (C4/C5-**C**H_3, NHC), 22.3 (CH(**C**H_3)$_2$, NHC), 34.0 (C(**C**H_3)$_3$, O^{t}Bu), 50.9 (**C**H(CH_3)$_2$, NHC), 72.3 (**C**(CH_3)$_3$, O^{t}Bu), 125.5 (C4/C5-**C**, NHC), 172.0 (**C**$_{NHC}$) ppm.

3.5.2 Synthesis of novel germylium-ylidenes

Synthesis of [(IPrMe)(B^{Dipp})Ge=Ge(B^{Dipp})(IPrMe)][BArF$_{24}$]$_2$, [(9)$_2$][BArF$_{24}$]$_2$

(IPrMe)(B^{Dipp})GeCl (0.750 g, 1.11 mmol) and Na[$BArF_{24}$] (0.984 g, 1.11 mmol) were combined in fluorobenzene (15 mL) at room temperature. The solution immediately turned a deep red; it was stirred for a further 1 h at room temperature, during which time a fine precipitate began to form, and then left for 30 min to allow this precipitate to settle. After filtration, the solution was concentrated and layered with hexane. Storage at −25°C for 3 d yielded deep red crystals, which were isolated, washed with a small amount of cold (−25°C) fluorobenzene (2 x 2 mL), and dried *in vacuo* to yield 0.812 g (0.540 mmol, 48.7%) of a red crystalline solid [Note that for this and other dimeric cations in this chapter, molar quantities given refer to the monomeric units].

Elemental microanalysis: found (calc. for $C_{69}H_{68}B_2F_{24}GeN_4$): C 54.98 (55.12)%, H 4.62 (4.56)%, N 3.71 (3.73)%

UV-Vis (fluorobenzene): λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 462 (9840)

Crystallographic data for [(9)$_2$][BArF$_{24}$]$_2$:

$C_{138}H_{136}B_4F_{48}Ge_2N_8$, M_r = 3006.99, triclinic, P-1, a = 17.0530(2) Å, b = 17.6136(2) Å, c = 28.6924(4) Å, α = 94.9379(11)°, β = 103.7992(10)°, γ = 106.4928(11)°, V = 7914.88(18) Å^3, Z = 2, R_1 = 0.0775 (28091, I>2σ{I}), wR_2 = 0.2186 (all 32903 unique reflections).

Generation of [(IPrMe)(B^{Dipp})Ge(L)][BArF$_{24}$], [9(L)][BArF$_{24}$]

[9(d$_8$-THF)][BArF$_{24}$] and **[9(d$_5$-pyridine)][BArF$_{24}$]** could be obtained as yellow and orange solutions respectively by dissolution of **[(9)$_2$][BArF$_{24}$]$_2$** in the respective deuterated solvents. Dissolution in minimal protio-solvent, followed by layering with hexane and storage for several days at room temperature, enabled the isolation of a small amount of yellow/orange crystals suitable for X-ray crystallography.

Spectroscopic data for [9(d_8-THF)][$BArF_{24}$]:

^{1}H NMR (400.2 MHz, d_8-THF, 298 K): 1.18 (d, 12H, $^{3}J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.24 (br. m, 12H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.29 (br. m, 12H, CH(C**H**$_3$)$_2$, NHC), 2.29 (s, 6H, C4/C5-C**H**$_3$, NHC), 3.24 (sept, 4H, $^{3}J_{HH}$ = 6.4 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.83 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, NHC), 6.43 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.26 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz, *m*-Ph, B^{Dipp}), 7.33 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, *p*-Ph, B^{Dipp}), 7.59 (s, 4H, *p*-Ph, $BArF_{24}$), 7.80 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d_8-THF, 298 K): −6 (**B**ArF_{24}), 34 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, d_8-THF, 298 K): 10.6 (C4/C5-**C**H$_3$, NHC), 21.8 (CH(**C**H$_3$)$_2$, NHC), 24.0, 26.6 (CH(**C**H$_3$)$_2$, B^{Dipp}), 29.5 (**C**H(CH$_3$)$_2$, B^{Dipp}), 55.0 (**C**H(CH$_3$)$_2$, NHC), 118.4 (br. m, $^{3}J_{CF}$ = 3.6 Hz, *p*-Ph, $BArF_{24}$), 124.2 (C4/C5-**C**, B^{Dipp}), 125.2 (*m*-Ph, B^{Dipp}), 125.7 (q, $^{1}J_{CF}$ = 271.8 Hz, **C**F$_3$, $BArF_{24}$), 129.5 (*p*-Ph, B^{Dipp}), 130.0 (C4/C5-**C**, NHC), 130.2 (qq, $^{3}J_{CB}$ = 2.4 Hz, $^{2}J_{CF}$ = 32.2 Hz, *m*-Ph, $BArF_{24}$), 135.8 (*o*-Ph, $BArF_{24}$), 140.4 (*i*-Ph, B^{Dipp}), 147.4 (*o*-Ph, B^{Dipp}), 163.0 (q, $^{1}J_{CB}$ = 50.1 Hz, *i*-Ph, $BArF_{24}$), 167.0 (**C**$_{NHC}$) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, d_8-THF, 298 K): −63.4 (BAr**F**$_{24}$) ppm.

Elemental microanalysis: found (calc. for $C_{73}H_{76}B_2F_{24}GeN_4O$): C 55.12 (55.65)%, H 4.73 (4.86)%, N 3.66 (3.56)%

Crystallographic data for [9(THF)][$BArF_{24}$]:

$C_{77}H_{84}B_2F_{24}GeN_4O_2$, M_r = 1647.69, monoclinic, $P2_1/c$, a = 13.1361(2) Å, b = 23.9448(4) Å, c = 26.3106(4) Å, α = 90°, β = 89.683(2)°, γ = 90°, V = 8275.6(2) Å^3, Z = 4, R_1 = 0.0847 (12843, I>2σ{I}), wR_2 = 0.2472 (all 14624 unique reflections).

Spectroscopic data for [9(d_5-pyridine)][$BArF_{24}$]:

^{1}H NMR (400.2 MHz, d_5-pyridine, 298 K): 1.10 (overlapping br. m, 12H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.10 (overlapping br. m, 12H, CH(C**H**$_3$)$_2$, NHC), 1.23 (d, 12H, $^{3}J_{HH}$ = 6.5 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 2.14 (s, 6H, C4/C5-C**H**$_3$), 3.37 (br. sept, 4H, C**H**(CH$_3$)$_2$, B^{Dipp}), 5.06 (sept, 2H, $^{3}J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$, NHC), 6.66 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.34 (br. m, 4H, *m*-Ph), 7.51 (t, 2H, $^{3}J_{HH}$ = 7.8 Hz, *p*-Ph), 7.84 (s, 4H, *p*-Ph, $BArF_{24}$), 8.43 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d_5-pyridine, 298 K): −6 (**B**ArF_{24}), 33 (**B**^{Dipp}) ppm.

Crystallographic data for [9(pyridine)][BArF$_{24}$]:

$C_{80.5}H_{79.5}B_2F_{24}GeN_6$, M_r = 1681.21, orthorhombic, Pba2, a = 22.8649(3) Å, b = 26.8024(3) Å, c = 13.23260(10) Å, α = 90°, β = 90°, γ = 90°, V = 8109.39(15) Å^3, Z = 4, R_1 = 0.0403 (15211, I>2σ{I}), wR_2 = 0.1066 (all 16848 unique reflections).

Generation of [(I-Me$_4$)(Ar^{Mes})Ge=Ge(Ar^{Mes})(I-Me$_4$)][WCA]$_2$, [(10)$_2$][WCA]$_2$

These compounds could not be satisfactorily synthesised on a preparatory scale. However, from combination of (I-Me$_4$)(Ar^{Mes})GeCl (0.100 g, 0.183 mmol) and Na[BArF$_{24}$] (0.162 g, 0.183 mmol) in fluorobenzene (10 mL) at room temperature, followed by stirring for 1 h, standing for 30 min, and subsequent filtration, concentration, layering with hexane and storage at −25°C for 2 weeks, could be obtained a small number of orange single crystals suitable for X-ray diffraction analysis.

Crystallographic data for [(10)$_2$][BArF$_{24}$]$_2$:

$C_{138}H_{108}B_2F_{50}Ge_2N_4$, M_r = 2939.11, triclinic, P-1, a = 12.67410(3) Å, b = 18.19210(3) Å, c = 29.74590(4) Å, α = 106.503(4)°, β = 98.776(4)°, γ = 91.520(4)°, V = 6481.25(15) Å^3, Z = 2, R_1 = 0.0954 (46319, I>2σ{I}), wR_2 = 0.3275 (all 54047 unique reflections).

In investigating the reactivity of this cation, (I-Me$_4$)(Ar^{Mes})GeCl (0.020 g, 0.0366 mmol) and Li[Al(OR^F)$_4$] (0.036 g, 0.0369 mmol) were combined in C_6D_5Br (0.5 mL) at room temperature to generate *in situ* a suspension of **[(10)$_2$][Al(OR^F)$_4$]$_2$**. Na[BArF$_{24}$] (0.033 g, 0.0372 mmol) was also competent for this reaction, although the crystallinity of Li[Al(OR^F)$_4$] resulted in greater convenience for small-scale reactions.

Spectroscopic data for [(10)$_2$][Al(OR^F)$_4$]$_2$:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298 K): 1.65 (br. s, 6H, C4/5-C**H**$_3$, NHC), 1.99 (br. s, 6H, *o*-C**H**$_3$, Mes), 2.17 (br. s, 6H, *o*-C**H**$_3$, Mes), 2.38 (s, 6H, *p*-C**H**$_3$, Mes), 3.06 (br. s, 6H, NC**H**$_3$, NHC), 6.55 (br. s, 2H, *m*-Ph, Mes), 6.90 (overlapping br., 4H, *m*-Ph, Mes and C_6H_3), 7.35 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph, C_6H_3) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, C_6D_5Br, 298K): −74.6 (C**F**$_3$, Al(OR^F)$_4$) ppm.

^{27}Al{^{1}H} NMR (104.3 MHz, C_6D_5Br, 298K): 35.5 (**Al**(OR^F)$_4$) ppm.

Satisfactory ^{13}C NMR data could not be obtained due to the poor solubility of this species.

UV-Vis (fluorobenzene): λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 441 (7380)

Spectroscopic data for [(10)$_2$][BArF$_{24}$]$_2$:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298K): 1.65 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 1.89 (br. s, 6H, *o*-C**H**$_3$, Mes), 2.16 (br. s, 6H, *o*-C**H**$_3$, Mes), 2.32 (s, 6H, *p*-C**H**$_3$, Mes), 2.99 (br. s, 6H, NC**H**$_3$, NHC), 6.54 (br. s, 2H, *m*-Ph, Mes), 6.92 (overlapping br., 4H, *m*-Ph, Mes and C_6H_3), 7.39 (br. m, 1H, *p*-Ph, C_6H_3), 7.79 (s, 4H, *p*-Ph, $BArF_{24}$), 8.39 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

Satisfactory ^{13}C NMR data could not be obtained due to the poor solubility of this species.

Generation of [(I-Me$_4$)(Ar^{Mes})Ge(THF)][Al(OR^F)$_4$], [10(THF)][Al(OR^F)$_4$]

This compound could be generated *in situ* from addition of excess THF (12.0 µL, 0.148 mmol, 4 equiv.) to a solution of **[(10)$_2$][Al(OR^F)$_4$]$_2$** (0.0366 mmol) in C_6D_5Br (0.5 mL) at room temperature.

Spectroscopic data for [10(THF)][Al(OR^F)$_4$]:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298 K): 1.71 (s, 6H, C4/5-C**H**$_3$, NHC), 2.16 (s, 6H, *o*-C**H**$_3$, Mes), 2.36 (s, 6H, *p*-C**H**$_3$, Mes), 2.51 (s, 6H, *o*-C**H**$_3$, Mes), 3.19 (s, 6H, NC**H**$_3$, NHC), 6.78 (s, 2H, *m*-Ph, Mes), 6.93-7.02 (overlapping, 4H, *m*-Ph, Mes and C_6H_3), 7.35 (overlapping m, 1H, *p*-Ph, C_6H_3) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, C_6D_5Br, 298K): −74.6 (C**F**$_3$, Al(OR^F)$_4$) ppm.

^{27}Al{^{1}H} NMR (104.3 MHz, C_6D_5Br, 298K): 35.4 (**Al**(OR^F)$_4$) ppm.

Satisfactory ^{13}C NMR data could not be obtained due to the poor solubility of this species.

Syntheses of [(NHC)(Ar)Ge][WCA]

These cations were prepared according to a common procedure, which is exemplified here for the case of NHC = IPrMe, Ar = Ar^{Mes}, WCA = Al(OR^F)$_4$ (**[12][Al(OR^F)$_4$]**). (IPrMe)(Ar^{Mes})GeCl (0.179 g, 0.297 mmol) and Li[Al(OR^F)$_4$] (0.290 g, 0.298 mmol) were combined in fluorobenzene (15 mL) at room temperature. The solution immediately turned a deep red; it was stirred for a further 1 h at room temperature, during which time a fine precipitate began to form, and then left for 30 min to allow this precipitate to settle. After filtration, the solution was concentrated and layered with hexane. Storage at −25°C for 2 weeks yielded deep red crystals, which were isolated, washed with a small amount of cold (−25°C) fluorobenzene (2 x 2 mL), and dried *in vacuo*, to yield 0.390 g (0.254 mmol, 85.3%) of a red crystalline solid.

Spectroscopic data for [12][Al(OR^F)$_4$]:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298 K): 1.07 (d, 12H, $^3J_{HH}$ = 6.5 Hz, CH(C**H**$_3$)$_2$, NHC), 2.01 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.26 (s, 12H, *o*-C**H**$_3$, Mes), 2.33 (s, 6H, *p*-C**H**$_3$, Mes), 4.00 (br. sept, 2H, C**H**(CH$_3$)$_2$, NHC), 6.96 (s, 4H, *m*-Ph, Mes), 7.08 (d, 2H, $^3J_{HH}$ = 7.1 Hz, *m*-Ph, C_6H_3), 7.55 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph, C_6H_3) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_5Br, 298 K): 10.3 (C4/C5-**C**H$_3$, NHC), 21.3 (*p*-**C**H$_3$, Mes), 21.4 (*o*-**C**H$_3$, Mes), 21.8 (CH(**C**H$_3$)$_2$, NHC), 53.6 (**C**H(CH$_3$)$_2$, NHC), 79.5 (br., O**C**(CF$_3$)$_3$, Al(OR^F)$_4$), 121.9 (q, $^1J_{CF}$ = 294.4 Hz, **C**F$_3$, Al(OR^F)$_4$), [signals for C4/C5-**C**, NHC, *m*- and *p*-Ph, C_6H_3, and *m*-Ph, Mes, obscured by those for C_6D_5Br], 132.4 (*i*-Ph, Mes), 137.3 (*o*-Ph, Mes), 140.0 (*p*-Ph, Mes), 143.6 (*o*-Ph, C_6H_3), 154.1 (*i*-Ph, C_6H_3), 168.0 (**C**$_{NHC}$) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, C_6D_5Br, 298K): −74.6 (C**F**$_3$, Al(OR^F)$_4$) ppm.

^{27}Al{^{1}H} NMR (104.3 MHz, C_6D_5Br, 298K): 35.4 (**Al**(OR^F)$_4$) ppm.

Elemental microanalysis: found (calc. for $C_{51}H_{45}AlF_{36}GeN_2O_4$): C 39.56 (39.95)%, H 3.33 (3.39)%, N 2.69 (2.62)%

Crystallographic data for [12][Al(OR^F)$_4$]:

$C_{53.25}H_{48}AlF_{36.25}GeN_2O_4$, M_r = 1568.25, triclinic, P-1, a = 14.5938(4) Å, b = 16.0784(3) Å, c = 28.1094(5) Å, α = 95.659(2)°, β = 92.317(2)°, γ = 94.000(2)°, V = 6540.2(2) Å^3, Z = 4, R_1 = 0.1253 (19084, I>2σ{I}), wR_2 = 0.3909 (all 23000 unique reflections).

For the case of [(IPrMe)(Ar^{Mes})Ge][BArF$_{24}$] (**[12][BArF$_{24}$]**), (IPrMe)(Ar^{Mes})GeCl (0.100 g, 0.166 mmol) and Na[BArF$_{24}$] (0.147 g, 0.166 mmol) were combined to give a small number of red single crystals, revealed by X-ray diffraction analysis to be the co-crystallite of [(IPrMe)(Ar^{Mes})Ge][BArF$_{24}$] (53%) and [(IPrMe)(Ar^{Mes})GeH(OH)][BArF$_{24}$] (47%).

Crystallographic data for [{12}$_{0.53}${(12)H(OH)}$_{0.47}$][BArF$_{24}$]:

$C_{79}H_{67.93}BF_{26}GeN_2O_{0.47}$, M_r = 1630.12, monoclinic, $P2_1/c$, a = 24.1331(2) Å, b = 13.2169(1) Å, c = 25.1121(2) Å, α = 90°, β = 108.399(1)°, γ = 90°, V = 7600.42(11) Å^3, Z = 4, R_1 = 0.0787 (15095, I>2σ{I}), wR_2 = 0.1915 (all 15938 unique reflections).

For the case of [(I-Me_4)(Ar^{Tripp})Ge][$BArF_{24}$] (**[11][$BArF_{24}$]**), (I-Me_4)(Ar^{Tripp})GeCl (0.100 g, 0.140 mmol) and Na[$BArF_{24}$] (0.124 g, 0.140 mmol) were combined to yield 0.178 g (0.115 mmol, 82.5%) of an orange crystalline solid.

Spectroscopic data for [11][$BArF_{24}$]:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298K): 1.20 (overlapping br. m, 15H, CH(C**H**$_3$)$_2$, Tripp), 1.37 (overlapping br. m, 21H, CH(C**H**$_3$)$_2$, Tripp), 1.66 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 3.03 (overlapping br. m, 6H, C**H**$(CH_3)_2$, Tripp), 3.03 (overlapping br. s, 6H, NC**H**$_3$, NHC), 7.19-7.39 (overlapping br., 7H, Ph, Tripp and C_6H_3), 7.78 (s, 4H, *p*-Ph, $BArF_{24}$), 8.37 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

Satisfactory ^{13}C NMR data could not be obtained due to the poor solubility of this species.

Crystallographic data for [11][$BArF_{24}$]:

$C_{81}H_{78}BF_{25}GeN_2$, M_r = 1637.85, monoclinic, Cc, a = 18.4835(3) Å, b = 18.9570(3) Å, c = 22.6395(4) Å, α = 90°, β = 105.764(2)°, γ = 90°, V = 7634.3(2) Å^3, Z = 4, R_1 = 0.0432 (10883, I>2σ{I}), wR_2 = 0.1155 (all 11376 unique reflections).

For the case of [(IPrMe)(Ar^{Tripp})Ge][$BArF_{24}$] (**[13][$BArF_{24}$]**), (IPrMe)(Ar^{Tripp})GeCl (0.200 g, 0.260 mmol) and Na[$BArF_{24}$] (0.230 g, 0.260 mmol) were combined to yield 0.097 g (0.0607 mmol, 23.3%) of a red crystalline solid.

Spectroscopic data for [13][$BArF_{24}$]:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298 K): 1.01 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, NHC), 1.20 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *o*-CH(C**H**$_3$)$_2$, Tripp), 1.28 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *o*-CH(C**H**$_3$)$_2$, Tripp), 1.38 (d, 12H, $^3J_{HH}$ = 7.0 Hz, *p*-CH(C**H**$_3$)$_2$, Tripp), 1.89 (s, 6H, C4/C5-C**H**$_3$, NHC), 3.00 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, *p*-C**H**$(CH_3)_2$, Tripp), 3.12 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, *o*-C**H**$(CH_3)_2$, Tripp), 3.80 (sept, 2H, $^3J_{HH}$ = 6.5 Hz, C**H**$(CH_3)_2$, NHC), 7.28 (overlapping d, 2H, *m*-Ph, C_6H_3), 7.29 (overlapping s, 4H, *m*-Ph, Tripp), 7.49 (overlapping t [with C_6D_5Br], 1H, *p*-Ph, C_6H_3), 7.76 (s, 4H, *p*-Ph, $BArF_{24}$), 8.37 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_5Br, 298 K): −6 (**B**ArF_{24}) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_5Br, 298 K): 10.2 (C4/C5-**C**H_3, NHC), 21.8 (CH(**C**$H_3)_2$, NHC), 23.0 (*o*-CH(**C**$H_3)_2$, Tripp), 23.9 (*p*-CH(**C**$H_3)_2$, Tripp), 26.8 (*o*-CH(**C**$H_3)_2$, Tripp), 31.5 (*o*-**C**$H(CH_3)_2$, Tripp), 34.4 (*p*-**C**$H(CH_3)_2$, Tripp), 53.8 (**C**$H(CH_3)_2$, NHC), 117.8 (br. m, $^3J_{CF}$ = 4.5 Hz, *p*-Ph, $BArF_{24}$), 122.9 (*m*-Ph, Tripp),

124.9 (q, $^{1}J_{CF}$ = 272.5 Hz, **C**F_3, $BArF_{24}$), 129.4 (C4/C5-**C**, NHC), [signals for *m*-Ph, $BArF_{24}$, and *i*-Ph, Tripp obscured by those for C_6D_5Br], 131.5 (*p*-Ph, C_6H_3), 131.8 (*m*-Ph, C_6H_3), 135.2 (*o*-Ph, $BArF_{24}$), 142.6 (*o*-Ph, C_6H_3), 148.3 (*o*-Ph, Tripp), 151.7 (*p*-Ph, Tripp), 156.4 (*i*-Ph, C_6H_3), 162.3 (q, $^{1}J_{CB}$ = 50.9 Hz, *i*-Ph, $BArF_{24}$), 167.7 (**C**$_{NHC}$) ppm.

$^{19}F\{^{1}H\}$ NMR (376.5 MHz, C_6D_5Br, 298 K): −62.1 (BAr**F**$_{24}$) ppm.

Crystallographic data for [13][BArF$_{24}$]:

$C_{79}H_{81}BF_{24}GeN_2$, M_r = 1597.85, orthorhombic, Pbca, a = 18.4687(1) Å, b = 23.1425(3) Å, c = 36.8932(4) Å, α = 90°, β = 90°, γ = 90°, V = 15768.6(3) Å^3, Z = 8, R_1 = 0.0704 (13476, I>2σ{I}), wR_2 = 0.2120 (all 16548 unique reflections).

Synthesis of [(IDipp)(DippNH)Ge][Al(OR^F)$_4$], [14][Al(OR^F)$_4$]

(IDipp)(DippNH)GeCl (0.200 g, 0.297 mmol) and Li[Al(OR^F)$_4$] (0.290 g, 0.298 mmol) were combined in fluorobenzene (15 mL) at room temperature. The solution immediately turned orange; it was stirred for a further 1 h at room temperature, during which time a fine precipitate began to form, and then left for 30 min to allow this precipitate to settle. After filtration, the solution was concentrated and layered with hexane. Storage at −25°C for 2 d yielded orange crystals, which were isolated, washed with a small amount of cold (−25°C) fluorobenzene (2 x 2 mL), and dried *in vacuo*, to yield 0.208 g (0.130 mmol, 43.5%) of an orange crystalline solid.

Spectroscopic data for [14][Al(OR^F)$_4$]:

[due to a difficulty in distinguishing between the Dipp groups of the NHC and NHDipp, these are not differentiated in the assignments below]

^{1}H NMR (400.2 MHz, CD_2Cl_2, 298 K): 0.93 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz), 1.30 (overlapping m, 24H) [both CH(C**H**$_3$)$_2$, Dipp], 2.33 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz), 2.56 (sept, 4H, $^{3}J_{HH}$ = 6.9 Hz) [both C**H**$(CH_3)_2$, Dipp], 3.75 (br. s, 1H, GeN**H**), 7.45-7.51 (overlapping d, 6H, *m*-Ph, Dipp), 7.62 (s, 2H, C4/C5-**H**, NHC), 7.67-7.75 (overlapping t, 3H, *p*-Ph, Dipp) ppm.

$^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 298K): 23.9, 24.9, 25.3 (CH(**C**H_3)$_2$, Dipp), 28.6, 30.1 (**C**H$(CH_3)_2$, Dipp), 79.6 (br., O**C**$(CF_3)_3$, Al(OR^F)$_4$), 121.8 (q, $^{1}J_{CF}$ = 293.7 Hz, **C**F_3, Al(OR^F)$_4$), 125.9, 126.2 (*m*-Ph, Dipp), 127.3

(C4/C5-**C**, NHC), 129.5, 130.9, 133.7 (*p*-Ph, Dipp), 136.7, 137.0 (*i*-Ph, Dipp), 143.0, 145.9 (*o*-Ph, Dipp), 170.8 ($\mathbf{C}_{NHC}$) ppm.

$^{19}F\{^{1}H\}$ NMR (376.5 MHz, CD_2Cl_2, 298K): −75.7 ($C\mathbf{F}_3$, $Al(OR^F)_4$) ppm.

$^{27}Al\{^{1}H\}$ NMR (104.3 MHz, CD_2Cl_2, 298K): 34.6 ($\mathbf{Al}(OR^F)_4$) ppm.

Elemental microanalysis: found (calc. for $C_{55}H_{54}AlF_{36}GeN_3O_4$): C 40.52 (41.17)%, H 3.24 (3.39)%, N 2.71 (2.62)%

Crystallographic data for [14][Al(OR^F)$_4$]:

$C_{55}H_{54}AlF_{36}GeN_3O_4$, M_r = 1604.58, monoclinic, $P2_1/c$, a = 11.4299(1) Å, b = 35.9074(2) Å, c = 16.0208(1) Å, α = 90°, β = 95.725(1)°, γ = 90°, V = 6542.43(8) Å^3, Z = 4, R_1 = 0.0543 (12523, I>2σ{I}), wR_2 = 0.1512 (all 13663 unique reflections).

Synthesis of [(IMes){(B^{Dipp})NH}Ge][BArF$_{24}$], [15][BArF$_{24}$]

(IMes){(B^{Dipp})NH}GeCl (0.150 g, 0.184 mmol) and $Na[BArF_{24}]$ (0.163 g, 0.184 mmol) were combined in fluorobenzene (15 mL) at room temperature. The solution immediately turned red; it was stirred for a further 1 h at room temperature, during which time a fine precipitate began to form, and then left for 30 min to allow this precipitate to settle. After filtration, the solution was concentrated and layered with hexane. Storage at −25°C for 1 week yielded red crystals, which were isolated, washed with a small amount of cold (−25°C) fluorobenzene (2 x 2 mL), and dried *in vacuo*, to yield 0.215 g (0.131 mmol, 71.1%) of a red crystalline solid.

Spectroscopic data for [15][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, CD_2Cl_2, 298 K): 0.83 (d, 12H, $^3J_{HH}$ = 7.0 Hz, $CH(C\mathbf{H}_3)_2$, B^{Dipp}), 1.12 (d, 12H, $^3J_{HH}$ = 7.0 Hz, $CH(C\mathbf{H}_3)_2$, B^{Dipp}), 1.81 (s, 12H, *o*-$C\mathbf{H}_3$, NHC), 2.11 (s, 1H, GeN**H**), 2.33 (s, 6H, *p*-$C\mathbf{H}_3$, NHC), 2.79 (sept, 4H, $^3J_{HH}$ = 7.0 Hz, $C\mathbf{H}(CH_3)_2$, B^{Dipp}), 6.13 (s, 2H, C4/C5-**H**, B^{Dipp}), 6.90 (s, 4H, *m*-Ph, NHC), 7.15 (overlapping d, 4H, $^3J_{HH}$ = 7.7 Hz, *m*-Ph, B^{Dipp}), 7.23 (s, 2H, C4/C5-**H**, NHC), 7.31 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *p*-Ph, B^{Dipp}), 7.56 (s, 4H, *p*-Ph, $BArF_{24}$), 7.73 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

$^{11}B\{^{1}H\}$ NMR (128.4 MHz, CD_2Cl_2, 298 K): −7 ($\mathbf{B}ArF_{24}$), 23 ($\mathbf{B}^{Dipp}$) ppm.

$^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 298 K): 17.6 (*o*-$C\mathbf{H}_3$, NHC), 21.5 (*p*-$C\mathbf{H}_3$, NHC), 24.0, 24.6 ($CH(C\mathbf{H}_3)_2$, B^{Dipp}), 28.8 ($C\mathbf{H}(CH_3)_2$, B^{Dipp}), 118.0 (br. m, $^3J_{CF}$ = 4.8 Hz, *p*-Ph, $BArF_{24}$), 118.6 (C4/C5-**C**, B^{Dipp}), 124.9 (*m*-

Ph, B^{Dipp}), 125.2 (q, $^{1}J_{CF}$ = 271.8 Hz, **C**F_3, $BArF_{24}$), 125.8 (C4/C5-**C**, NHC), 128.9 (*p*-Ph, B^{Dipp}), 129.4 (qq, $^{3}J_{CB}$ = 2.9 Hz, $^{2}J_{CF}$ = 30.5 Hz, *m*-Ph, $BArF_{24}$), 130.9 (*m*-Ph, NHC), 134.2 (*o*-Ph, NHC), 135.4 (*o*-Ph, $BArF_{24}$), 137.4 (*i*-Ph, B^{Dipp}), 142.7 (*p*-Ph, NHC), 146.7 (*o*-Ph, B^{Dipp}), 162.3 (q, $^{1}J_{CB}$ = 49.6 Hz, *i*-Ph, $BArF_{24}$), 171.3 (**C**$_{NHC}$) ppm. [signal for *i*-Ph, NHC not observed/obscured]

$^{19}F\{^{1}H\}$ NMR (376.5 MHz, CD_2Cl_2, 298 K): −62.9 (BAr**F**$_{24}$) ppm.

Crystallographic data for [15][BArF$_{24}$]:

$C_{79}H_{73}B_2F_{24}GeN_5$, M_r = 1642.63, monoclinic, $P2_1$, a = 13.2764(3) Å, b = 14.6563(3) Å, c = 20.1260(4) Å, α = 90°, β = 92.218(2)°, γ = 90°, V = 3913.24(14) Å^3, Z = 2, R_1 = 0.0608 (16984, I>2σ{I}), wR_2 = 0.1753 (all 19448 unique reflections).

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Chapter IV

Small Molecule Activation by Novel Germanium Cations

4.1 Introduction

4.1.1 E-H bond activation by germylium-ylidenes

Small molecule activation by germylenes is well-established,[1,2] with recent years seeing the development of compounds capable of the oxidative addition of traditionally challenging, catalytically-relevant substrates such as dihydrogen and ammonia.[3–5] As compared to such neutral germylenes, germylium-ylidenes possess, by virtue of their lone pair but also positive charge, a potentially accentuated ambiphilicity and "transition metal-like" reactivity.[6] Furthermore, it has been suggested that cationic species, following addition, have a greater disposition towards reductive elimination and reversibility,[7,8] a phenomenon not yet achieved by neutral germylenes.[2] This stability of neutral Ge^{IV} products also extends to other onward reactions, which have similarly not been seen; whereas, the enhanced electrophilicity of cationic analogues might be expected to lead to further reaction following oxidative addition, which is obviously crucial towards the construction of catalytic cycles. Precedent to inspire such a hypothesis can be found in silicon chemistry, where the high reactivity of silylium ions (for example, in abstracting halides and as Lewis acids), has led to varied applications in catalysis.[9,10]

However, the strategies typically used to stabilise germylium-ylidenes (for instance, the use of bulky or cyclic π-donor ligands,[11–16] or multiple neutral ligands)[17] often leads to a quenching of their potentially fascinating reactivity. Thus, while their pronounced electrophilicity has repeatedly been demonstrated (by, for example, coordination of Lewis bases),[14,15,18] only recently have a small number of germylium-ylidenes been reported which are capable of oxidative bond activation.[7,8,19,20] However, each of these systems exhibit deficiencies that make it clear that further exploration in this area is urgently needed. Thus, although the reversible activation of boranes and silanes facilitated by **1.67-IDipp** (Figure 4.1) is fascinating, it is clearly desirable to try and replicate this reactivity with non-transition metal-stabilised cations.[7] The siloxy-substituted cation **1.69**, while capable of the activation

of the polar C-Cl bond in dichloromethane, presumably features an insufficiently strong donor ligand to facilitate the addition of more challenging small molecules.[20] The alkyl-substituted cation **1.33** can also activate dichloromethane, however reactivity studies towards E-H bonds resulted only in the isolation of $[IDippH]^+$-containing species, suggesting insufficient stabilisation of the transient Ge^{IV} product by the alkyl donor.[19] Finally, the terphenyl-substituted **1.63**, postulated as a transient intermediate generated *in situ* (by dihydrogen elimination from $[(Ar^{Tripp})GeH_2]^+$, which is unstable above 0°C), exhibits interesting, albeit uncontrollable, reactivity (with solvent and flanking ligand moieties), suggesting a strong donor ligand alone, while engendering a reactive element centre, is insufficient to enable the isolation and controlled reactivity of a germylium-ylidene.[8]

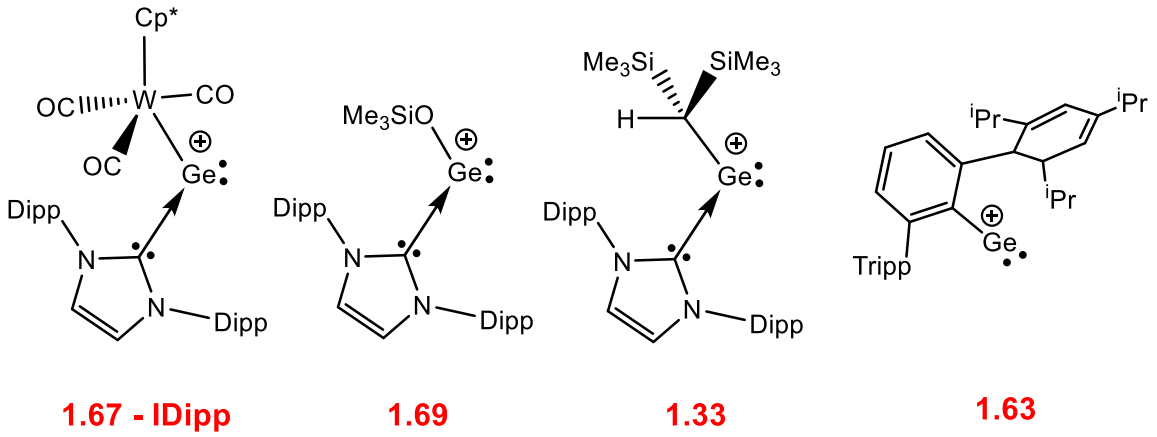
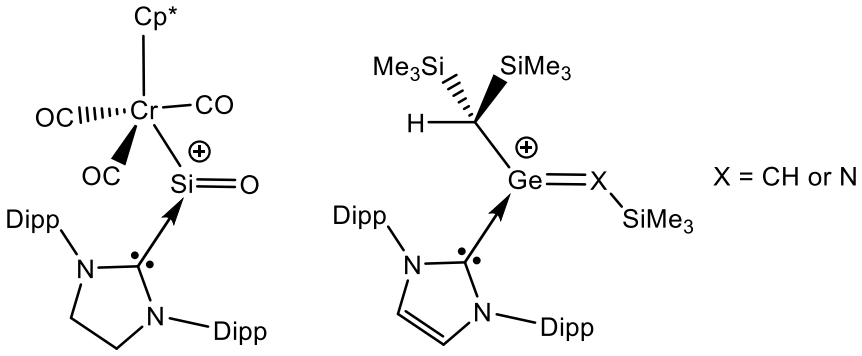


Figure 4.1: Germylium-ylidenes reported to be capable of oxidative addition (counteranion: $[BArF_{24}]^-$, apart from $[Al(OR^F)_4]^-$ far right)

4.1.2 Electrostatic stabilisation of multiple bonds involving germanium

Of the many examples of heteronuclear multiple bonds involving germanium,[21] the vast majority have been stabilised by some combination of bulky substituents,[22–26] resonance delocalisation,[27–37] and/or additional neutral donors.[38–40] However, these approaches are clearly detrimental to potential reactivity across the multiple bond once isolated. As an alternative, a recently applied strategy within the Aldridge group, of using a positive charge to provide an electrostatic disincentive to aggregration,[19] has enabled the isolation of three-coordinate multiply bonded germanium systems featuring considerably less bulky ligands (**{1.33}XSiMe$_3$**, X = CH or N). Such an approach has also been utilised by Filippou in the synthesis of a transition metal-stabilised Si=O bond (**1.68**).[41] With the eventual aim of replicating the fascinating reactivity of transition metal-carbon/nitrogen multiple bonds,[42–44] the

targeting of such cationic main group analogues featuring (relative to neutral systems) reduced steric hindrance, localisation of multiple bond character, increased electrophilicity, and increased polarisation of the Ge=X bond is perceived as ideal.



1.68 **(1.33)XSiMe$_3$**

Figure 4.2: Cationic heteronuclear multiple bonds involving group 14 elements (counteranion: [BArF$_{24}$]$^-$ for all)

4.2 Project aims

The boryl- or terphenyl-substituted cations synthesised in Chapter 3 are ideal candidates as isolable, non-transition metal-stabilised germylium-ylidenes capable of the activation of E-H bonds. Kinetically, calculations suggest that the HOMO-LUMO gap of **[9][BArF$_{24}$]** (132 kJ mol^{-1}) is smaller than that of germylenes capable of the oxidative addition of dihydrogen.[3–5,7] From a thermodynamic perspective these calculations also suggest the exergonic nature of oxidative addition of H_2 by model cations of the form [(I-Me$_4$)(R)Ge]$^+$ (ΔG = −21.8 and −30.0 kcal mol^{-1} for R = Ph and Bpin, respectively). There are many types of bonds for which oxidative reactivity towards would be interesting to explore.[2] Silanes, for instance, are a traditional "germylene trap";[45–48] boranes, while less frequently deployed in bond-activation studies with germylenes,[4,49,50] are interesting substrates due to their catalytic relevance in hydroboration; dihydrogen and ammonia are also catalytically relevant and rarely activated by main group compounds.[2] If oxidative addition can be achieved, then it will be intriguing to assess the potential onward reactivity of the Ge^{IV} products, either towards reductive elimination, or potentially with nucleophiles that may initiate reactions via attack at the electrophilic cationic species.

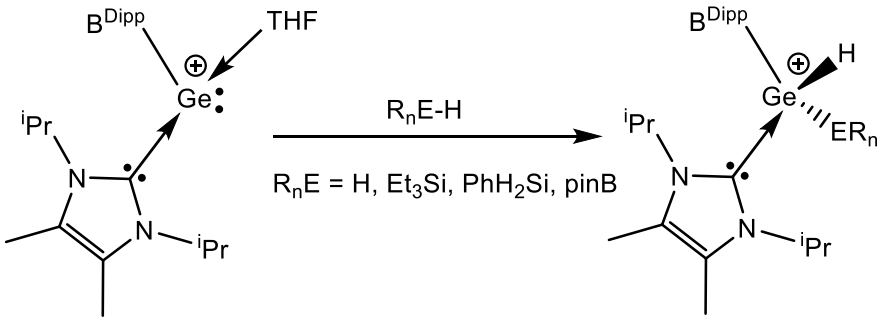
The isolation of boryl- or terphenyl-substituted analogues of **(1.33)XSiMe$_3$**[19] will also be explored, via the reaction of germylium-ylidenes with trimethylsilylazide and trimethylsilylazidomethane. The

impact of the differing steric and electronic profile of the ligands on the structure and reactivity of the formed compounds will be interesting to assess.

4.3 Results and discussion

4.3.1 Activation of E-H bonds by a THF-coordinated boryl-substituted germanium cation

Given the insolubility of **[(9)$_2$][BArF$_{24}$]$_2$** in non-donor deuterated solvents, and the difficulties found in large-scale reactivity studies in Schlenk flasks due to extreme air- and moisture-sensitivity, the most effective means for reactivity investigation was found to be the dissolution of bulk-prepared **[(9)$_2$][BArF$_{24}$]$_2$** in d$_8$-THF in a J. Young's NMR tube, yielding a solution of **[9(d$_8$-THF)][BArF$_{24}$]**.



*Scheme 4.1: E-H bond activation by **[9(d$_8$-THF)][BArF$_{24}$]** (counteranion omitted)*

Upon exposure to an atmosphere of H$_2$, a yellow sample of **[9(d$_8$-THF)][BArF$_{24}$]** in d$_8$-THF lightens gradually over several days at room temperature. As well as a new set of resonances corresponding to the NHC and boryl ligands, the ^{1}H NMR spectrum (see Figure 4.3) contains a potential Ge-H signal (integrating as 2 protons per set of ligand resonances) at 4.17 ppm, which is in the expected range (cf. (Ar^{Mes}){(Me$_3$Si)$_3$Si}GeH$_2$, 3.90 ppm [C$_6$D$_6$];[4] {(Me$_3$Si)$_2$N}(B^{Dipp})GeH$_2$, 4.63 ppm [C$_6$D$_6$];[4] (Ar^{Mes})$_2$GeH$_2$, 4.61 ppm [C$_7$D$_8$];[3] [(IDipp){Cp*W(CO)$_3$}GeH$_2$][BArF$_{24}$], 3.78 ppm [d$_4$-*o*-dichlorobenzene];[7] {(B^{Dipp})(Me$_3$Si)N}{Ar*(^{i}Pr$_3$Si)NZn}GeH$_2$, 3.88 ppm [C$_6$D$_6$]).[5] Furthermore, following reaction, the ^{11}B and ^{13}C NMR spectra feature pronounced upfield shifts in the signals arising from germanium-bonded atoms, from respectively 34 and 167.0 ppm in **[9(d$_8$-THF)][BArF$_{24}$]**, to 23 and 145.5 ppm. The formation of [(IPrMe)(B^{Dipp})GeH$_2$][BArF$_{24}$] (**[(9)H$_2$][BArF$_{24}$]**) is thus strongly implied by NMR data.

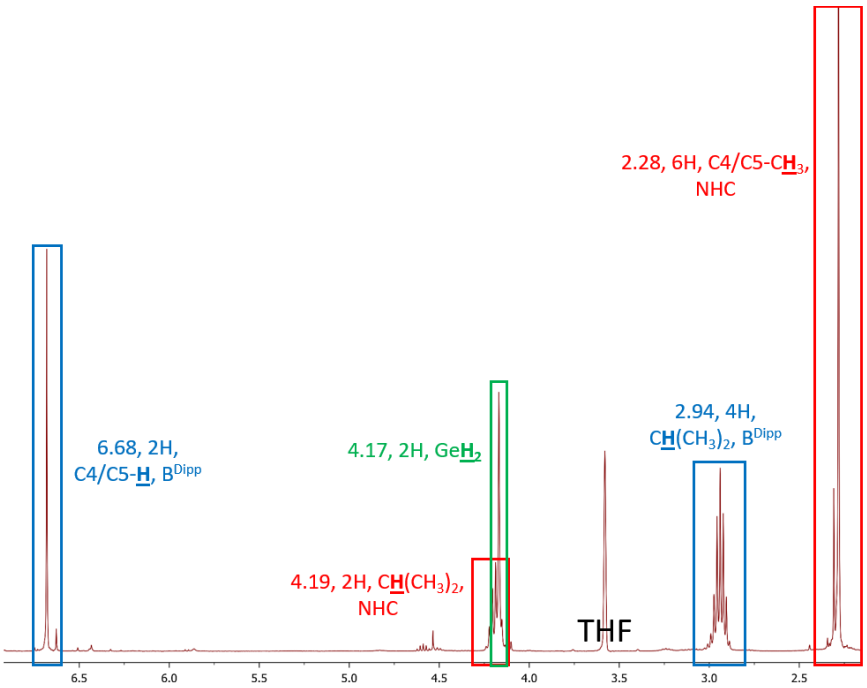


*Figure 4.3: Excerpt from the ^{1}H NMR spectrum of **[(9)H$_2$][BArF$_{24}$]**. Chemical shifts in ppm. Resonances due to Ph of B^{Dipp}, CH(C**H**$_3$)$_2$ of NHC and B^{Dipp}, and [BArF$_{24}$]$^-$ are not shown.*

X-ray crystallographic studies confirmed the formation of the dihydride species, a rare example of a germylium dihydride.[7,8] The B-Ge-C$_{NHC}$ angle widens on oxidation (106.4° average in **[(9)$_2$][BArF$_{24}$]$_2$**, 100.9(2)° in **[9(THF)][BArF$_{24}$]**, to 114.40(9)° in **[(9)H$_2$][BArF$_{24}$]**), as observed in other oxidative addition reactions of metallylenes.[4] This reflects the fact that the shortening of the Ge-B and Ge-C$_{NHC}$ bonds on oxidation (2.091/2.009 Å respective averages in **[(9)$_2$][BArF$_{24}$]$_2$**, 2.127(5)/2.074(5) Å in **[9(THF)][BArF$_{24}$]**, 2.048(2)/1.991(2) Å in **[(9)H$_2$][BArF$_{24}$]**) leads to the substituents moving apart in angular terms to minimise the increase in steric repulsion. Evident in the structure is a close approach between a fluorine of the [BArF$_{24}$]$^-$ anion and the germanium centre (3.523(2) Å, slightly smaller than the sum of the van der Waals radii [3.58 Å]),[51] likely arising due to packing effects because of the lack of steric bulk on that face of the germanium centre.

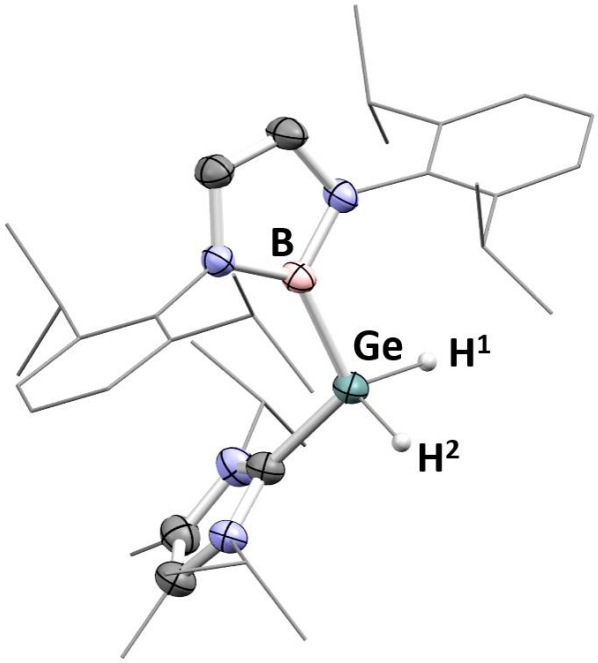


Figure 4.4: Structure of ***[(9)H$_2$][BArF$_{24}$]****. For clarity, [BArF$_{24}$]$^-$ counteranion and hydrogen atoms (other than Ge**H**$_2$) omitted, and B^{Dipp} Dipp and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-B: 2.048(2), Ge-C$_{NHC}$: 1.991(2), B-Ge-C$_{NHC}$: 114.40(9)*

As would be expected, the addition of silanes (Et_3SiH and $PhSiH_3$) and boranes (HBpin) to solutions of **[9(d$_8$-THF)][BArF$_{24}$]** also leads to decolourisation, and conversion to new products identifiable by NMR spectroscopy. These reactions appear to proceed more rapidly (within minutes at room temperature), reflecting the more polar nature of these bonds. As well as new sets of resonances corresponding to the NHC and boryl ligands, potential Ge-H signals can be identified in the ^{1}H NMR spectra at 4.17, 4.02 and 4.14 ppm, respectively. In the case of $PhSiH_3$ this signal is particularly informative, as it is split into a doublet of doublets due to coupling to the diastereotopic Si**H**$_2$Ph protons (doublets at 3.65 and 4.38 ppm). These ^{1}H NMR spectra are suggestive of more sterically crowded, unsymmetrical species as compared to the dihydride. For instance, the ^{1}H NMR spectrum resulting from the reaction with Et_3SiH features two resonances for each of the boryl and NHC C**H**$(CH_3)_2$ isopropyl environments, as well as for the NHC backbone methyl groups, as opposed to single resonances in the spectrum of the dihydride. Furthermore, there are two SiC**H**$_2CH_3$ resonances, consistent with these protons being rendered diastereotopic and so magnetically inequivalent due to the adjacent chiral germanium centre. Heteronuclear ^{29}Si and ^{11}B NMR spectroscopy also indicate small molecule incorporation, with new signals at 4.0 ppm (vs. ca. 0 ppm for Et_3SiH), −54.9 ppm (vs. ca. −60 ppm for $PhSiH_3$) and 21 ppm (vs.

ca. 28 ppm for HBpin) respectively, as well as characteristic upfield shifts[52,53] of the ^{11}B NMR boryl signal to 25, 24 and 24 ppm, respectively (from 34 ppm for **[9(d$_8$-THF)][BArF$_{24}$]**). Thus, there is strong evidence for oxidative addition of the silanes and borane to form [(IPrMe)(B^{Dipp})GeH(SiEt$_3$)][BArF$_{24}$] (**[(9)H(SiEt$_3$)][BArF$_{24}$]**), [(IPrMe)(B^{Dipp})GeH(SiH$_2$Ph)][BArF$_{24}$] (**[(9)H(SiH$_2$Ph)][BArF$_{24}$]**) and [(IPrMe)(B^{Dipp})GeH(Bpin)][BArF$_{24}$] (**[(9)H(Bpin)][BArF$_{24}$]**), respectively.

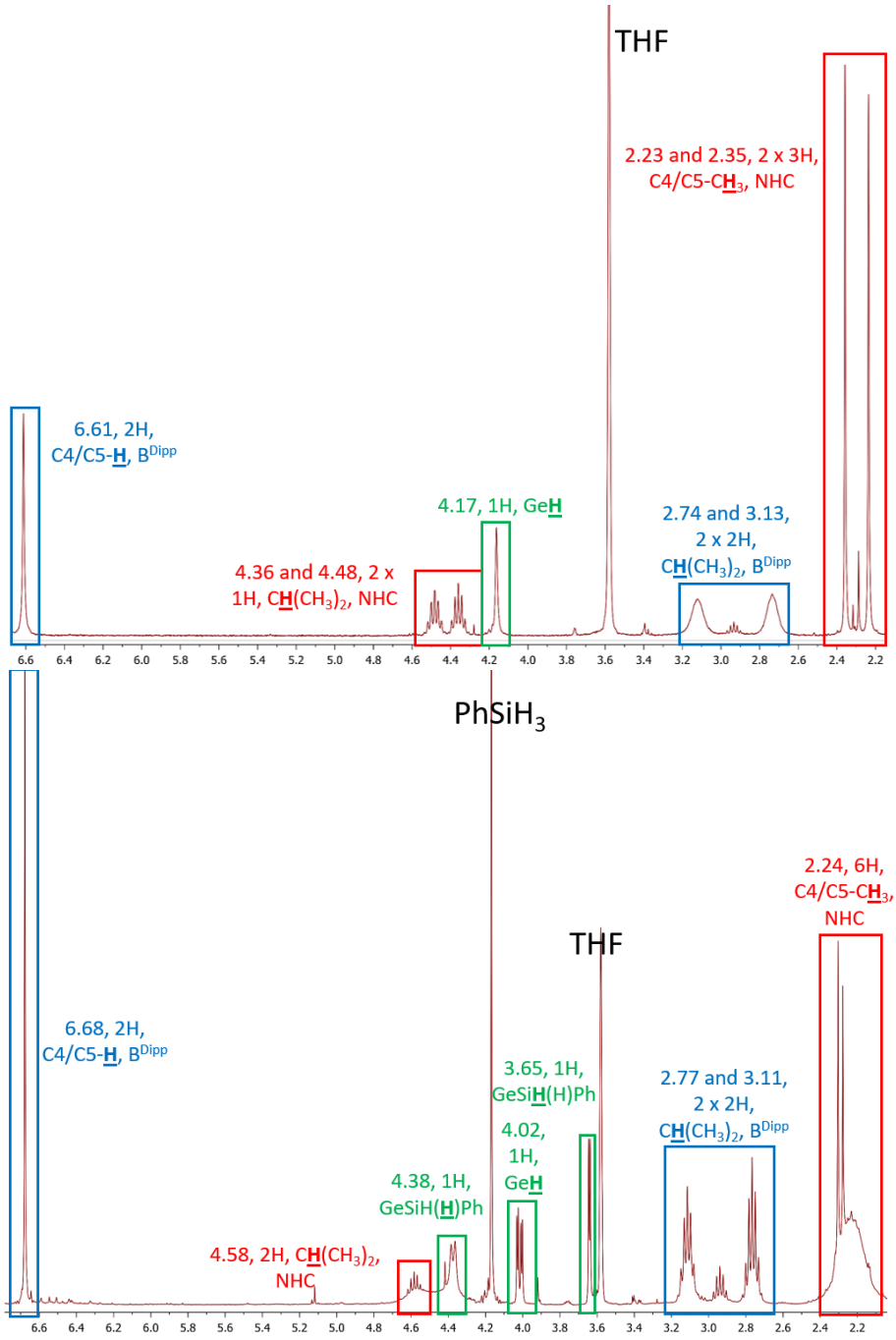


*Figure 4.5: Excerpts from the ^{1}H NMR spectra of **[(9)H(SiEt$_3$)][BArF$_{24}$]** (top) and **[(9)H(SiH$_2$Ph)][BArF$_{24}$]** (bottom). Chemical shifts in ppm. Resonances due to Ph of B^{Dipp}, CH(C**H**$_3$)$_2$ of NHC and B^{Dipp}, and [BArF$_{24}$]$^-$ are not shown. Extraneous signals are due to small amounts of **[(9)H$_2$][BArF$_{24}$]** (vide infra).*

Oxidative addition of the silanes could be confirmed by X-ray crystallography, however for the borane case the product proved too moisture-sensitive for this to be possible. Predictably, the steric bulk of the SiH_2Ph and $SiEt_3$ ligands leads to a reduced B-Ge-C_{NHC} angle as compared to the dihydride (110.4(1)° and 109.3(2)°, respectively, vs. 114.40(9)°). An interesting structural feature of **[(9)H(SiH_2Ph)][$BArF_{24}$]** in the solid state is a stacking interaction between the silicon centre and the SiH_2Ph phenyl ring (shortest C-Si distance of 3.778 Å, slightly smaller than the sum of the van der Waals radii [3.80 Å]).[51] This hints at ligand-centred electrophilicity in these Ge^{IV} compounds. Though the activation of silanes by germylenes has long been known,[45–48] **[(9)H($SiEt_3$)][$BArF_{24}$]** represents one of just a few structurally characterised examples of the activation of Et_3SiH,[46,54,55] and there are no published structures regarding $PhSiH_3$. There are only a few examples of the oxidative addition of less polar B-H bonds at germanium.[4,7,49,50]

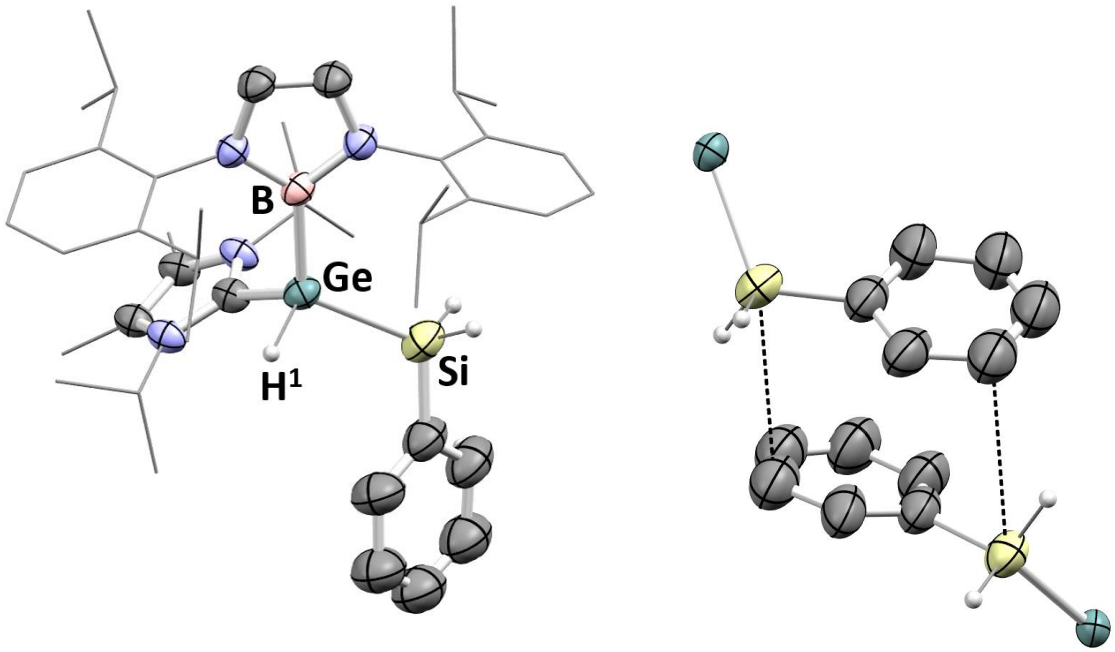


*Figure 4.6: Structure of **[(9)H(SiH_2Ph)][$BArF_{24}$]** (L) and stacking interaction in **[(9)H(SiH_2Ph)][$BArF_{24}$]** (R). For clarity, $[BArF_{24}]^-$ counteranion and hydrogen atoms (other than Ge**H** and Si**H**$_2$Ph) omitted, and B^{Dipp} Dipp and NHC ^{i}Pr and Me groups shown in wireframe format (L), and only the $GeSiH_2Ph$ moiety is shown (R). Key bond lengths (Å) and angles (°): Ge-B: 2.042(3), Ge-C_{NHC}: 2.000(3), Ge-Si: 2.383(1), B-Ge-C_{NHC}: 110.4(1), B-Ge-Si: 117.8(1), C_{NHC}-Ge-Si: 110.5(1)*

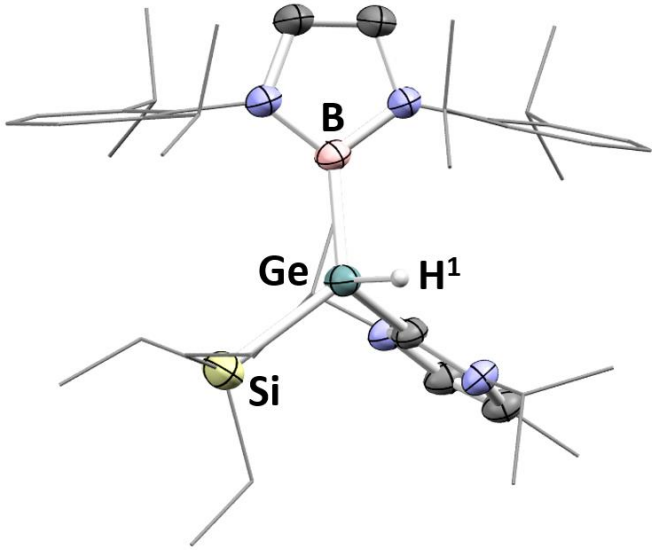
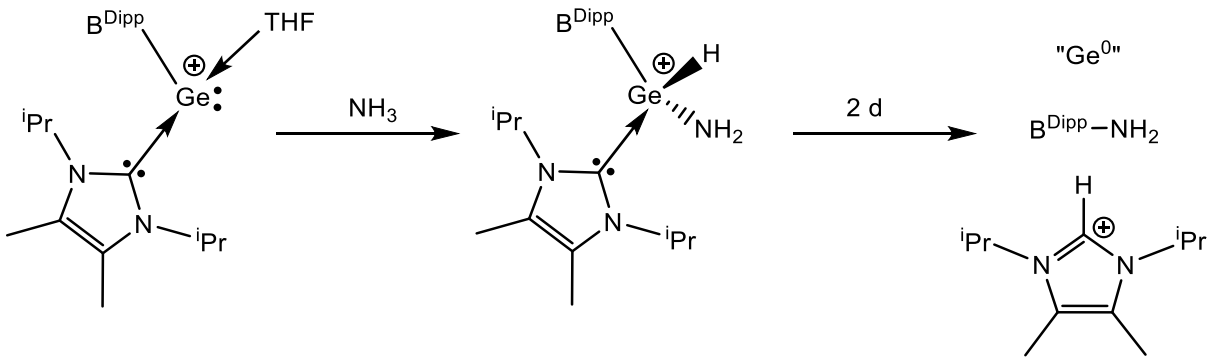


Figure 4.7: Structure of ***[(9)H(SiEt$_3$)][BArF$_{24}$]****. For clarity, [BArF$_{24}$]$^-$ counteranion and hydrogen atoms (other than Ge**H**) omitted, and B^{Dipp} Dipp, NHC ^{i}Pr and Me, and SiEt$_3$ Et groups, shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-B: 2.064(5), Ge-C$_{NHC}$: 2.030(5), Ge-Si: 2.444(6), B-Ge-C$_{NHC}$: 109.3(2), B-Ge-Si: 123.0(2), C$_{NHC}$-Ge-Si: 105.5(2)*

Upon exposure to an atmosphere of NH_3, a sample of **[9(d$_8$-THF)][BArF$_{24}$]** lightens rapidly, and an initial ^{1}H NMR spectrum (within 5 minutes) reveals conversion to a new product. In addition to a new set of ligand resonances, this spectrum features broad singlets at 5.66 ppm (1H) and at 0.32 ppm (2H), in the range expected for Ge-H and Ge-NH_2 moieties, respectively (cf. (Ar^{Mes}){(Me$_3$Si)$_3$Si}GeH(NH_2), 5.10 and −0.06 ppm [C_6D_6];[4] (Ar^{Mes})$_2$GeH(NH_2), 5.47 and −0.37 ppm [C_7D_8];[3] (Ar^{Dipp})$_2$GeH(NH_2), 5.84 and −0.37 ppm [C_6D_6]).[3] The formation of [(IPrMe)(B^{Dipp})GeH(NH_2)][BArF$_{24}$], **[(9)H(NH_2)][BArF$_{24}$]**, is thus suggested. However, subsequent monitoring of this reaction mixture by ^{1}H NMR spectroscopy reveals the appearance (within minutes) of a signal at 8.76 ppm, in the region characteristic of imidazolium NC(**H**)N resonances,[56] as well as a new set of signals for the boryl ligand. Within 2 d at room temperature complete conversion to this new product is observed. Removal of the solvent and extraction with hexane enables the isolation and identification of the known borylamine B^{Dipp}NH_2.[53]



*Scheme 4.2: Ammonia activation by **[9(d$_8$-THF)][BArF$_{24}$]** (counteranion omitted)*

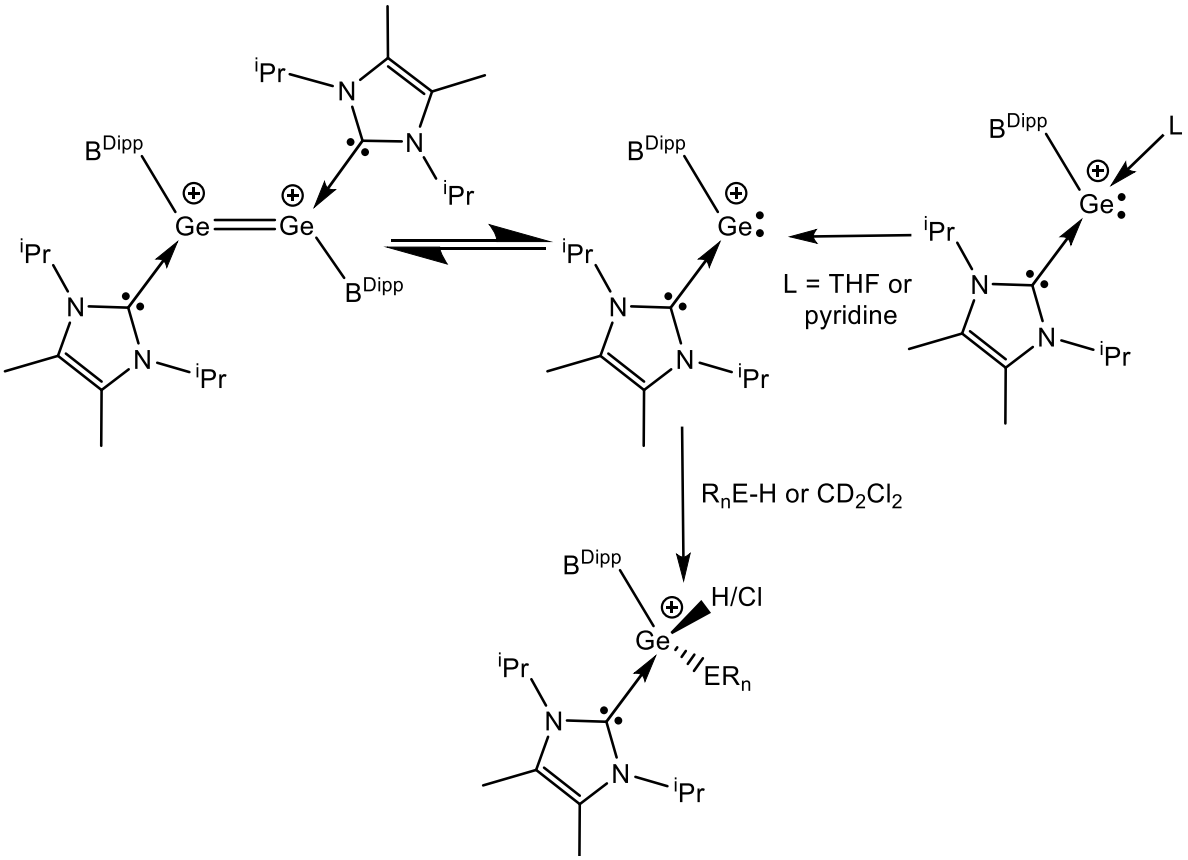
That **[(9)H(NH$_2$)][BArF$_{24}$]** is the least stable of the Ge^{IV} species studied in this work is predictable given the relative destabilisation of the (less electron-rich) Ge^{IV} state by the σ-withdrawing amido group, and the relative stabilisation of a putative Ge^{II}-NH$_2$ species by π-donation (with the necessary orbital overlap likely to be more favourable in this less crowded system). Reductive elimination following addition of ammonia has been observed for tin systems (e.g. following reaction of (B^{Dipp})$_2$Sn with NH$_3$),[53] but not for germanium (e.g. (Ar$^{Mes/Dipp}$)$_2$GeH(NH$_2$)[3] and (Ar^{Mes}){(Me$_3$Si)$_3$Si}GeH(NH$_2$) are stable compounds).[4] That elimination occurs specifically in this system is consistent with the relatively greater propensity for elimination observed in cationic (as opposed to charge neutral) Ge^{IV} species.[7,8] That the boryl-containing product is not {(B^{Dipp})GeNH$_2$}$_n$ is due to the favourable formation of B^{Dipp}NH$_2$ both thermodynamically, given the strong B-N bond, and kinetically, due to the electrophile/nucleophile coupling. Consistently, {(B^{Dipp})GeNH$_2$}$_n$ is unknown, and (B^{Dipp})$_2$Sn reacts with NH$_3$ via stepwise addition then elimination to reduced tin species, B^{Dipp}H and B^{Dipp}NH$_2$ (despite (B^{Dipp})Sn(μ$_2$-NH$_2$)$_2$Sn(B^{Dipp}) being known).[53]

Two possible strategies were attempted to stabilise the Ge^{IV}-NH$_2$ species to enable its isolation and characterisation. The first strategy derives from the fact that potentially there may be coordination of a further equivalent of ammonia during addition, and hence the presence of a stronger donor may act to stabilise the Ge^{IV}-NH$_2$ species further. However, the elimination was observed to take place over a similar time period when one equivalent of DMAP was added. The second strategy draws on the hypothesis that the Ge^{IV}-NH$_2$ product may be stable in isolation, but that it is attack of excess ammonia on the boryl group that causes decomposition. Hence, attempts to reduce the concentration of ammonia were made: the sample was less rigorously degassed before addition of NH$_3$ (only one *freeze-*

pump-thaw cycle rather than three), and then removal of the ammonia atmosphere was attempted (though this cannot be achieved by *freeze-pump-thaw* due to the freezing point of ammonia being higher than that of THF, the sample was purged with argon for an extended period). However, the elimination nevertheless proceeded at a similar rate, and hence the intrinsic instability of this species was accepted. Reactions with amines were attempted, in the hope they may offer more stable germanium-containing products (cf. (B^{Dipp})Ge{$N(SiMe_3)_2$}),[4] however either a complex mixture from which nothing could be isolated ($^tBuNH_2$) or no reaction ($DippNH_2$ or $(Me_3Si)_2NH$) was observed.

4.3.2 Bond activation by a boryl-substituted germanium cation in other solvents

Upon addition of CD_2Cl_2 to a red sample of solid **[(9)$_2$][BArF$_{24}$]$_2$**, almost immediately after dissolution the solution rapidly decolourises; the clean ^{1}H NMR spectrum of this colourless product, and an ^{11}B NMR signal at 22 ppm, are suggestive of the oxidative addition of CD_2Cl_2, which presumably traps out the monomeric form of the cation. There are no examples of neutral germylenes reacting with dichloromethane,[2,57] and it is a widely applied solvent for germylium-ylidenes,[11,14–16] with there being just a small number of examples of reactive cations capable of affording C-Cl bond activation.[19,20]



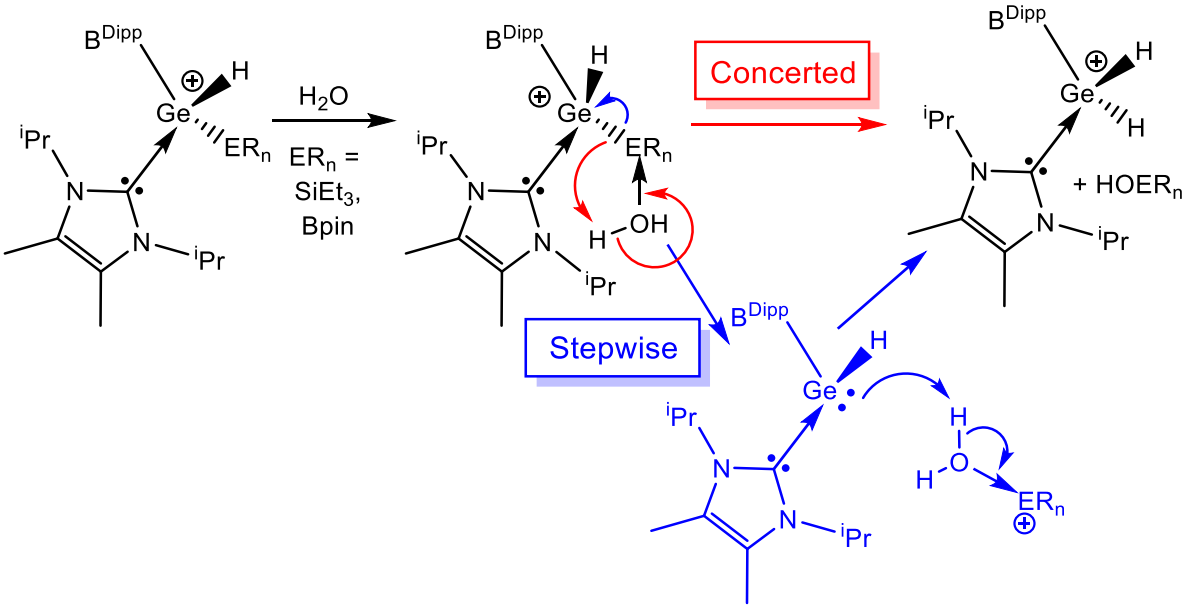
*Scheme 4.3: Bond activation by **[9][BArF$_{24}$]** in various solvents (counteranion omitted)*

Addition of Et_3SiH to a solution of **[(9)$_2$][BArF$_{24}$]$_2$** in fluorobenzene leads to slow decolourisation, qualitatively much more slowly than in THF (as also observed by slower conversion to product by ^{11}B NMR spectroscopy, over a period of several hours rather than a few minutes). Furthermore, addition of Et_3SiH to a solution of **[9(d$_5$-pyridine)][BArF$_{24}$]** in d_5-pyridine leads to a very slow reaction at room temperature (starting material still remains even after addition of a large excess of Et_3SiH and storage for several weeks at room temperature), with full conversion to the product requiring heating at 60°C for 10 h. In both cases, removal of volatiles and redissolution in CD_2Cl_2 reveals the product to be the same as that from the reaction in THF (**[(9)H(SiEt$_3$)][BArF$_{24}$]**), according to ^1H NMR spectroscopy.

Theoretical work has suggested the activation of E-H bonds by germylenes generally involves coordination of the substrate with the germylene LUMO,[58] implying that occupation of this LUMO by a donor will block this pathway and considerably slow or even quench the reaction (with the donor needing to dissociate first). Leigh in particular has extensively studied the kinetics of simple metallylenes (e.g. Me_2Ge) in solution, and shown that donor solvents either inhibit reactions[59–64] or promote alternative ones involving initial germylene nucleophilic attack.[65] There are many examples of donor-coordinated germylenes reacting more slowly (if at all), and progressively so with increasing donor strength. For example, regarding a series of donor-stabilised silylated germylenes synthesised by Marschner, PMe_3-coordinated germylenes were found reactive in C-H activation chemistry while NHC-coordinated analogues were not;[66,67] furthermore, Baines found that whereas *in situ*-generated Mes_2Ge reacts with Et_3SiH,[68] its NHC adduct does not;[69] finally, a PMe_3-coordinated germylene was found to undergo very sluggish reactions with germylene-trapping reagents.[70] Thus, it is expected that **[9][BArF$_{24}$]** reacts more slowly when coordinated by a stronger donor solvent or in a donor-acceptor complex with itself. The explanation may be more thermodynamic, in terms of skewing an equilibrium of dissociation away from a two-coordinate species, or kinetic, by increasing the activation energy of a mechanism involving initial ejection of an additional donor.

4.3.3 Onward reactivity of boryl-substituted germylium hydrides

Throughout the investigation of the reactivity of **[9][BArF$_{24}$]** towards E-H bonds, a frequently observed side product was the germylium dihydride species **[(9)H$_2$][BArF$_{24}$]**. A proposed mechanism for the formation of this product involves initial attack of adventitious moisture at boron/silicon (a three-coordinate boron adjacent to a cationic centre would be expected to be extremely electrophilic, while the greater electronegativity of germanium as compared to silicon[71] would lead to significant positive charge at silicon, i.e. partial silylium ion character). Subsequent breaking of the Ge-E bond and proton-transfer to germanium would then generate the observed dihydride. These steps can be thought of in terms of two limiting mechanistic possibilities following initial attack of water at B/Si: either (i) a concerted process (with concomitant elimination of an R$_n$EOH species, R$_n$E = pinB or Et$_3$Si, red in Scheme 4.4), or (ii) a stepwise process involving attack of a Ge^{II} hydride at an ejected [(H$_2$O)ER$_n$]$^+$ cationic adduct (to generate the dihydride and an R$_n$EOH species, blue in Scheme 4.4). Stable [(H$_2$O)SiR$_3$]$^+$ adducts are known as isolated species (with carborane counteranions and albeit slightly bulkier R groups, = ^{i}Pr,[72] ^{t}Bu),[73] and the protonation of germylenes with acids (e.g. HCN, HN$_3$, HBF$_4$) has also been reported.[74]



Scheme 4.4: Attack of adventitious moisture resulting in germylium dihydride formation (counteranion omitted)

In reality, the situation is likely to be somewhere in between: as electron density is transferred from E to Ge, the germanium centre becomes progressively more basic and the coordinated water

progressively more acidic (as the positive charge and so electrophilicity of E builds up),* until such point that the deprotonation can be afforded. Of course, this assumes that the steric hindrance of R_nE is not so great as to prevent intramolecular attack, though given the extremely unbulky neighbouring hydride ligand it seems likely that the coordinated water is able to approach the germanium centre sufficiently closely to enable deprotonation. The eliminated R_nEOH can then attack another molecule of germylium monohydride, to produce a further equivalent of dihydride and R_nEOER_n (consistent with this is the lack of observation of an –OH signal in the ^{1}H NMR spectra, and a single set of "R" alkyl resonances). In order to investigate this reactivity in a more controlled fashion, one equivalent of a stock solution of PhOH was added to **[(9)H(SiEt$_3$)][BArF$_{24}$]** or **[(9)H(Bpin)][BArF$_{24}$]**, generating the expected dihydride as well as $PhOSiEt_3$[75] or PhOBpin[76] within minutes at room temperature. Such reactivity of Ge^{IV} species towards water and alcohols is quite unprecedented, and presumably occurs in this system because of the increased electrophilicity of the cation relative to neutral analogues, as well as the relatively high basicity of the germanium centre due to the strongly donating ligands.[77]

Various attempts were made to investigate reversibility/triggered elimination following oxidative addition in the systems studied in this work. Variable temperature NMR at elevated temperature reveals no hint of reversibility in the reactions of **[9][BArF$_{24}$]** with H_2, $PhSiH_3$, Et_3SiH or HBpin. The addition of substrates that have precedent for triggering elimination (NHCs[78–81] and amines),[82] or that a small molecule could be transferred to (for instance, azobenzene), either resulted in decomposition or no reaction. The oxidative addition products were also heated in various solvents for prolonged periods. Heating **[(9)H(SiEt$_3$)][BArF$_{24}$]** for several days in d_8-THF leads to slow but selective conversion to a new product; quantitative conversion according to ^{1}H NMR spectroscopy was achieved after 5 d at 60°C in the presence of an excess of Et_3SiH. The ^{1}H NMR spectrum of the product curiously features the same integration of the boryl, NHC and $SiEt_3$ ligand moieties, but with different chemical shifts. That the ^{1}H NMR spectrum (specifically the $SiEt_3$ resonances) remains unchanged after washing with either toluene or hexane, or prolonged heating under vacuum, suggests the continued incorporation

*For example, the pKa of $(H_2O)B(C_6F_5)_3$ is 8.6,[238] considerably lower than the pKa of uncoordinated water.

of the $SiEt_3$ moiety in the germanium-containing product, as opposed to a possible elimination. Furthermore, the more symmetrical nature of the ^1H NMR spectrum (for instance, one resonance for the NHC C**H**$(CH_3)_2$ isopropyl environment as opposed to two in the starting material) implies a decrease in steric crowding at the germanium centre, while the single resonance for the SiC**H**$_2CH_3$ environment (as opposed to two in the starting material) illustrates that these protons are no longer diastereotopic, and so no longer adjacent to a chiral germanium centre.

Single crystals suitable for X-ray diffraction could be grown by layering a concentrated fluorobenzene solution with hexane, and suggest the formation of $[(IPrMe)(B^{Dipp})GeH(C_4D_8OSiEt_3)][BArF_{24}]$ (**[(9)H(C_4D_8OSiEt_3)][$BArF_{24}$]**), via the insertion of d_8-THF into the Ge-Si bond. However, significant disorder in the moiety at the end of the alkyl chain precludes definitive crystallographic confirmation that this is the product. Further evidence can be found in the ^{29}Si NMR spectrum, which features a signal at 17.4 ppm, consistent with a species of the form $ROSiEt_3$ (cf. $^nC_5H_{11}OSiEt_3$, $\delta(^{29}Si)$ = 17.9 ppm [$CDCl_3$]).[75] Furthermore, ESI mass spectrometry confirms the mass of the cationic product; the reaction could also be performed in protio-THF, with ESI mass spectrometry revealing the expected mass difference to the deuterated product. The ^1H NMR spectrum of **[(9)H(C_4H_8OSiEt_3)][$BArF_{24}$]** (in CD_2Cl_2) features resonances for the boryl, NHC and $SiEt_3$ moieties essentially identical to those of the deuterated analogue in CD_2Cl_2 (largest deviation of 0.03 ppm), with the only difference between the spectra being an additional multiplet at 3.34 ppm arising from the OC**H**$_2$ protons and further multiplets arising from $OCH_2(CH_2)_3Ge$ protons (mostly obscured by $CH(CH_3)_2$ isopropyl signals, except for a visible multiplet at 1.09 ppm); in the ^{13}C NMR spectrum, these correspond to resonances at 61.7 ppm and 35.9 ppm, respectively.

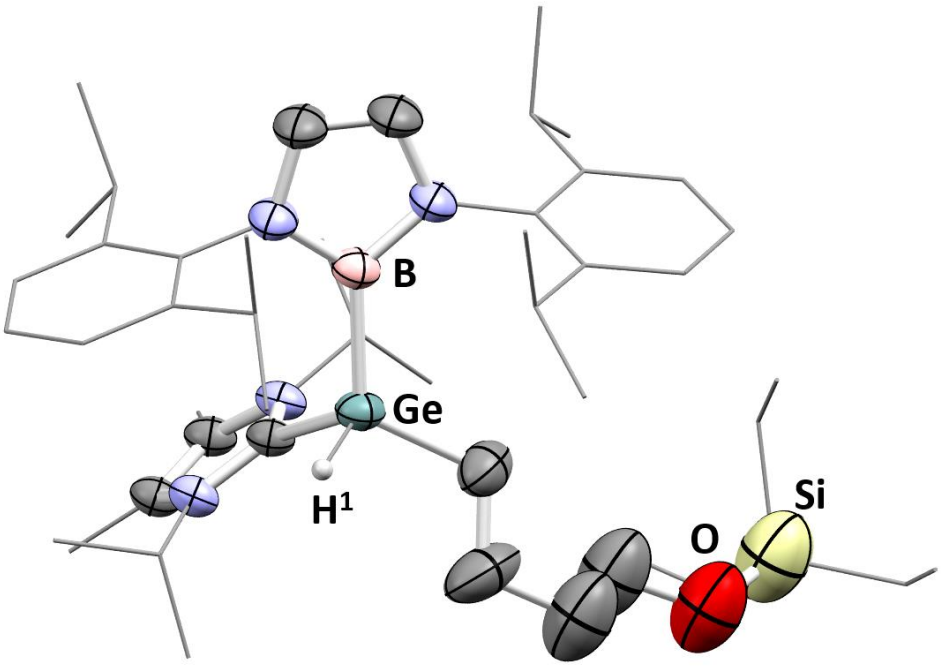
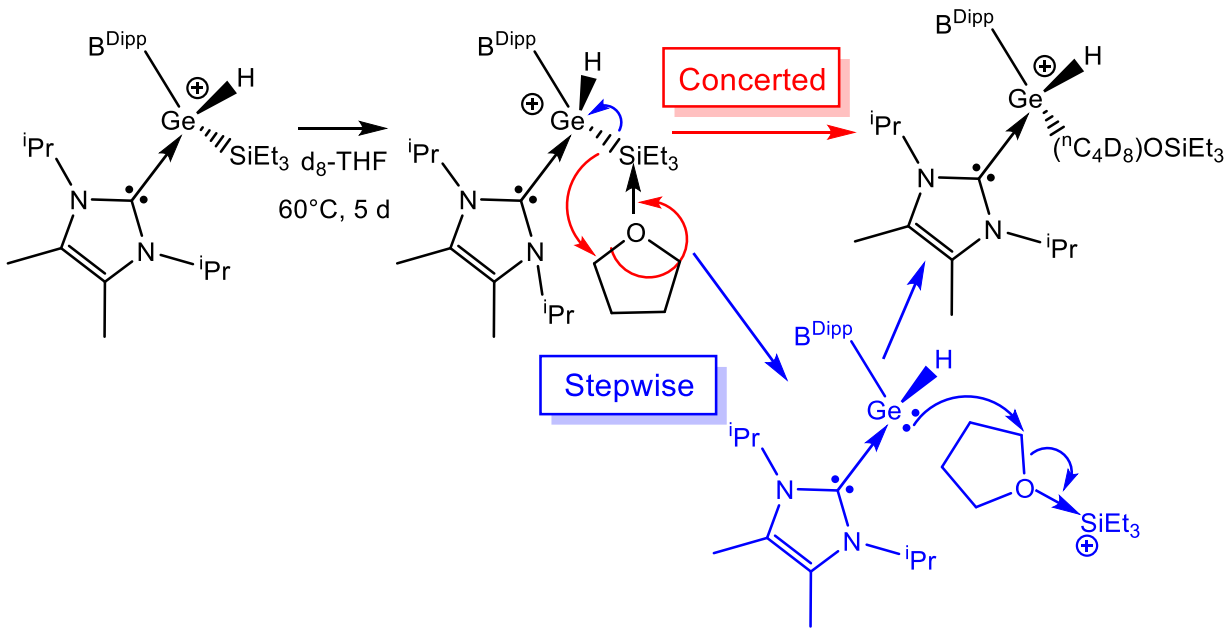


Figure 4.8: Structure of ***[(9)H(C$_4$D$_8$OSiEt$_3$)][BArF$_{24}$]****. For clarity, [BArF$_{24}$]$^-$ counteranion and hydrogen atoms (other than Ge**H**) omitted, and B^{Dipp} Dipp, NHC ^{i}Pr and Me, and SiEt$_3$ Et groups, shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-B: 2.047(4), Ge-C$_{NHC}$: 2.005(3), Ge-C$_{THF}$: 1.969(4), B-Ge-C$_{NHC}$: 110.8(1), C$_{NHC}$-Ge-C$_{THF}$: 107.1(2), B-Ge-C$_{THF}$: 118.7(2)*

The mechanism for this reaction is likely similar to that involving water, i.e. initial attack of THF at the $SiEt_3$ ligand, followed by ring-opening due to attack by the germanium centre, either in a concerted manner or with initial elimination of a $[(THF)SiEt_3]^+$ moiety, again with the likelihood that the real situation will be intermediate between these extremes. The formation of $[(THF)SiR_3]^+$ species has been studied in solution,[83] while ring-opening of coordinated THF by nucleophiles is well-known (*vide infra*). The considerably more forcing conditions required in this case as compared to the reaction with water reflect the influence of the greater steric bulk (hence slower attack at $SiEt_3$ by THF and at THF by germanium), the reduced entropic driver (due to a lack of eventual elimination), and the smaller partial positive charge on the THF α-C vs. the proton of water, which all presumably outweigh the greater stabilisation of the partially positively charged silicon by the stronger donor THF. The use of an excess of Et_3SiH was found to increase the rate of this reaction (with no further rate enhancement beyond ca. 5 equivalents), potentially reflecting the ability of Et_3SiH to stabilise a silylium-like intermediate (cf. $[Et_3Si\text{-}H\text{-}SiEt_3][BArF_{20}]$).[84] It should be noted that during repetitions of this reaction occasionally a viscous solution resulted in the NMR tube, consistent with the polymerisation of THF (which

germanium cations have precedent for initiating),[13,14] though no specific circumstance could be identified that caused this instead of the more controlled reactivity otherwise observed.



Scheme 4.5: Potential mechanisms of THF insertion to give ***[(9)H(C$_4$D$_8$OSiEt$_3$)][BArF$_{24}$]*** *(counteranion omitted)*

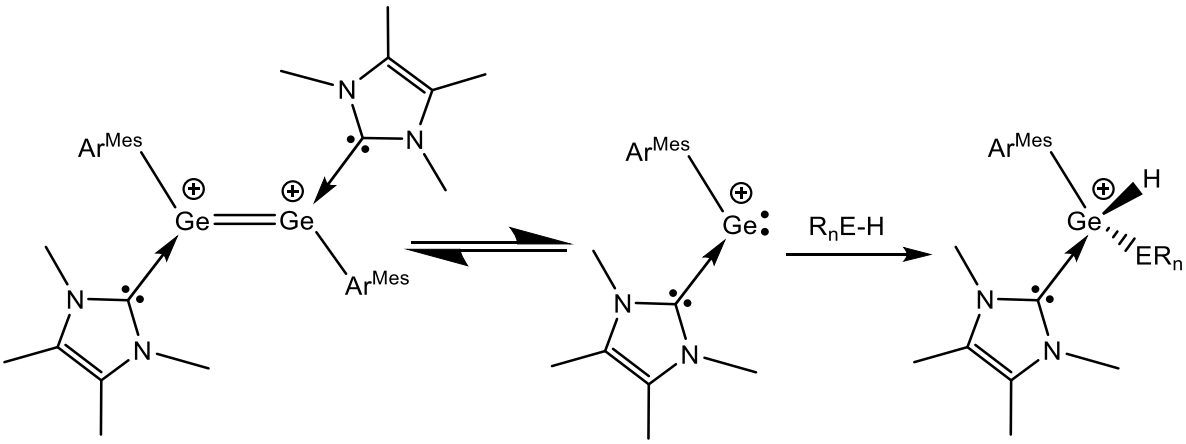
In order to confirm the plausibility of the attack of water/THF at $SiEt_3$, as well as the potential intermediacy of a Ge^{II} hydride, nucleophiles less prone to further reaction were investigated. A solution of **[(9)H(SiEt$_3$)][BArF$_{24}$]** in d_5-pyridine is stable at room temperature, and only decomposition to [IPrMeH][$BArF_{24}$] and (B^{Dipp})H was observed on heating. However, the addition of DMAP to **[(9)H(SiEt$_3$)][BArF$_{24}$]** in CD_2Cl_2 resulted in the appearance of a new resonance in the ^{29}Si NMR spectrum at 36.8 ppm almost immediately at room temperature, presumably reflecting the greater nucleophilicity of DMAP compared to THF and pyridine. This signal is consistent with the formation of the species [(DMAP)$SiEt_3$]$^+$, which could be generated independently *in situ* from Et_3SiCl, AgOTf and DMAP in CD_2Cl_2 and shown to have the same chemical shift; this chemical shift is also similar to that of the previously reported analogue [(DMAP)$SiMe_3$][OTf]: δ(^{29}Si) = 31.6 ppm [$CDCl_3$].[85] However, the putative (IPrMe)(B^{Dipp})GeH co-product proved unstable in CD_2Cl_2 (decomposing over 2 d at room temperature) and could not be characterised/isolated, while attempts to independently generate such a compound (for instance, from (IPrMe)(B^{Dipp})GeCl and K[BEt_3H]) proved similarly unsuccessful. While not providing much insight into the subsequent mechanism, these observations are at least consistent with an initial attack at $SiEt_3$ by water/THF.

The cationic polymerisation of THF has been known since the 1930s, when Meerwein utilised oxonium salts as initiators,[86,87] with a wide variety of Brønsted and Lewis acids having since been deployed for this purpose (including trialkylsilylium salts).[83] There are many examples of the stoichiometric ring-opening of THF (most simply and initially done using hydrohalic acids),[88] involving initial activation of THF due to coordination at, for example, oxophilic early transition metal or lanthanide/actinide centres (e.g. titanium,[89–92] zirconium,[93–100] hafnium,[101] yttrium,[102] samarium,[103–106] lutetium,[107,108] neodymium, thulium, lanthanum,[108] uranium[109–113] and thorium),[114] or s-block elements (e.g. lithium,[115] berylium,[116] and magnesium),[117] or organic groups (e.g. acylium ions,[118] acyl chlorides,[119] carbenes[120] and bromonium cations),[121] or more rarely at main group element centres (e.g boron,[122–136] aluminium[137–142] and silylium ions).[143] The resulting further polarisation of the C-O bond thus increases susceptibility to nucleophilic attack at the α-C, by, for example, phosphines[93,95,99,100,124,126] and arsines[107] (or phosphides[102,106,134] and arsenides),[104] carbenes,[128,135] alcohols[120,138] (or alkoxides),[127,129] amines,[97,125,126,141] cyclopentadienides,[103,108,113,140] hydrides[96,115,142] or halides,[90–92,109–111,114,116,117,123,131,132] resulting in the incorporation of a molecule of ring-opened THF between electrophile (O-bound) and nucleophile (C-bound) (less common is the initial attack of phosphorus at oxygen).[144,145] Some of these examples, where the electrophile and nucleophile are initially present but not interacting with one another, clearly fall within the realm of Frustrated Lewis Pair chemistry;[99,100,124–126,128,134,135] others involve coordination at a central element, followed by intramolecular attack of a ligand, resulting in an O-bound alkoxide ligand.[104,111,114,116] However, the reactivity observed in this case, involving initial attack of THF at a ligand followed by ring-opening of the activated THF by the central element (resulting in a C-bound ligand), is quite unprecedented, especially given the involvement of germanium (though germylenes have acted as the electrophile in intermolecular THF ring-opening).[146] The only (slightly) related example, from Sekiguchi, involves activation of THF (by initial coordination at boron) across a transient Ge=B bond to give a cyclic product, though clearly this is quite distinct given the reactivity is across a double bond.[147] Again, as with the reactivity towards water, it is apparent that the positive charge, in combination with the strong donor

ligands at germanium, embues **[(9)H(SiEt$_3$)][BArF$_{24}$]** with unique ambiphilic character that primes it for such reactivity.

4.3.4 Activation of E-H bonds by a terphenyl-substituted germanium cation

Given the fascinating reactivity shown by **[9][BArF$_{24}$]**, comparison of the reactivity of a terphenyl-substituted analogue was clearly of interest. However, preparative-scale synthesis and reactivity of the terphenyl-substituted cations proved challenging, primarily due to their extreme moisture-sensitivity. The most fruitful means for reactivity studies came through the use of *in situ*-generated solutions of **[(10)$_2$][Al(OR^F)$_4$]$_2$** in C_6D_5Br in J. Young's NMR tubes (Li[Al(OR^F)$_4$] being preferred to Na[BArF$_{24}$] given its crystallinity and so ability to be more accurately weighed out for small-scale reactions).



*Scheme 4.6: Small molecule activation by **[10][Al(OR^F)$_4$]** (counteranion omitted)*

Hence, reactivity studies could be undertaken with analogous substrates to **[9][BArF$_{24}$]**. Upon addition of Et_3SiH, $PhSiH_3$ or HBpin to a C_6D_5Br solution of **[(10)$_2$][Al(OR^F)$_4$]$_2$**, the solutions rapidly decolourised. The ^{1}H NMR spectra provide evidence for the clean formation of new products, with sharp new resonances corresponding to the methyl groups of the NHC and terphenyl ligands. Furthermore, the spectra feature signals in the region characteristic of germanium hydrides (*vide supra*), at 5.03 (singlet), 3.57 (doublet of doublets) and 4.50 (singlet) ppm, respectively, as well as respectively new resonances for the silyl ethyl groups (with characteristic inequivalence of the diastereotopic SiC$\underline{\mathbf{H}}_2$CH$_3$ protons), two doublets (at 3.88 and 4.91 ppm) corresponding to the Si$\underline{\mathbf{H}}_2$Ph protons, and new resonances for the Bpin methyl groups. Heteronuclear NMR spectra (new signals at 11.0 and −53.3 ppm in the ^{29}Si NMR spectra, and 22 ppm in the ^{11}B NMR spectrum, respectively) are also consistent with small molecule

incorporation, and the formation of the oxidative addition products [(I-Me_4)(Ar^{Mes})GeH($SiEt_3$)][$Al(OR^F)_4$] (**[(10)H($SiEt_3$)][$Al(OR^F)_4$]**), [(I-Me_4)(Ar^{Mes})GeH(SiH_2Ph)][$Al(OR^F)_4$] (**[(10)H(SiH_2Ph)][$Al(OR^F)_4$]**), and [(I-Me_4)(Ar^{Mes})GeH(Bpin)][$Al(OR^F)_4$] (**[(10)H(Bpin)][$Al(OR^F)_4$]**). The lack of effect from the counteranion on reactivity could be confirmed by the addition of Et_3SiH to an *in situ*-generated solution of **[$(10)_2$][$BArF_{24}$]$_2$**, yielding a ^{1}H NMR spectrum essentially identical to that of the $[Al(OR^F)_4]^-$ analogue (maximum deviation of a given chemical shift between the two of 0.1 ppm).

In addition to the evidence from NMR data, in the case of the reaction with $PhSiH_3$, single crystals suitable for X-ray diffraction could be obtained from a concentrated solution in C_6D_5Br, providing definitive proof of oxidative addition and the formation of the monomeric product **[(10)H(SiH_2Ph)][$Al(OR^F)_4$]**. This in turn provides further evidence for the dissociation of the solid state dimer **[$(10)_2$][$Al(OR^F)_4$]$_2$** into monomer units in non-donor solvents. This structure can be compared with the analogous boryl-substituted compound **[(9)H(SiH_2Ph)][$BArF_{24}$]**. Despite the smaller NHC, the C_{NHC}-Ge-Si angle is smaller in this case (99.2(1)° vs. 110.5(1)°), due to the shorter Ge-C_{Ar} bond (1.960(4) Å, vs. 2.042(3) Å for Ge-B) and more sterically imposing terphenyl ligand (6-membered central ring vs. 5-membered of boryl). Interestingly, the Ge-Si bond is marginally shorter in this case (2.374(2) Å vs. 2.383(1) Å), presumably reflecting the proportionally greater s-character of the germanium bond to the more electropositive boron as compared to that to carbon, and hence in the terphenyl product the relatively higher s-character of the Ge-Si bond.[148] The shorter Ge-C_{NHC} bond (1.981(5) Å vs. 2.000(3) Å) can be ascribed to the less bulky N-substituents of the NHC.

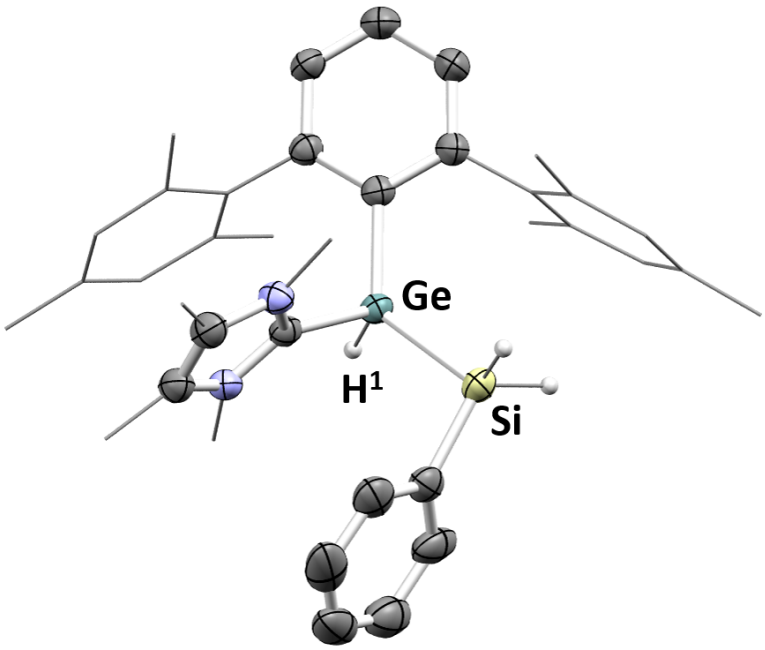


Figure 4.9: Structure of ***[(10)H(SiH$_2$Ph)][Al(OR^F)$_4$]****. For clarity, [Al(OR^F)$_4$]$^-$ counteranion and hydrogen atoms (other than Ge**<u>**H**</u>** and Si**<u>**H**</u>**$_2$Ph) omitted, and Ar^{Mes} Mes and NHC Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-C$_{Ar}$: 1.960(4), Ge-C$_{NHC}$: 1.981(5), Ge-Si: 2.374(2), C$_{Ar}$-Ge-C$_{NHC}$: 106.8(2), C$_{Ar}$-Ge-Si: 125.5(1), C$_{NHC}$-Ge-Si: 99.2(1)*

Exposure of a C_6D_5Br solution of **[(10)$_2$][Al(OR^F)$_4$]$_2$** to an atmosphere of H_2 results in slow conversion to a new product (over several days at room temperature). Although definitive crystallographic characterisation of this product could not be achieved, the similarly symmetrical ^{1}H NMR spectrum to **[(9)H$_2$][BArF$_{24}$]** (featuring a germanium hydride signal at 4.54 ppm) strongly suggests the formation of the germylium dihydride [(I-Me$_4$)(Ar^{Mes})GeH$_2$][Al(OR^F)$_4$], **[(10)H$_2$][Al(OR^F)$_4$]**. Further evidence comes from the fact that this same species could be generated via the addition of PhOH to solutions of **[(10)H(Bpin)][Al(OR^F)$_4$]** (and was seen as a common side product when manipulating **[(10)H(R)][Al(OR^F)$_4$]** species, presumably due to reactions with adventitious moisture). It was also hoped that, as compared to **[(9)H(NH$_2$)][BArF$_{24}$]**, the use of a terphenyl ligand might provide a more stable germanium-containing product following oxidative addition of ammonia, given the lack of B-N bond formation as a driving force for elimination. While {(B^{Dipp})GeNH$_2$}$_n$ is unknown, (Ar$^{Dipp/Tripp}$)Ge(μ$_2$-NH$_2$)$_2$Ge(Ar$^{Dipp/Tripp}$) have been synthesised.[149,150] Further inspiration for such a strategy can be found in tin chemistry, as (Ar$^{Mes/Dipp}$)$_2$Sn reacts with NH_3 to give (Ar$^{Mes/Dipp}$)Sn(μ$_2$-NH$_2$)$_2$Sn(Ar$^{Mes/Dipp}$) (albeit via concerted arene elimination rather than a stepwise mechanism),[3,151] whereas (B^{Dipp})$_2$Sn undergoes oxidative addition followed by elimination to form reduced tin species, B^{Dipp}H and B^{Dipp}NH$_2$.[53] Upon

exposure of a C_6D_5Br solution of **[(10)$_2$][Al(OR^F)$_4$]$_2$** to an atmosphere of NH_3, a new set of signals in the ^{1}H NMR spectrum suggest the oxidative addition of ammonia (Ge-H signal at 5.76 ppm, Ge-NH_2 signal at 0.05 ppm); however, this species can be observed to decompose over a period of 2 d. Although [I-Me_4H][Al(OR^F)$_4$] can be identified as the NHC-containing product, in contrast to the boryl analogue there is no clean formation of a single terphenyl-containing product, with several different species observable in the ^{1}H NMR spectrum. {(Ar^{Mes})$GeNH_2$}$_n$ is, unlike its Ar^{Dipp} and Ar^{Tripp} analogues,[149,150] unreported, and attempts in this work to synthesise it for comparison proved unsuccessful.

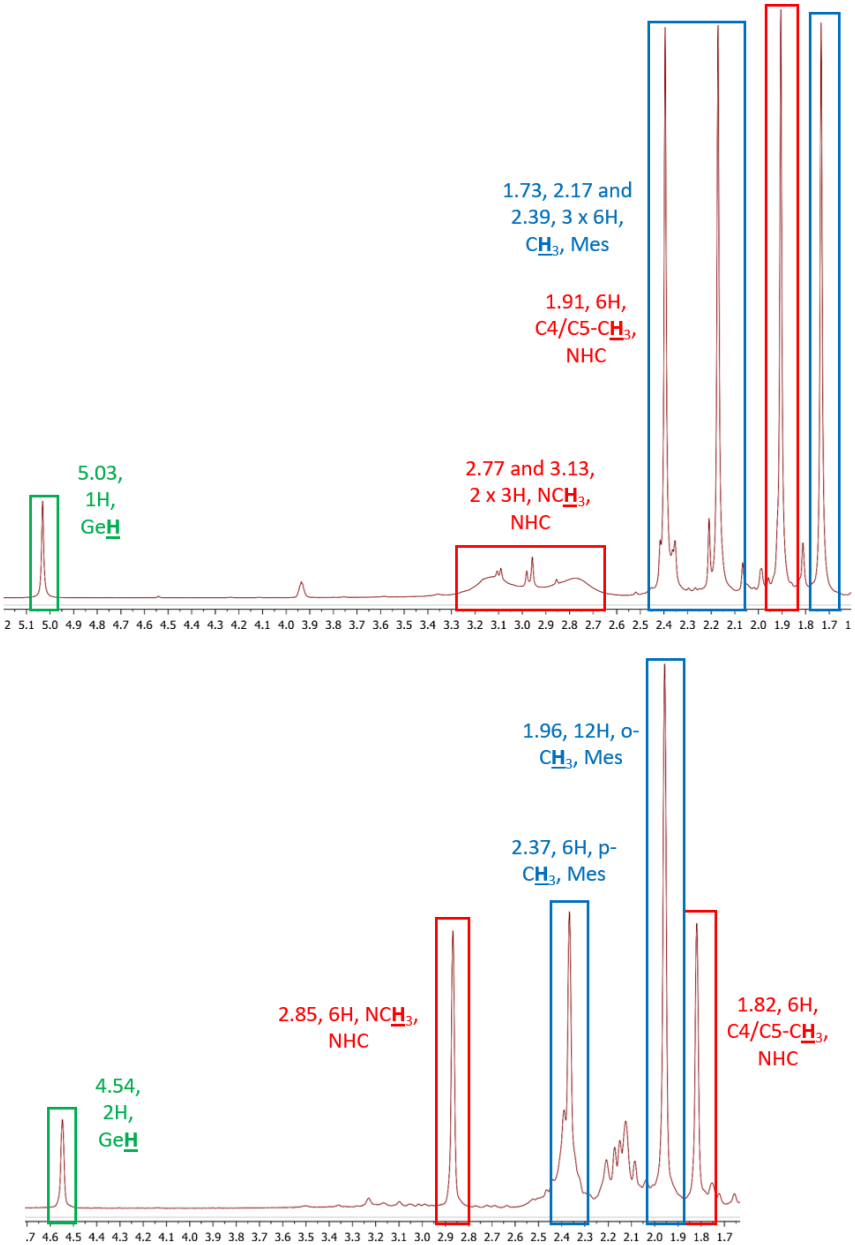
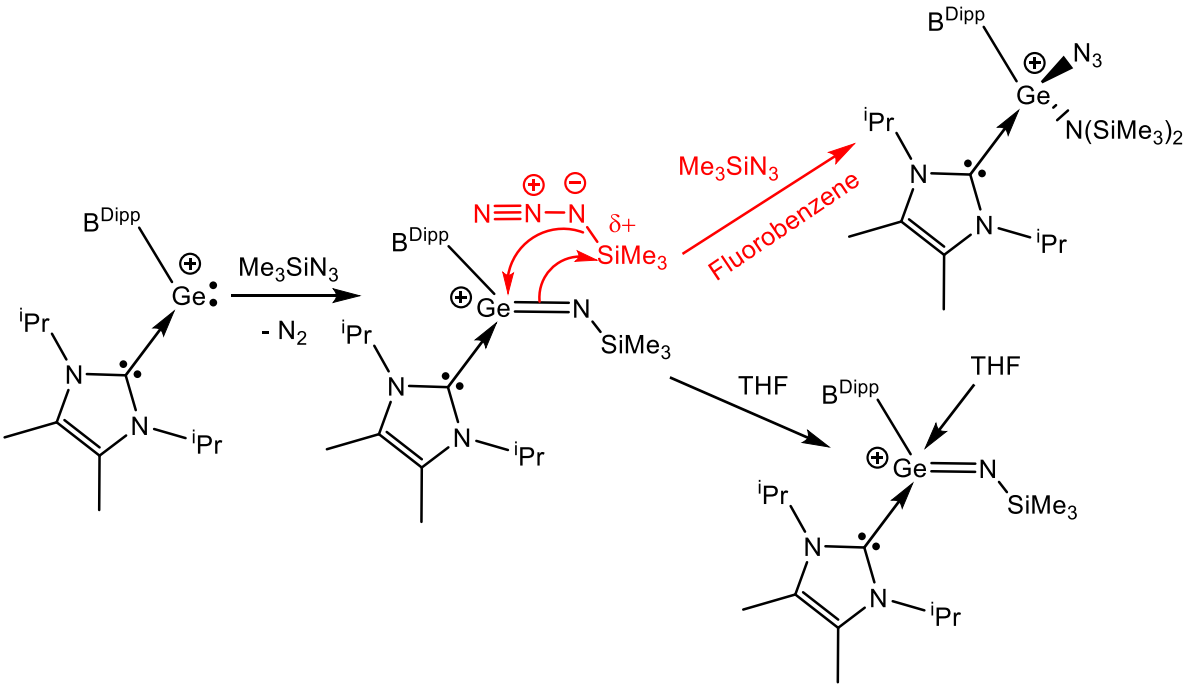


*Figure 4.10: Excerpts from the ^{1}H NMR spectra of **[(10)H(SiEt$_3$)][Al(OR^F)$_4$]** (top) and **[(10)H$_2$][Al(OR^F)$_4$]** (bottom). Chemical shifts in ppm. Resonances due to $SiEt_3$ and aryl signals of Ar^{Mes} are not shown.*

4.3.5 Reactivity of a boryl-substituted germanium cation towards trimethylsilylazide and trimethylsilylazidomethane

Given the fascinating reactivity of **1.33** towards Me_3SiXN_2 reagents (X = CH or N), in forming sterically unprotected examples of germanium-carbon/nitrogen double bonds,[19] the reactivity of **[9][BArF$_{24}$]** towards these substrates was expected to be of significant interest. After 2 h the ^{1}H NMR spectrum of a mixture of **[9(d$_8$-THF)][BArF$_{24}$]** and one equivalent of Me_3SiN_3 in d_8-THF is consistent with the formation of a single new product. Integration of $SiMe_3$ methyl signals suggests the incorporation of one $SiMe_3$ unit per ligand moiety (with no change even after the addition of a considerable excess of Me_3SiN_3).



*Scheme 4.7: Reactivity of **[9][BArF$_{24}$]** towards Me_3SiN_3 in THF or fluorobenzene (counteranion omitted)*

Intriguingly, however, when the reaction was carried out instead in fluorobenzene, using a slight excess of Me_3SiN_3, removal of the volatiles and subsequent ^{1}H NMR spectroscopy in d_8-THF revealed a mixture of products. The product obtained from the reaction in THF was the second most abundant (ca. 30%), with the major product (ca. 40%) being a different species, and smaller amounts of other products also being observed. Single crystals of the major product (whose identity could be confirmed by redissolution of the crystals in d_8-THF and comparison of the ^{1}H NMR spectra) could be obtained from this reaction mixture, and were revealed by X-ray diffraction to contain the germylium azide/amide

[(IPrMe)(B^{Dipp})GeN_3{$N(SiMe_3)_2$}][$BArF_{24}$], **[(9)N_3{$N(SiMe_3)_2$}][$BArF_{24}$]**, consistent with the addition of two equivalents of Me_3SiN_3 (Scheme 4.7). We hypothesise that, in the donor solvent THF, a germa-imine of the form [(d_8-THF)(IPrMe)(B^{Dipp})Ge=N($SiMe_3$)][$BArF_{24}$] (**[(d_8-THF)9(N$SiMe_3$)][$BArF_{24}$]**) is generated, with a molecule of THF coordinated at the cationic germanium centre, blocking any further reactivity. There is precedent for polarised multiple bonds involving group 14 elements leading to the coordination of THF and other donor solvents (which can often only be removed by prolonged heating under vacuum, if at all).[27,31,152,153] However, in the non-donor solvent fluorobenzene, there is no such coordination, and a further molecule of Me_3SiN_3 can add across the multiple bond. This is in contrast to the behavior observed for **1.33**, which was found to form a germa-imine in either fluorobenzene or bromobenzene,[19] and reflects the lesser combined steric demand of the ligands in this case (hence this cation being dimeric in the solid state, as compared to the monomeric **1.33**). Such solvent-dependent reactivity of group 14 elements towards azides is quite unprecedented, and reflects the ability of the charge of **[9][$BArF_{24}$]** to profoundly influence its reactivity. Regarding the regioselectivity of the addition of the second equivalent of Me_3SiN_3, there are examples of such additions across germa-imines to give either a tetrazole via [3+2] cycloaddition or an azide/amide via 1,2-addition;[154–156] the formation of the latter in this instance is consistent with the general observation that more polarised Ge=N bonds react via this pathway[156] - though it is conceivable that the tetrazole may be one of the minor products observed.

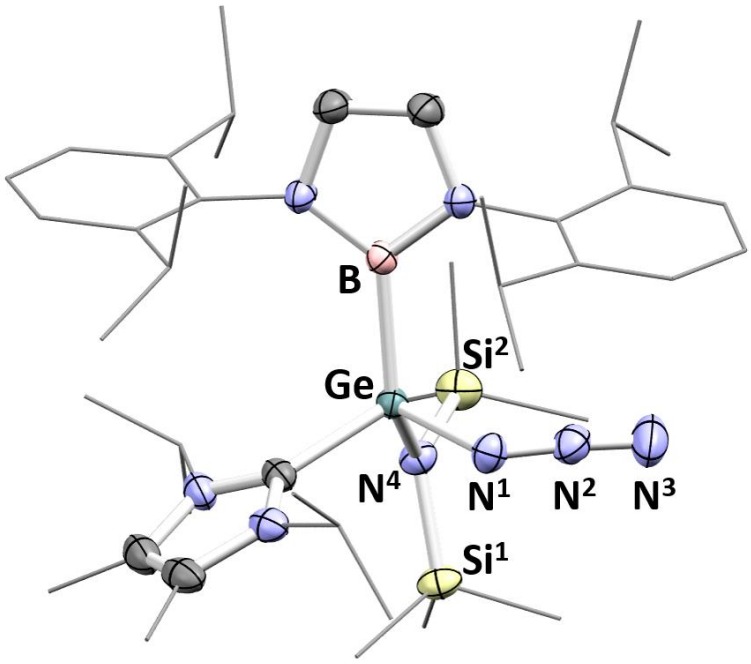


Figure 4.11: Structure of ***[(9)N$_3${N(SiMe$_3$)$_2$}][BArF$_{24}$]****. For clarity, [BArF$_{24}$]$^-$ counteranion and hydrogen atoms omitted, and B^{Dipp} Dipp, NHC ^{i}Pr and Me, and SiMe$_3$ Me groups, shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-B: 2.104(3), Ge-N^4: 1.859(2), Ge-N^1: 1.895(3), N^1-N^2: 1.225(3), N^2-N^3: 1.127(3), Ge-C$_{NHC}$: 2.016(2), C$_{NHC}$-Ge-N^4: 104.4(1), C$_{NHC}$-Ge-N^1: 100.6(1), C$_{NHC}$-Ge-B: 110.9(1), B-Ge-N^1: 106.3(1), B-Ge-N^4: 128.5(1), N^4-Ge-N^1: 102.6(1), Ge-N^1-N^2: 118.0(2), N^1-N^2-N^3: 174.8(3)*

Compound **[(9)N$_3${N(SiMe$_3$)$_2$}][BArF$_{24}$]** represents a relatively rare example of a germanium azide – in particular, the first germylium azide (there are two previous examples of germylium-ylidene azides),[157,158] the first Ge^{IV} azide coordinated by an NHC (there are two NHC-coordinated Ge^{II} azides),[158,159] and the first germanium (or indeed heavier main group) azide substituted by a boryl group. Structural metrics of **[(9)N$_3${N(SiMe$_3$)$_2$}][BArF$_{24}$]** can be compared to those of two other Ge^{IV} azides, (Ar^{Mes})$_2$GeH(N$_3$)[74] and Mes$_3$GeN$_3$,[160] which are given in Table 4.1.

	[(9)N$_3${N(SiMe$_3$)$_2$}][BArF$_{24}$]	(Ar^{Mes})$_2$GeH(N$_3$)[74]	Mes$_3$GeN$_3$[160]
Ge-N^1 (Å)	1.895(3)	1.909(4)	1.895(9)
Ge-N^1-N^2 (°)	118.0(2)	117.3(4)	119.0(7)
N^1-N^2-N^3 (°)	174.8(3)	177.0(5)	175(1)
N^1-N^2/N^2-N^3 (Å)	1.225(3)/1.127(3)	1.231(6)/1.201(5)	1.210(15)/1.171(16)
(N^1-N^2)-(N^2-N^3) (pm)	9.8 (8.7%)	3.0 (2.5%)	3.9 (3.3%)

Table 4.1: Structural metrics of ***[(9)N$_3${N(SiMe$_3$)$_2$}][BArF$_{24}$]*** *compared to analogous compounds (% given is that by which (N^1-N^2) is greater than (N^2-N^3))*

The Ge-N^1 distance is consistent with the other Ge^{IV} azides, as are the Ge-N^1-N^2 and N^1-N^2-N^3 angles.[74,160,161] However, what is noticeable is the greater discrepancy between the N-N bond lengths (N^1-N^2 and N^2-N^3) as compared to these other examples. The values for these other cases are quite representative of germanium azides, and indeed an exhaustive assessment of all structurally characterised germanium azides (ca. 30 examples) reveals that **[(9)N_3{$N(SiMe_3)_2$}][$BArF_{24}$]** has a larger difference between the N-N bond lengths than nearly all published germanium azides,[154,156–159,162–177] with the exception of {$CpW(CO)(PMe_3)_2$}$Ge(N_3)_3$,[178] where the mean distance difference of 11.2 pm is likely to be influenced by interaction with the transition metal centre.[†]

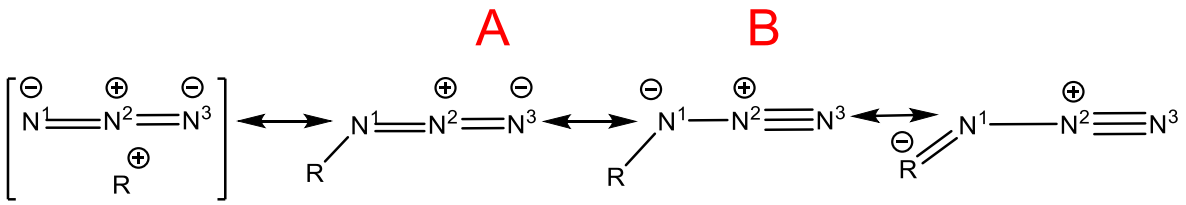


Figure 4.12: Ionic (A) and covalent (B) resonance structures for azides, and possible extreme forms depending on the nature of R

Azides can be represented by two possible resonance structures – either the more "ionic" (A) form (towards, e.g. NaN_3, with equal N^1-N^2 and N^2-N^3 distances) or the more "covalent" (B) form (e.g. HN_3, where N^1-N^2 is 10.6 pm (9.3%) longer than N^2-N^3).[179] Alkyl azides are more towards the covalent form, with aryl azides even more so due to the potential for delocalisation of the resulting charge at N^1 (from average values for many examples, N^1-N^2 is 8.3 pm (7.3%) longer than N^2-N^3 for R = $C(sp^3)$, but 11.5 pm (10.2%) longer for R = $C(sp^2)$).[180] West found that for Mes_3SiN_3 the bond lengths are approximately equal (with N^2-N^3 being 1.2 pm (1.0%) longer than N^1-N^2), with the explanation that the greater polarity of the Si-N_3 bond (compared to C-N_3) disfavours the resonance form B featuring a negatively charged N^1.[181] Whereas, in Mes_3GeN_3, the lesser electronegativity difference compared to the silicon case results in a greater contribution of the B resonance structure, so N^1-N^2 being the longer bond (as is

[†]Ph_3GeN_3 exhibits a disordered structure with one azide moiety featuring $d(N^1\text{-}N^2)>d(N^2\text{-}N^3)$ by 10 pm and the other with $d(N^1\text{-}N^2)<d(N^2\text{-}N^3)$.[239] This was ascribed to the presence of two or more quasi-degenerate ground states featuring different canonical forms of the azide moiety, with the selection of one over the other depending on the exigences of crystal packing.[240] Hence, this former distance difference is not truly representative of the overall bonding picture. There is one further example featuring a large difference,[241] but this was due to an error in the processing of the crystal structure and has subsequently been corrected to a more normal value.[242,243]

also observed in the majority of other germanium azides).[160] The even more extreme N^1-N^2/N^2-N^3 difference observed in **[(9)N_3{$N(SiMe_3)_2$}][$BArF_{24}$]** can be ascribed to the greater possibility of N^1 to Ge electron donation to satiate the electron deficiency at the cationic germanium centre when the azide is in the B resonance form, and hence the correspondingly greater contribution of this to the structure as compared to neutral systems. One can also think of this in terms of the extreme ionic canonical form featuring a separation of charges (and thus an extra positive charge at germanium) being especially unfavourable for an already cationic germanium centre. Though it might thus be expected for the Ge-N^1 bond to be shorter than in other Ge^{IV} azides, there is clearly the opposing effect in this case of the greater combined steric demand of the ancillary ligands as compared to these other examples, with the two effects approximately cancelling out to result in a similar bond length. A final structural observation, and evidence for the preceding point, is the B-Ge-N^4 angle of 128.5(1)°, which is the largest distortion from ideal tetrahedral geometry seen in any of the Ge^{IV} compounds examined in this study.

Azides can be identified in their infrared spectra primarily by the asymmetric stretching band, typically appearing at ca. 2100 cm^{-1} (the symmetric stretch, at ca. 1300 cm^{-1}, is ordinarily less intense and more variable in position, and hence is less diagnostic and harder to assign).[182] In organic azides, in which the B resonance form (and thus a triple bond) predominates, then the value is higher (e.g. 2141 cm^{-1} for both HN_3 and MeN_3),[182] while ionic azides feature lower values (e.g. 2002 cm^{-1} for CsN_3),[183] though exceptions are known to these trends (as observed by West in some silicon azides).[181] In the IR spectrum of **[(9)N_3{$N(SiMe_3)_2$}][$BArF_{24}$]**, the asymmetric and symmetric stretches can be identified at 2120 and 1280 cm^{-1}, respectively. This value for the asymmetric stretch is large in comparison to most other reported examples of Ge^{IV} azides, such as 2104 cm^{-1} for $(Ar^{Mes})_2GeH(N_3)$[74] and 2090 cm^{-1} for Mes_3GeN_3,[184] though examples of higher values do exist, such as 2145 cm^{-1} for $(CF_3)_3GeN_3$.[176] The IR spectrum is thus consistent with the X-ray data and the suggested greater contribution in this case of the covalent resonance form B.

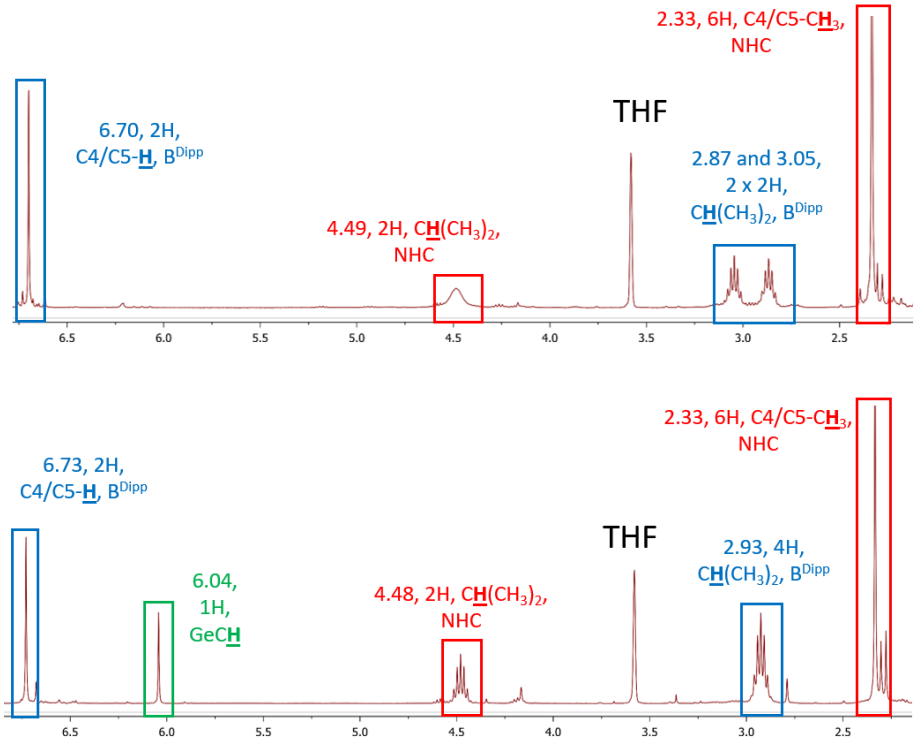
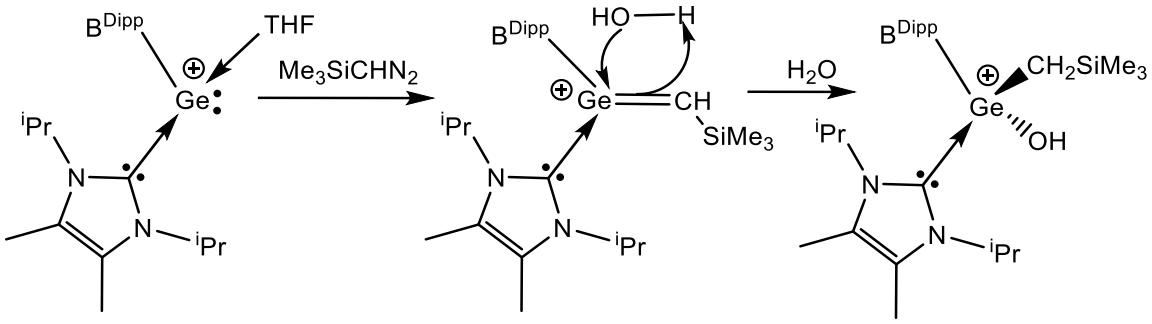


Figure 4.13: Excerpts from the ^{1}H NMR spectra of ***[(d$_8$-THF)9(NSiMe$_3$)][BArF$_{24}$]*** *(top) and* ***[9{CH(SiMe$_3$)}][BArF$_{24}$]*** *(bottom). Chemical shifts in ppm. Resonances due to Ph of B^{Dipp}, CH(C**H**$_3$)$_2$ of NHC and B^{Dipp}, SiMe$_3$ and [BArF$_{24}$]$^-$ are not shown, and that due to C4/C5-C**H**$_3$ is cropped for clarity.*

Addition of Me_3SiCHN_2 to **[9(d$_8$-THF)][BArF$_{24}$]** also leads to the formation of a new species identifiable by ^{1}H NMR spectroscopy. In addition to a new set of ligand resonances, and one for a $SiMe_3$ moiety, the ^{1}H NMR spectrum features a singlet (integrating as 1 proton per set of ligand and $SiMe_3$ resonances) at 6.04 ppm, in the region expected for a Ge=C**H** resonance (cf. 5.02 ppm [CD_2Cl_2] for **(1.33)CH{SiMe$_3$}**), thus providing evidence for the formation of the monomeric germene [(IPrMe)(B^{Dipp})Ge=CH(SiMe$_3$)][BArF$_{24}$], **[9{CH(SiMe$_3$)}][BArF$_{24}$]**. Furthermore, the ^{1}H NMR spectrum is highly symmetric as compared to the corresponding germa-imine (featuring, for example, one resonance for the boryl C**H**$(CH_3)_2$ isopropyl environment, as opposed to two in the spectrum of the germa-imine, see Figure 4.13), suggesting a significantly less sterically crowded germanium centre. This implies three-coordination and the absence of coordinated THF, which is reasonable given the less polarised nature of the Ge=C vs. Ge=N bond.



Scheme 4.8: Germene formation, and subsequent activation of adventitious moisture (counteranion omitted)

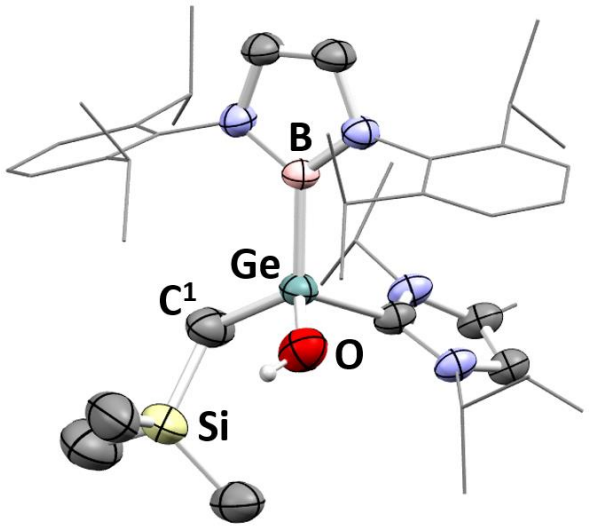


Figure 4.14: Structure of ***[9(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$]****. For clarity, [BArF$_{24}$]$^-$ counteranion and hydrogen atoms other than GeO**H** omitted, and B^{Dipp} Dipp and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge-B: 2.059(3), Ge-O: 1.850(4), Ge-C$_{alkyl}$: 1.927(5), Ge-C$_{NHC}$: 2.024(4), B-Ge-O: 108.6(2), B-Ge-C$_{alkyl}$: 118.5(2), B-Ge-C$_{NHC}$: 111.2(2), O-Ge-C$_{alkyl}$: 105.1(2), O-Ge-C$_{NHC}$: 105.3(2), C$_{alkyl}$-Ge-C$_{NHC}$: 107.2(2)*

Unfortunately, however, the only single crystals suitable for X-ray diffraction that could be obtained from this reaction were identified as [(IPrMe)(B^{Dipp})Ge(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$] (**[9(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$]**), presumably obtained via the activation of adventitious moisture. The activation of water and alcohols across germanium-carbon double bonds is well-known,[27,152,185] with especially high reactivity expected in this system because of the positive charge. Germanium hydroxide groups are not uncommon,[26,27,29,160,186–215] though **[9(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$]** represents the first example substituted by either a boryl group or an NHC. The germanium-oxygen bond in **[9(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$]** (1.850(4) Å) is relatively long compared to other Ge^{IV} examples (cf. 1.77(1) Å in (Ar^{Mes})$_2$GeH(OH)[207] and 1.805(3) Å in Mes$_3$Ge(OH))[160] and even longer than some Ge^{II} examples (cf. 1.828(1) Å in Roesky's NacNac-stabilised germanium hydroxide),[197] though longer Ge-OH bonds are known, such as 1.885(3) Å in (*o*-^{t}BuC$_6$H$_4$)$_3$Ge(OH).[203] As well as the bulky ancillary ligands, this above-

average length is also likely influenced by the electropositive boryl group, the bond to which features relatively more s-character than one to, say, an aryl group, thus leading to more p-character in the bond to oxygen.[148] The polar O-H bond probabilises the presence of interesting additional interactions, given the myriad examples of such observed in other germanium hydroxide compounds. Some of these compounds associate via intermolecular hydrogen bonding interactions between the hydroxide groups,[190,196,197,210,213] which predictably do not occur in this case (shortest O···O distance: 9.841(6) Å) because of the considerable ligand steric bulk. Intermolecular O-H···Aryl ("nonclassical hydrogen bond") interactions have been suggested in another example with bulky ligands;[195] Power, in $(Ar^{Mes})_2Ge(OH)_2$, observed *intra*molecular examples of such interactions between the hydroxide groups and the flanking aryl rings of the terphenyl ligands, with O-H···$Mes_{centroid}$ distances as short as 2.374 Å.[191] There is no evidence for such interactions in this case (either inter- or intramolecularly, the latter disproved by O···$Dipp_{centroid}$ distances of 4.550/5.420 Å), with the greater combined ligand steric bulk and the lessened approach of the flanking rings to the germanium centre (as a result of the 5- rather than 6-membered central ring) presumably precluding this.[203,206] Other germanium hydroxides feature intramolecular interactions between the hydroxide groups and nitrogen atoms in the backbone of ligands.[188,192,194,200,202,209] In **[9(OH)(CH_2SiMe_3)][$BArF_{24}$]**, there is evidence for intramolecular interactions, though of a slightly different type. It can be seen that the NHC^{plane} is nearly exactly coincident with the C_{NHC}-Ge-O plane (dihedral angle: 5.8°), which enables an extremely close approach of a C-H bond of an NHC isopropyl group to the oxygen (2.113 Å). This distance is consistent with a C-H···O weak interaction.[216–218]

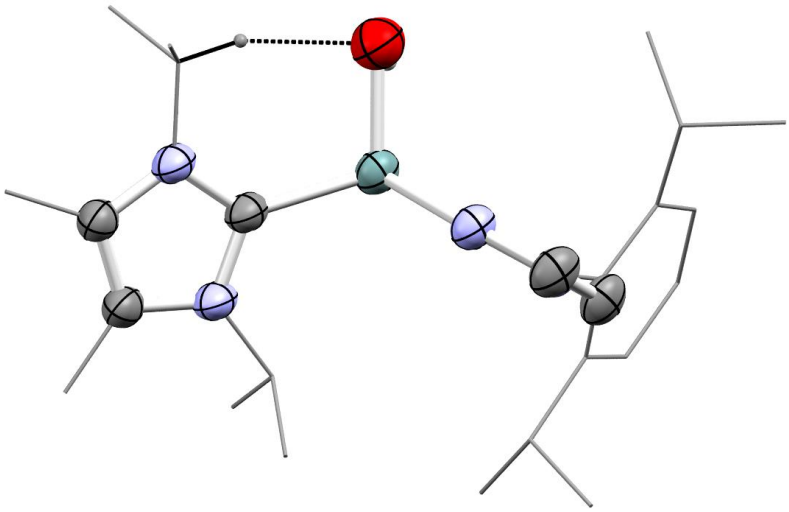
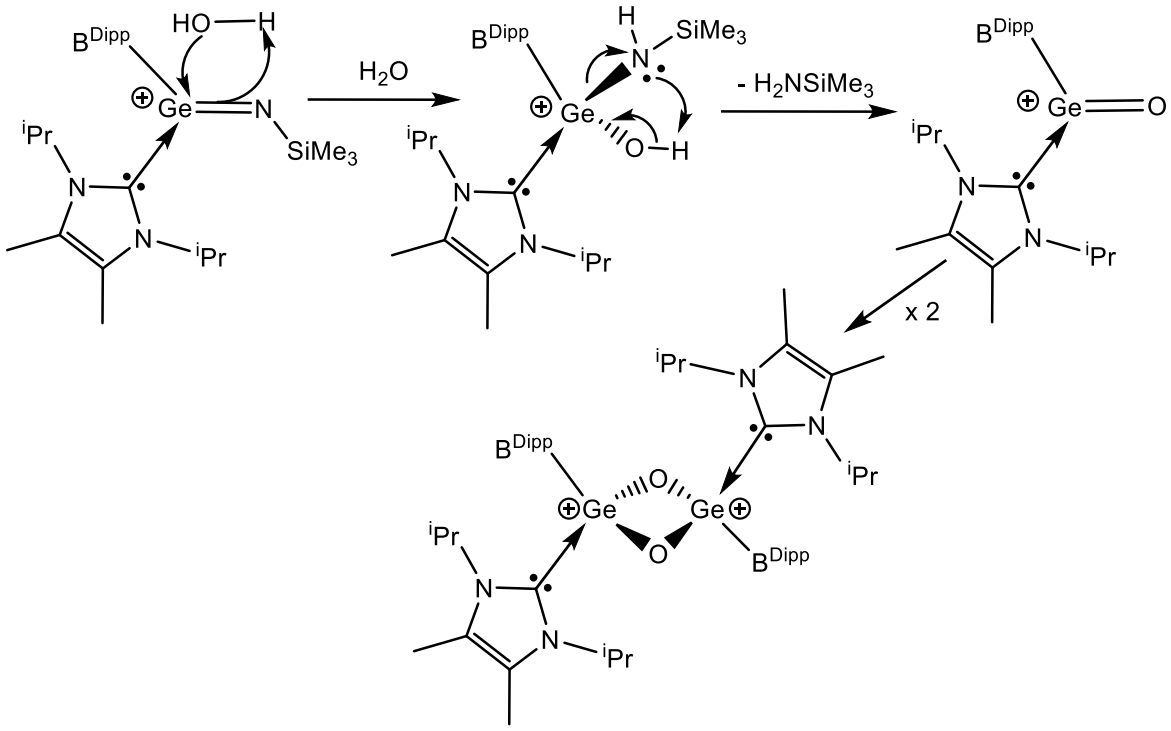


Figure 4.15: Illustration of short C-H···O contact (compared to Figure 4.14, additionally one Dipp group of B^{Dipp} and the CH_2SiMe_3 ligand omitted for clarity)

Mechanistically, the formation of the hydroxide in the above case can be compared with that of another unintended side-product. Single crystals could be obtained from a concentrated THF solution of **[(THF)9(NSiMe$_3$)][BArF$_{24}$]** layered with hexane, and were revealed by X-ray diffraction to contain the germanium μ-oxo dimer [(IPrMe)(B^{Dipp})Ge(μ$_2$-O)$_2$Ge(B^{Dipp})(IPrMe)][BArF$_{24}$]$_2$, **[9(μ$_2$-O)$_2$9][BArF$_{24}$]$_2$**. It is conceivable that, whereas in the alkyl case the reaction with adventitious moisture stops after the addition of a single equivalent of water across the multiple bond, in this case the proximity of a hydroxide group and the lone pair of the NHSiMe$_3$ moiety resulting from the first step leads to deprotonation of the hydroxide, and so to the formation of a transient germanone that dimerises to give the observed product. Only one three-coordinate germanone has been synthesised ({Eind}$_2$Ge=O),[26] and that in this case there is insufficient ligand steric bulk to stabilise a germanone is predictable given the failure to form one from reactions of the bulkier **1.33** with oxygen-atom sources.[19]



Scheme 4.9: Activation of adventitious moisture by a germa-imine (counteranion omitted)

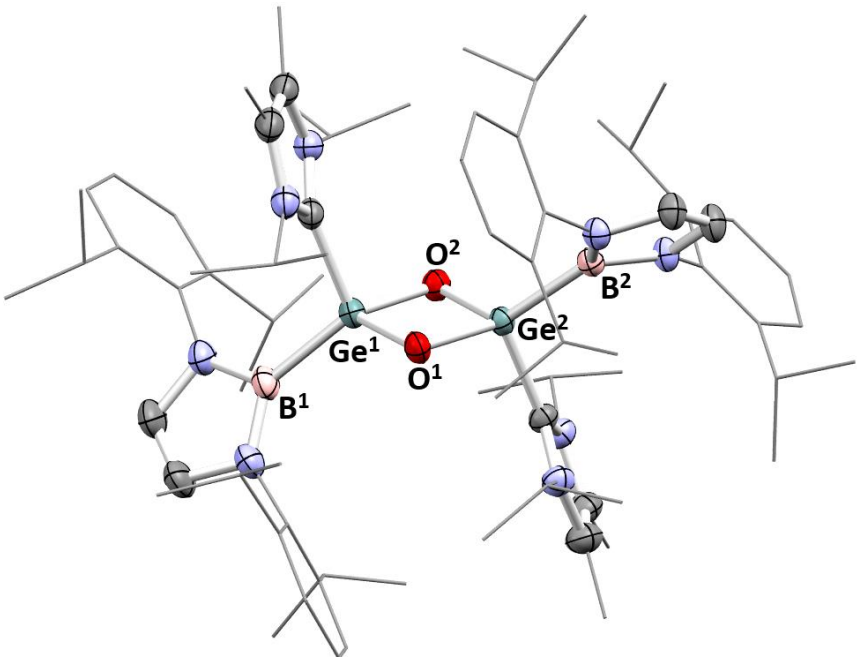


Figure 4.16: Structure of ***[9(μ$_2$-O)$_2$9][BArF$_{24}$]$_2$****. For clarity, [BArF$_{24}$]$^-$ counteranions and hydrogen atoms omitted, and B^{Dipp} Dipp and NHC^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Ge^1-B^1: 2.072(5), Ge^2-B^2: 2.071(4), Ge^1-C$_{NHC}$^{1}: 2.004(3), Ge^2-C$_{NHC}$^{2}: 2.005(3), Ge^1-O^1: 1.816(3), Ge^1-O^2: 1.822(2), Ge^2-O^1: 1.826(2), Ge^2-O^2: 1.819(3), B^1-Ge^1-C$_{NHC}$^{1}: 111.2(2), B^2-Ge^2-C$_{NHC}$^{2}: 108.5(1), B^1-Ge^1-O^1: 119.8(2), B^1-Ge^1-O^2: 125.3(2), B^2-Ge^2-O^1: 120.8(1), B^2-Ge^2-O^2: 126.8(1), C$_{NHC}$^{1}-Ge^1-O^1: 106.4(1), C$_{NHC}$^{1}-Ge^1-O^2: 103.8(1), C$_{NHC}$^{2}-Ge^2-O^1: 106.5(1), C$_{NHC}$^{2}-Ge^2-O^2: 104.6(1), O^1-Ge^1-O^2: 86.8(1), O^1-Ge^2-O^2: 86.6(1), Ge^1-O^1-Ge^2: 93.3(1), Ge^1-O^2-Ge^2: 93.3(1)*

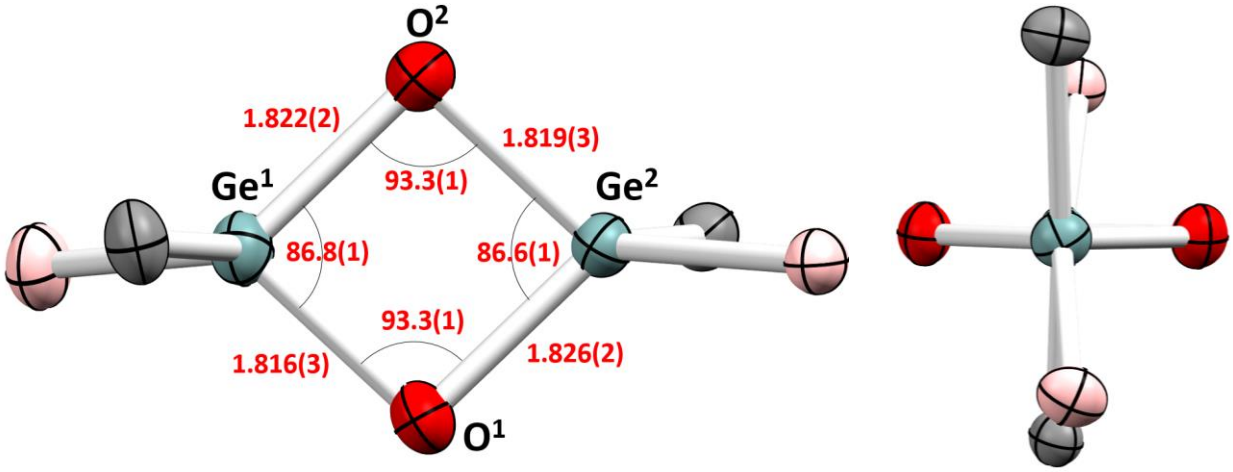


Figure 4.17: Lengths (Å) and angles (°) of Ge_2O_2 core (L); Newman projection along Ge-Ge axis (R)

This dioxadigermetane contains a central Ge_2O_2 core, which is almost square and nearly perfectly planar (torsion angle: 0.9(1)°, sum of internal angles: 360°, dihedral angles between Ge-O-Ge and O-Ge-O planes: 1.3° and 1.2°, respectively). The transannular distance between the germanium centres (2.6484(7) Å) is much greater than twice the covalent radius of germanium (2.42 Å),[219] thus implying no meaningful direct bonding interaction (as is the case with the distance between the oxygen centres: 2.499(3) Å). The ligands on each germanium centre are approximately perpendicularly disposed with respect to this central ring (dihedral angles between each B-Ge-C_{NHC} plane and the central Ge_2O_2 plane: 87.2° and 87.5°). There is an *E* orientation of the ligands about this central core, with the B-Ge-C_{NHC} planes twisted slightly with respect to one another (see Newman projection above, dihedral angle between these planes: 7.0°). That said, the structural metrics of the ligands on either side of the core are very similar (Ge-B: 2.072(5)/2.071(4) Å; Ge-C_{NHC}: 2.004(3)/2.005(3) Å; B-Ge-C_{NHC}: 111.2(2)°/108.5(1)°; dihedral angles between NHC^{plane} and the Ge_2O_2 plane of 74.0°/70.2°, and analogously for B^{plane} of 51.0°/46.8°). The boryl groups are oriented further away from the central plane than the NHC ligands, as would be expected given their greater steric bulk (mean angles: B-Ge-O, 123.2°; C_{NHC}-Ge-O, 105.3°).

Though there are various other examples of germanium μ-oxo dimers,[193,220–237] **[9(μ$_2$-O)$_2$9][BArF$_{24}$]$_2$** represents the first cationic one, as well as the first substituted by either a boryl group or an NHC. The

planar Ge_2O_2 core is consistent with almost all of these examples.[‡] The structural metrics are also similar, as illustrated by a comparison of these in Table 4.2 with those of $\{(Me_3Si)_2N\}_2Ge(\mu_2\text{-}O)_2Ge\{N(SiMe_3)_2\}_2$ (**4.1**)[231] and $\{(H_2C(Me_3Si)_2C)_2\}Ge(\mu_2\text{-}O)_2Ge\{(C(SiMe_3)_2CH_2)_2\}$ (**4.2**).[235] The mean Ge-O distance (1.821 Å) is predictably considerably longer than in the germanone (1.6468(5) Å)[26] and is in keeping with those of other μ-oxo dimers, with the deviation between individual Ge-O lengths far from the largest that has been observed[225,229,236] (e.g. 1.799(8) Å and 1.875(6) Å in $\{Me_2Si(DippN)_2\}Ge(\mu_2\text{-}O)_2Ge\{(NDipp)_2SiMe_2\}$).[222] The Ge-O-Ge and O-Ge-O angles are also typical. Although it might be thought that the bringing together of two cationic units would result in a large Ge···Ge separation, the distance in this case is not atypically large.

	$[9(\mu_2\text{-}O)_29][BArF_{24}]_2$	**4.1**	**4.2**
Mean Ge-O distance (Å)	1.821	1.805	1.821
Mean Ge-O-Ge (°)	93.3	92.5	94.5
Mean O-Ge-O (°)	86.7	87.5	85.5
Ge···Ge separation (Å)	2.6484(7)	2.607(2)	2.6748(3)

*Table 4.2: Structural metrics of **$[9(\mu_2\text{-}O)_29][BArF_{24}]_2$** compared to analogous compounds*

4.4 Conclusions

In this chapter, the reactivity of the germylium-ylidenes synthesised in Chapter 3 has been explored. The boryl-substituted **[9][BArF$_{24}$]** has been found, primarily as the THF-adduct **[9(d$_8$-THF)][BArF$_{24}$]**, to be capable of the activation of a variety of small molecules, including dihydrogen, ammonia, silanes and boranes, representing the first isolable non-transition metal-stabilised germylium-ylidene capable of the oxidative addition of E-H bonds. Reactivity in other solvents has also provided insight into the behavior of these cations. The onward reactivity of Ge^{IV} products has demonstrated the unique reactivity of cations as compared to their neutral analogues; thus, elimination following addition of ammonia illustrates a greater propensity for reductive elimination, while ligand-centred

[‡]With the exception of $(2,6\text{-}Et_2C_6H_3)_2Ge(\mu_2\text{-}O)_2Ge(2,6\text{-}Et_2C_6H_3)_2$, which features a slightly puckered core, with dihedral angles between the Ge-O-Ge and O-Ge-O planes of 8.8(2)° and 8.4(1)°, respectively.[220]

electrophilicity was demonstrated through reactions with THF and water/alcohols. A terphenyl-substituted example was found to have similar reactivity towards E-H bonds, despite the weaker donor ligand. Attempts towards the formation of multiple bonds enabled the formation of the first boryl-substituted examples of germanium azide, hydroxide and μ-oxo dimer species.

4.5 Synthesis and characterisation of novel compounds

4.5.1 Small molecule activation by [9][BArF$_{24}$]

Generation of [(IPrMe)(B^{Dipp})GeH$_2$][BArF$_{24}$], [(9)H$_2$][BArF$_{24}$]

A J. Young's NMR tube containing a solution of **[9(d$_8$-THF)][BArF$_{24}$]** (0.050 g, 0.0333 mmol) in d$_8$-THF (0.5 mL) was degassed via three *freeze-pump-thaw* cycles, and back-filled with an atmosphere of H_2 at room temperature. Monitoring via ^{1}H NMR spectroscopy confirmed complete conversion to the product after 7 d at room temperature. Single crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution of [(IPrMe)(B^{Dipp})GeH(Bpin)][BArF$_{24}$] with hexane, followed by storage at −25°C for several days. Note that in this and subsequent procedures, the mass given refers to that of **[(9)$_2$][BArF$_{24}$]$_2$**, and the molar quantities given refer to the monomeric unit.

Spectroscopic data for [(9)H$_2$][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, d$_8$-THF, 298 K): 1.17 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.20 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.28 (d, 12H, $^3J_{HH}$ = 7.1 Hz, CH(C**H**$_3$)$_2$, NHC), 2.28 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.94 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.17 (s, 2H, Ge**H**$_2$), 4.19 (overlapping sept, 2H, $^3J_{HH}$ = 7.1 Hz, C**H**(CH$_3$)$_2$, NHC), 6.68 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.31-7.42 (m, 6H, Ph, B^{Dipp}), 7.58 (s, 4H, *p*-Ph, BArF$_{24}$), 7.80 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d$_8$-THF, 298 K): −6 (**B**ArF$_{24}$), 23 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, d$_8$-THF, 298 K): 10.6 (C4/C5-**C**H$_3$, NHC), 21.2 (CH(**C**H$_3$)$_2$, NHC), 23.9, 25.8 (CH(**C**H$_3$)$_2$, B^{Dipp}), 29.7 (**C**H(CH$_3$)$_2$, B^{Dipp}), 56.2 (**C**H(CH$_3$)$_2$, NHC), 118.4 (br. m, $^3J_{CF}$ = 4.8 Hz, *p*-Ph, BArF$_{24}$), 125.0 (overlapping C4/C5-**C** and *m*-Ph, B^{Dipp}), 125.7 (q, $^1J_{CF}$ = 273.0 Hz, **C**F$_3$, BArF$_{24}$), 129.9 (*p*-Ph, B^{Dipp}), 130.2 (qq, $^3J_{CB}$ = 3.6 Hz, $^2J_{CF}$ = 32.2 Hz, *m*-Ph, BArF$_{24}$), 131.8 (C4/C5-**C**, NHC), 135.8 (*o*-Ph, BArF$_{24}$), 138.7 (*i*-Ph, B^{Dipp}), 145.5 (**C**$_{NHC}$), 146.7 (*o*-Ph, B^{Dipp}), 163.0 (q, $^1J_{CB}$ = 50.1 Hz, *i*-Ph, BArF$_{24}$) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, d$_8$-THF, 298 K): −63.4 (BAr**F**$_{24}$) ppm.

Crystallographic data for [(9)H$_2$][BArF$_{24}$]:

$C_{69}H_{70}B_2F_{24}GeN_4$, M_r = 1505.50, triclinic, P-1, a = 13.1107(5) Å, b = 13.1292(5) Å, c = 21.3354(7) Å, α = 82.898(3)°, β = 76.234(3)°, γ = 84.452(3)°, V = 3531.0(2) Å^3, Z = 2, R_1 = 0.0509 (11890, I>2σ{I}), wR_2 = 0.1436 (all 14561 unique reflections).

Generation of [(IPrMe)(B^{Dipp})GeH(NH$_2$)][BArF$_{24}$], [(9)H(NH$_2$)][BArF$_{24}$]

A J. Young's NMR tube containing a solution of **[9(d$_8$-THF)][BArF$_{24}$]** (0.050 g, 0.0333 mmol) in d$_8$-THF (0.5 mL) was degassed via three *freeze-pump-thaw* cycles, and back-filled with an atmosphere of NH_3 at room temperature. Monitoring via ^{1}H NMR spectroscopy confirmed complete conversion to the product after ca. 5 min at room temperature. Full characterising data could not be obtained due to the short-lived nature of this species.

Spectroscopic data for [(9)H(NH$_2$)][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, d$_8$-THF, 298 K): 0.32 (s, 2H, GeN**H**$_2$), 1.01 (d, 6H, $^3J_{HH}$ = 7.0 Hz), 1.18 (overlapping d, 12H), 1.23 (overlapping d, 6H), 1.37 (d, 6H, $^3J_{HH}$ = 7.0 Hz), 1.41 (d, 6H, $^3J_{HH}$ = 6.8 Hz) [all CH(C**H**$_3$)$_2$, B^{Dipp} and NHC], 2.28 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.88 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.07 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.68 (br. sept, 2H, C**H**(CH$_3$)$_2$, NHC), 5.66 (s, 1H, Ge**H**), 6.65 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.27-7.48 (m, 6H, Ph, B^{Dipp}), 7.58 (s, 4H, *p*-Ph, BArF$_{24}$), 7.80 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d$_8$-THF, 298 K): −6 (**B**ArF$_{24}$), 23 (**B**^{Dipp}) ppm.

Generation of [(IPrMe)(B^{Dipp})GeH(SiEt$_3$)][BArF$_{24}$], [(9)H(SiEt$_3$)][BArF$_{24}$]

Et$_3$SiH (5.3 µL, 0.0333 mmol, 1 equiv.) was added to a solution of **[9(d$_8$-THF)][BArF$_{24}$]** (0.050 g, 0.0333 mmol) in d$_8$-THF (0.5 mL) in a J. Young's NMR tube at room temperature. The solution immediately changed colour from yellow to colourless, and ^{1}H NMR spectroscopy revealed complete conversion to the product (within ca. 5 min at room temperature). Alternatively, the reaction could be performed on the same scale in fluorobenzene or d$_5$-pyridine, in which case the reaction mixture was respectively stirred for 3 h at room temperature or heated at 60°C for 10 h, after which the volatiles were removed *in vacuo*, and the residue dissolved in CD_2Cl_2. ^{1}H NMR spectroscopy in each case revealed complete conversion to the product. Single crystals suitable for X-ray diffraction were obtained by layering a

concentrated fluorobenzene solution (0.0333 mmol) with hexane, followed by storage at −25°C for several days (yielding 0.020 g, 0.0123 mmol, 37.1%).

Spectroscopic data for [(9)H(SiEt$_3$)][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, d$_8$-THF, 298 K): 0.20 (m, 3H, $^{2/3}J_{HH}$ = 7.9 Hz, SiC**H**(H)CH$_3$, SiEt$_3$), 0.49 (m, 3H, $^{2/3}J_{HH}$ = 7.3 Hz, SiCH(**H**)CH$_3$, SiEt$_3$), 0.70 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, NHC), 0.77 (t, 9H, $^3J_{HH}$ = 7.9 Hz, SiCH$_2$C**H**$_3$, SiEt$_3$), 1.14 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.17 (br. m, 12H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.33 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(C**H**$_3$)$_2$, NHC), 1.43 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.57 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, NHC), 1.61 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, NHC), 2.23 (s, 3H, C4/C5-C**H**$_3$, NHC), 2.35 (s, 3H, C4/C5-C**H**$_3$, NHC), 2.74 (br. sept, 2H, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.13 (br. sept, 2H, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.17 (s, 1H, Ge**H**), 4.36 (sept, 1H, $^3J_{HH}$ = 7.3 Hz, C**H**(CH$_3$)$_2$, NHC), 4.48 (sept, 1H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, NHC), 6.61 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.10-7.40 (m, 6H, Ph, B^{Dipp}), 7.58 (s, 4H, *p*-Ph, BArF$_{24}$), 7.80 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{1}H NMR (400.2 MHz, CD$_2$Cl$_2$, 298 K): 0.12 (m, 3H, $^{2/3}J_{HH}$ = 7.8 Hz, SiC**H**(H)CH$_3$, SiEt$_3$), 0.41 (m, 3H, $^{2/3}J_{HH}$ = 7.6 Hz, SiCH(**H**)CH$_3$, SiEt$_3$), 0.64 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH(C**H**$_3$)$_2$, NHC), 0.73 (t, 9H, $^3J_{HH}$ = 7.6 Hz, SiCH$_2$C**H**$_3$, SiEt$_3$), 1.12 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.15 (br. m, 12H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.27 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH(C**H**$_3$)$_2$, NHC), 1.38 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.48 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, NHC), 1.53 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, NHC), 2.14 (s, 3H, C4/C5-C**H**$_3$, NHC), 2.25 (s, 3H, C4/C5-C**H**$_3$, NHC), 2.66 (br. sept, 2H, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.05 (br. sept, 2H, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.09 (s, 1H, Ge**H**), 4.30 (sept, 1H, $^3J_{HH}$ = 7.3 Hz, C**H**(CH$_3$)$_2$, NHC), 4.41 (sept, 1H, $^3J_{HH}$ = 7.1 Hz, C**H**(CH$_3$)$_2$, NHC), 6.45 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.13-7.39 (m, 6H, Ph, B^{Dipp}), 7.56 (s, 4H, *p*-Ph, BArF$_{24}$), 7.72 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d$_8$-THF, 298 K): −6 (**B**ArF$_{24}$), 25 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, d$_8$-THF, 298 K): 5.9 (Si**C**H$_2$CH$_3$, SiEt$_3$), 8.4 (SiCH$_2$**C**H$_3$, SiEt$_3$), 10.8, 10.9 (C4/C5-**C**H$_3$, NHC), 21.2, 21.4, 21.6 (CH(**C**H$_3$)$_2$, NHC), 22.8, 23.1, 26.3, 27.0 (CH(**C**H$_3$)$_2$, B^{Dipp}), 29.5, 29.9 (**C**H(CH$_3$)$_2$, B^{Dipp}), 55.2, 56.2 (**C**H(CH$_3$)$_2$, NHC), 118.4 (br. m, $^3J_{CF}$ = 3.6 Hz, *p*-Ph, BArF$_{24}$), 125.1, 125.3 (C4/C5-**C** and *m*-Ph, B^{Dipp}), 125.7 (q, $^1J_{CF}$ = 273.6 Hz, **C**F$_3$, BArF$_{24}$), 129.8 (*p*-Ph, B^{Dipp}), 130.2 (qq, $^3J_{CB}$ = 3.6 Hz, $^2J_{CF}$ = 31.0 Hz, *m*-Ph, BArF$_{24}$), 132.2 (C4/C5-**C**, NHC), 135.8 (*o*-Ph, BArF$_{24}$), 139.8 (*i*-Ph, B^{Dipp}), 146.6 (*o*-Ph, B^{Dipp}), 151.1 (**C**$_{NHC}$), 163.0 (q, $^1J_{CB}$ = 48.9 Hz, *i*-Ph, BArF$_{24}$) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, d$_8$-THF, 298 K): −63.4 (BAr**F**$_{24}$) ppm.

$^{29}Si\{^{1}H\}$ NMR (99.3 MHz, d_8-THF, 298 K): 4.0 (Ge**Si**Et_3) ppm.

Crystallographic data for [(9)H(SiEt$_3$)][BArF$_{24}$]:

$C_{78}H_{86.50}B_2F_{24.5}GeN_4Si$, M_r = 1667.81, monoclinic, $P2_1/c$, a = 13.1239(2) Å, b = 24.0267(3) Å, c = 26.8456(3) Å, α = 90°, β = 90.023(1)°, γ = 90°, V = 8465.06(19) Å^3, Z = 4, R_1 = 0.0775 (12989, I>2σ{I}), wR_2 = 0.2277 (all 17260 unique reflections).

Generation of [(IPrMe)(B^{Dipp})GeH(SiH$_2$Ph)][BArF$_{24}$], [(9)H(SiH$_2$Ph)][BArF$_{24}$]

$PhSiH_3$ (6.2 µL, 0.0500 mmol, 1.5 equiv.) was added to a solution of **[9(d$_8$-THF)][BArF$_{24}$]** (0.050 g, 0.0333 mmol) in d_8-THF (0.5 mL) in a J. Young's NMR tube at room temperature. The solution immediately changed colour from yellow to colourless, and ^{1}H NMR spectroscopy revealed complete conversion to the product (within ca. 5 min at room temperature). Single crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution (0.0333 mmol) with hexane, followed by storage at room temperature for several days (yielding 0.030 g, 0.0186 mmol, 55.9%).

Spectroscopic data for [(9)H(SiH$_2$Ph)][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, d_8-THF, 298 K): 0.68 (br. m, 3H, CH(C**H**$_3$)$_2$, NHC), 0.93 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.04 (br. m, 3H, CH(C**H**$_3$)$_2$, NHC), 1.16 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.21 (d, 6H, $^{3}J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.34 (br. m, 3H, CH(C**H**$_3$)$_2$, NHC), 1.45 (d, 6H, $^{3}J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.60 (br. m, 3H, CH(C**H**$_3$)$_2$, NHC), 2.24 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 2.77 (sept, 2H, $^{3}J_{HH}$ = 6.7 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.11 (sept, 2H, $^{3}J_{HH}$ = 6.7 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.65 (d, 1H, $^{3}J_{HH}$ = 3.3 Hz, GeSi**H**(H)Ph), 4.02 (dd, 1H, $^{3}J_{HH}$ = 3.4, 8.8 Hz, Ge**H**), 4.38 (d, 1H, $^{3}J_{HH}$ = 8.7 Hz, GeSiH(**H**)Ph), 4.58 (br. sept, 2H, C**H**(CH$_3$)$_2$, NHC), 6.68 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.10-7.43 (m, 11H, Ph, PhSi and B^{Dipp}), 7.59 (s, 4H, *p*-Ph, BArF$_{24}$), 7.81 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

$^{11}B\{^{1}H\}$ NMR (128.4 MHz, d_8-THF, 298 K): −6 (**B**ArF$_{24}$), 24 (**B**^{Dipp}) ppm.

$^{13}C\{^{1}H\}$ NMR (100.6 MHz, d_8-THF, 298 K): 10.6, 10.7 (C4/C5-**C**H$_3$, NHC), 21.2, 22.7 (CH(**C**H$_3$)$_2$, NHC), 23.4, 23.9, 26.0, 26.8 (CH(**C**H$_3$)$_2$, B^{Dipp}), 29.5, 29.9 (**C**H(CH$_3$)$_2$, B^{Dipp}), 51.6, 56.2 (**C**H(CH$_3$)$_2$, NHC), 118.4 (br. m, $^{3}J_{CF}$ = 3.6 Hz, *p*-Ph, BArF$_{24}$), 125.2, 125.3 (C4/C5-**C** and *m*-Ph, B^{Dipp}), 125.7 (q, $^{1}J_{CF}$ = 273.0 Hz, **C**F$_3$, BArF$_{24}$), 128.8 (*i*-Ph, PhSi), 129.1 (*m*-Ph, PhSi), 129.6 (*p*-Ph, B^{Dipp}), 130.0 (*p*-Ph, PhSi), 130.2 (qq, $^{3}J_{CB}$ = 2.4 Hz, $^{2}J_{CF}$

= 32.2 Hz, *m*-Ph, $BArF_{24}$), 131.6 (C4/C5-**C**, NHC), 135.8 (*o*-Ph, $BArF_{24}$), 136.2 (*o*-Ph, PhSi), 139.1 (*i*-Ph, B^{Dipp}), 146.6 (*o*-Ph, B^{Dipp}), 147.1 ($\underline{\mathbf{C}}_{NHC}$), 163.0 (q, $^{1}J_{CB}$ = 50.1 Hz, *i*-Ph, $BArF_{24}$) ppm.

$^{19}F\{^{1}H\}$ NMR (376.5 MHz, d_8-THF, 298 K): −63.4 ($BAr\underline{\mathbf{F}}_{24}$) ppm.

$^{29}Si\{^{1}H\}$ NMR (79.5 MHz, d_8-THF, 298 K): −54.9 ($Ge\underline{\mathbf{Si}}H_2Ph$) ppm.

Elemental microanalysis: found (calc. for $C_{75}H_{76}B_2F_{24}GeN_4Si$): C: 56.39 (55.89)%, H: 4.67 (4.75)%, N: 3.39 (3.48)%

Crystallographic data for [(9)H(SiH₂Ph)][BArF₂₄]:

$C_{75}H_{76}B_2F_{24}GeN_4Si$, M_r = 1611.73, monoclinic, P2/c, a = 27.8824(9) Å, b = 13.5656(4) Å, c = 43.9247(14) Å, α = 90°, β = 93.686(3)°, γ = 90°, V = 16579.8(9) Å^3, Z = 8, R_1 = 0.0558 (17251, I>2σ{I}), wR_2 = 0.1107 (all 17323 unique reflections).

Generation of [(IPrMe)(B^{Dipp})GeH(Bpin)][BArF₂₄], [(9)H(Bpin)][BArF₂₄]

HBpin (4.8 µL, 0.0333 mmol, 1 equiv.) was added to a solution of **[9(d₈-THF)][BArF₂₄]** (0.050 g, 0.0333 mmol) in d_8-THF (0.5 mL) in a J. Young's NMR tube at room temperature. The solution immediately changed colour from yellow to colourless, and ^{1}H NMR spectroscopy revealed complete conversion to the product (within ca. 5 min at room temperature). Full characterising data could not be obtained due to the extreme moisture-sensitivity of this compound.

Spectroscopic data for [(9)H(Bpin)][BArF₂₄]:

^{1}H NMR (400.2 MHz, d_8-THF, 298 K): 0.96 (s, 12H, C4/C5-C$\underline{\mathbf{H}}_3$, Bpin), 0.96 (overlapping d, 6H, CH(C$\underline{\mathbf{H}}_3$)$_2$, B^{Dipp}), 1.14 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, CH(C$\underline{\mathbf{H}}_3$)$_2$, B^{Dipp}), 1.17 (overlapping d, 3H, CH(C$\underline{\mathbf{H}}_3$)$_2$, NHC), 1.19 (d, 6H, $^{3}J_{HH}$ = 7.0 Hz, CH(C$\underline{\mathbf{H}}_3$)$_2$, B^{Dipp}), 1.28 (br. d, 3H, CH(C$\underline{\mathbf{H}}_3$)$_2$, NHC), 1.41 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, CH(C$\underline{\mathbf{H}}_3$)$_2$, B^{Dipp}), 1.57 (br. d, 6H, CH(C$\underline{\mathbf{H}}_3$)$_2$, NHC), 2.28 (br. s, 6H, C4/C5-C$\underline{\mathbf{H}}_3$, NHC), 2.78 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, C$\underline{\mathbf{H}}$(CH$_3$)$_2$, B^{Dipp}), 3.10 (br. sept, 2H, C$\underline{\mathbf{H}}$(CH$_3$)$_2$, B^{Dipp}), 4.14 (s, 1H, Ge$\underline{\mathbf{H}}$), 4.46 (br. sept, 2H, C$\underline{\mathbf{H}}$(CH$_3$)$_2$, NHC), 6.57 (s, 2H, C4/C5-$\underline{\mathbf{H}}$, B^{Dipp}), 7.21-7.40 (m, 6H, Ph, B^{Dipp}), 7.58 (s, 4H, *p*-Ph, $BArF_{24}$), 7.80 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

$^{11}B\{^{1}H\}$ NMR (128.4 MHz, d_8-THF, 298 K): −6 ($\underline{\mathbf{B}}ArF_{24}$), 21 ($\underline{\mathbf{B}}$pin), 24 ($\underline{\mathbf{B}}^{Dipp}$) ppm.

$^{13}C\{^{1}H\}$ NMR (100.6 MHz, d_8-THF, 298 K): 10.8 (C4/C5-$\underline{\mathbf{C}}H_3$, NHC), 21.2, 22.7 (CH($\underline{\mathbf{C}}H_3$)$_2$, NHC), 23.8, 23.9 (CH($\underline{\mathbf{C}}H_3$)$_2$, B^{Dipp}), 25.4 (C4/C5-$\underline{\mathbf{C}}H_3$, Bpin), 26.1, 26.6 (CH($\underline{\mathbf{C}}H_3$)$_2$, B^{Dipp}), 29.6, 29.7 ($\underline{\mathbf{C}}$H(CH$_3$)$_2$, B^{Dipp}), 56.2

(**C**H(CH$_3$)$_2$, NHC), 86.8 (C4/C5-**C**, Bpin), 118.4 (br. m, $^3J_{CF}$ = 4.8 Hz, *p*-Ph, BArF$_{24}$), 125.09 (C4/C5-**C**, B^{Dipp}), 125.09 (*m*-Ph, B^{Dipp}), 125.7 (q, $^1J_{CF}$ = 271.8 Hz, **C**F$_3$, BArF$_{24}$), 129.7 (*p*-Ph, B^{Dipp}), 130.2 (qq, $^3J_{CB}$ = 3.6 Hz, $^2J_{CF}$ = 31.0 Hz, *m*-Ph, BArF$_{24}$), [signal for C4/C5-**C**, NHC not observed/obscured by those for BArF$_{24}$], 135.8 (*o*-Ph, BArF$_{24}$), 139.3 (*i*-Ph, B^{Dipp}), 146.7 (**C**$_{NHC}$), 147.0 (*o*-Ph, B^{Dipp}), 163.0 (q, $^1J_{CB}$ = 48.9 Hz, *i*-Ph, BArF$_{24}$) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, d$_8$-THF, 298 K): −63.4 (BAr**F**$_{24}$) ppm.

Reaction of [(9)$_2$][BArF$_{24}$]$_2$ with CD$_2$Cl$_2$

Upon dissolution of **[(9)$_2$][BArF$_{24}$]$_2$** in CD$_2$Cl$_2$ (0.5 mL) in a J. Young's NMR tube at room temperature, a briefly red solution decolourised within ca. 2 min, and ^{1}H NMR spectroscopy revealed complete conversion to a new product (within ca. 5 min at room temperature).

Spectroscopic data:

^{1}H NMR (400.2 MHz, CD$_2$Cl$_2$, 298 K): 1.00 (d, 6H, $^3J_{HH}$ = 7.0 Hz), 1.11 (d, 6H, $^3J_{HH}$ = 6.7 Hz), 1.17 (overlapping d, 6H), 1.19 (overlapping d, 6H), 1.37 (d, 6H, $^3J_{HH}$ = 7.0 Hz), 1.43 (d, 6H, $^3J_{HH}$ = 6.9 Hz) [all CH(C**H**$_3$)$_2$, B^{Dipp} and NHC], 2.24 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 2.82 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 2.96 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.41 (br. sept, 2H, C**H**(CH$_3$)$_2$, NHC), 6.57 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.24-7.45 (m, 6H, Ph, B^{Dipp}), 7.57 (s, 4H, *p*-Ph, BArF$_{24}$), 7.74 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, CD$_2$Cl$_2$, 298 K): −7 (**B**ArF$_{24}$), 22 (**B**^{Dipp}) ppm.

Reactions of [(9)H(SiEt$_3$)][BArF$_{24}$] and [(9)H(Bpin)][BArF$_{24}$] with PhOH

PhOH (28.2 μl, 1.77 M solution in THF, 0.0500 mmol, 1.5 equiv.) was added to an *in situ*-generated solution of **[(9)H(SiEt$_3$)][BArF$_{24}$]** or **[(9)H(Bpin)][BArF$_{24}$]** (0.0333 mmol) in d$_8$-THF (0.5 mL) in a J. Young's NMR tube at room temperature. ^{1}H NMR spectroscopy revealed complete conversion to **[(9)H$_2$][BArF$_{24}$]** (within ca. 5 min at room temperature), as well as PhOSiEt$_3$[75] or PhOBpin,[76] respectively. PhOSiEt$_3$ could be identified by comparison of ^{29}Si NMR resonances; PhOBpin could be identified by comparison of ^{1}H and ^{11}B NMR resonances (reported in d$_8$-THF in **2.3.9**).

Generation of [(IPrMe)(B^{Dipp})GeH(C$_4$D$_8$OSiEt$_3$)][BArF$_{24}$], [(9)H(C$_4$D$_8$OSiEt$_3$)][BArF$_{24}$]

An *in situ*-generated solution of **[(9)H(SiEt$_3$)][BArF$_{24}$]** (0.0333 mmol) in d$_8$-THF (0.5 mL) in a J. Young's NMR tube was heated with a further excess of Et$_3$SiH (26.6 µL, 0.166 mmol, 5 equiv.) at 60°C for 5 d, after which time complete conversion to the product was observed by ^{1}H NMR spectroscopy. Single crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution (0.0333 mmol) with hexane, followed by storage at −25°C for several days (yielding 0.020 g, 0.0118 mmol, 35.3%).

Spectroscopic data for [(9)H(C$_4$D$_8$OSiEt$_3$)][BArF$_{24}$]:

^{1}H NMR (499.9 MHz, d$_8$-THF, 298 K): 0.50 (q, 6H, $^3J_{HH}$ = 7.9 Hz, SiC**H**$_2$CH$_3$, SiEt$_3$), 0.87 (t, 9H, $^3J_{HH}$ = 8.1 Hz, SiCH$_2$C**H**$_3$, SiEt$_3$), 0.97 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.16 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.20 (overlapping d, 3H, CH(C**H**$_3$)$_2$, NHC), 1.21 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.28 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, NHC), 1.41 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.54 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, NHC), 2.31 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 2.80 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.07 (sept, 2H, $^3J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.38 (br. sept, 2H, C**H**(CH$_3$)$_2$, NHC), 4.52 (br. s, 1H, Ge**H**), 6.66 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.25-7.42 (m, 6H, Ph, B^{Dipp}), 7.57 (s, 4H, *p*-Ph, BArF$_{24}$), 7.79 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{1}H NMR (499.9 MHz, CD$_2$Cl$_2$, 298 K): 0.48 (q, 6H, $^3J_{HH}$ = 7.9 Hz, SiC**H**$_2$CH$_3$, SiEt$_3$), 0.85 (t, 9H, $^3J_{HH}$ = 8.2 Hz, SiCH$_2$C**H**$_3$, SiEt$_3$), 0.91 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.15 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.18 (overlapping d, 3H, CH(C**H**$_3$)$_2$, NHC), 1.19 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.23 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, NHC), 1.36 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.54 (overlapping d, 6H, CH(C**H**$_3$)$_2$, NHC), 2.21 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 2.72 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.00 (sept, 2H, $^3J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.29 (br. sept, 2H, C**H**(CH$_3$)$_2$, NHC), 4.44 (br. s, 1H, Ge**H**), 6.49 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.20 (d, 2H, $^3J_{HH}$ = 7.9 Hz, *m*-Ph, B^{Dipp}), 7.30 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph, B^{Dipp}), 7.39 (t, 2H, $^3J_{HH}$ = 7.8 Hz, *p*-Ph, B^{Dipp}), 7.56 (s, 4H, *p*-Ph, BArF$_{24}$), 7.72 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d$_8$-THF, 298 K): −6 (**B**ArF$_{24}$), 24 (**B**^{Dipp}) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, d$_8$-THF, 298 K): −63.4 (BAr**F**$_{24}$) ppm.

^{29}Si{^{1}H} NMR (99.3 MHz, d$_8$-THF, 298 K): 17.4 (O**Si**Et$_3$) ppm.

ESI-MS (+): Predicted: 837.5921; Found: 837.5864

Crystallographic data for [(9)H($C_4D_8OSiEt_3$)][$BArF_{24}$]:

$C_{79}H_{92}B_2F_{24}GeN_4OSi$, M_r = 1691.86, monoclinic, $P2_1/c$, a = 13.2539(2) Å, b = 23.6210(4) Å, c = 26.8839(4) Å, α = 90°, β = 91.4860(10)°, γ = 90°, V = 8413.7(2) Å^3, Z = 4, R_1 = 0.0841 (14156, I>2σ{I}), wR_2 = 0.2567 (all 17437 unique reflections).

Generation of [(IPrMe)(B^{Dipp})GeH($C_4H_8OSiEt_3$)][$BArF_{24}$], [(9)H($C_4H_8OSiEt_3$)][$BArF_{24}$]

An *in situ*-generated solution of **[(9)H($SiEt_3$)][$BArF_{24}$]** (0.0333 mmol) in THF (0.5 mL) in a J. Young's NMR tube was heated with a further excess of Et_3SiH (26.6 µL, 0.166 mmol, 5 equiv.) at 60°C for 5 d, after which time the volatiles were removed *in vacuo*, and the residue dissolved in CD_2Cl_2. ^{1}H NMR spectroscopy revealed complete conversion to the product.

Spectroscopic data for [(9)H($C_4H_8OSiEt_3$)][$BArF_{24}$]:

^{1}H NMR (400.2 MHz, CD_2Cl_2, 298 K): 0.48 (q, 6H, $^3J_{HH}$ = 8.1 Hz, SiC**H**$_2$CH$_3$, $SiEt_3$), 0.85 (t, 9H, $^3J_{HH}$ = 8.1 Hz, SiCH$_2$C**H**$_3$, $SiEt_3$), 0.91 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.09 (t, 2H, $^3J_{HH}$ = 5.9 Hz, C**H**$_2$, OCH$_2$(C**H**$_2$)$_3$Ge) [other CH_2 signals obscured due to overlap with those for CH(C**H**$_3$)$_2$], 1.15 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.18 (overlapping d, 3H, CH(C**H**$_3$)$_2$, NHC), 1.19 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.23 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, NHC), 1.36 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.51 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, NHC), 2.19 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 2.73 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.01 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.34 (m, 2H, $^3J_{HH}$ = 6.0 Hz, OC**H**$_2$), 4.31 (br. sept, 2H, C**H**(CH$_3$)$_2$, NHC), 4.46 (br. s, 1H, Ge**H**), 6.50 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.20 (dd, 2H, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 7.7 Hz, *m*-Ph, B^{Dipp}), 7.30 (dd, 2H, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 7.7 Hz, *m*-Ph, B^{Dipp}), 7.39 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *p*-Ph, B^{Dipp}), 7.57 (s, 4H, *p*-Ph, $BArF_{24}$), 7.73 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, CD_2Cl_2, 298 K): −7 (**B**ArF_{24}), 24 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 298 K): 4.8 (Si**C**H$_2$CH$_3$, $SiEt_3$), 7.0 (SiCH$_2$**C**H$_3$, $SiEt_3$), 11.1 (C4/C5-**C**H$_3$, NHC), 12.9 (**C**H$_2$, OCH$_2$(**C**H$_2$)$_3$Ge), 23.0, 23.4 (CH(**C**H$_3$)$_2$, NHC), 23.6, 24.6, 26.0, 26.7 (CH(**C**H$_3$)$_2$, B^{Dipp}), 29.0, 29.3 (**C**H(CH$_3$)$_2$, B^{Dipp}), 35.9 (**C**H$_2$, OCH$_2$(**C**H$_2$)$_3$Ge), 54.9 (**C**H(CH$_3$)$_2$, NHC), 61.7 (O**C**H$_2$), 118.0 (br. m, $^3J_{CF}$ = 3.8 Hz, *p*-Ph, $BArF_{24}$), 124.3, 124.4 (C4/C5-**C** and *m*-Ph, B^{Dipp}), 125.2 (q, $^1J_{CF}$ = 272.8 Hz, **C**F$_3$, $BArF_{24}$), 128.3 (*p*-Ph, B^{Dipp}), 129.47 (qq, $^3J_{CB}$ = 2.9 Hz, $^2J_{CF}$ = 31.5 Hz, *m*-Ph, $BArF_{24}$), 129.47 (C4/C5-**C**, NHC), 135.4

(*o*-Ph, $BArF_{24}$), 138.1 (*i*-Ph, B^{Dipp}), 146.0, 146.3 (*o*-Ph, B^{Dipp}), 148.9 ($\underline{\mathbf{C}}_{NHC}$), 162.3 (q, $^{1}J_{CB}$ = 48.6 Hz, *i*-Ph, $BArF_{24}$) ppm.

ESI-MS (+): Predicted: 829.54; Found: 829.54

4.5.2 Small molecule activation by [10][Al(OR^F)$_4$]

Generation of [(I-Me$_4$)(Ar^{Mes})GeH$_2$][Al(OR^F)$_4$], [(10)H$_2$][Al(OR^F)$_4$]

A J. Young's NMR tube containing an *in situ*-generated suspension of **[(10)$_2$][Al(OR^F)$_4$]$_2$** (0.0366 mmol) (see **3.5.2**) in C_6D_5Br (0.5 mL) was degassed via three *freeze-pump-thaw* cycles, and back-filled with an atmosphere of H_2 at room temperature. Monitoring via ^{1}H NMR spectroscopy confirmed complete conversion to the product after 7 d at room temperature. Note that in this and subsequent procedures, the molar quantities given for **[(10)$_2$][Al(OR^F)$_4$]$_2$** refer to the monomeric unit. For this and all other compounds detailed in **4.5.2**, extreme moisture-sensitivity precluded full characterising data from being obtained.

Spectroscopic data for [(10)H$_2$][Al(OR^F)$_4$]:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298K): 1.82 (s, 6H, C4/C5-C$\underline{\mathbf{H}}_3$, NHC), 1.96 (s, 12H, *o*-C$\underline{\mathbf{H}}_3$, Mes), 2.37 (s, 6H, *p*-C$\underline{\mathbf{H}}_3$, Mes), 2.85 (s, 6H, NC$\underline{\mathbf{H}}_3$, NHC), 4.54 (s, 2H, Ge$\underline{\mathbf{H}}_2$), 6.88 (s, 4H, *m*-Ph, Mes), 7.10 (overlapping d [with C_6D_5Br], 2H, *m*-Ph, C_6H_3), 7.57 (t, 1H, $^{3}J_{HH}$ = 7.5 Hz, *p*-Ph, C_6H_3) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_5Br, 298K): 8.0 (C4/C5-$\underline{\mathbf{C}}H_3$, NHC), 20.4 (*o*-$\underline{\mathbf{C}}H_3$, Mes), 21.1 (*p*-$\underline{\mathbf{C}}H_3$, Mes), 33.7 (N$\underline{\mathbf{C}}H_3$, NHC), 79.5 (br., O$\underline{\mathbf{C}}(CF_3)_3$, Al(OR^F)$_4$), 121.9 (q, $^{1}J_{CF}$ = 294.4 Hz, $\underline{\mathbf{C}}F_3$, Al(OR^F)$_4$), 128.8 (*m*-Ph, Mes), 129.0 (C4/C5-$\underline{\mathbf{C}}$, NHC), [signals for *m*- and *p*-Ph, C_6H_3 obscured by those for C_6D_5Br], 135.4 (*o*-Ph, Mes), 138.0, 138.1 (*i*- and *p*-Ph, Mes), 145.7 ($\underline{\mathbf{C}}_{NHC}$), 148.1 (*o*-Ph, C_6H_3), 154.0 (*i*-Ph, C_6H_3) ppm.

^{19}F NMR (376.5 MHz, C_6D_5Br, 298K): −74.6 (C$\underline{\mathbf{F}}_3$, Al(OR^F)$_4$) ppm.

^{27}Al NMR (104.3 MHz, C_6D_5Br, 298K): 35.4 ($\underline{\mathbf{Al}}$(OR^F)$_4$) ppm.

Generation of [(I-Me$_4$)(Ar^{Mes})GeH(NH$_2$)][Al(OR^F)$_4$], [(10)H(NH$_2$)][Al(OR^F)$_4$]

A J. Young's NMR tube containing an *in situ*-generated suspension of **[(10)$_2$][Al(OR^F)$_4$]$_2$** (0.0366 mmol) in C_6D_5Br (0.5 mL) was degassed via three *freeze-pump-thaw* cycles, and back-filled with an atmosphere of NH_3 at room temperature. Monitoring via ^{1}H NMR spectroscopy confirmed complete

conversion to the product after ca. 5 min at room temperature. Full characterising data could not be obtained due to the short-lived nature of this species.

Spectroscopic data for [(10)H(NH$_2$)][Al(OR^F)$_4$]:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298K): 0.05 (s, 2H, GeN**H**$_2$), 1.77 (s, 6H), 1.93 (s, 6H), 2.06 (s, 6H), 2.35 (s, 6H) [all either C4/C5-C**H**$_3$, NHC, or C**H**$_3$, Mes], 3.04 (s, 6H, NC**H**$_3$, NHC), 5.76 (s, 1H, Ge**H**), 6.82 (s, 2H, *m*-Ph, Mes), 6.90 (s, 2H, *m*-Ph, Mes), 7.06 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph, C_6H_3), 7.56 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-Ph, C_6H_3) ppm.

Generation of [(I-Me$_4$)(Ar^{Mes})GeH(SiEt$_3$)][Al(OR^F)$_4$], [(10)H(SiEt$_3$)][Al(OR^F)$_4$]

Et_3SiH (5.9 µL, 0.0366 mmol, 1 equiv.) was added to an *in situ*-generated suspension of **[(10)$_2$][Al(OR^F)$_4$]$_2$** (0.0366 mmol) in C_6D_5Br (0.5 mL) in a J. Young's NMR tube at room temperature. The suspension was sonicated in an ultrasonic bath for 20 min at room temperature, with the colour progressively changing from orange to yellow. After this period, ^{1}H NMR spectroscopy revealed complete conversion to the product.

Spectroscopic data for [(10)H(SiEt$_3$)][Al(OR^F)$_4$]:

^{1}H NMR (499.9 MHz, C_6D_5Br, 298K): 0.21 (m, 3H, $^{2/3}J_{HH}$ = 7.7 Hz, SiC**H**(H)CH_3, $SiEt_3$), 0.40 (m, 3H, $^{2/3}J_{HH}$ = 7.3 Hz, SiCH(**H**)CH_3, $SiEt_3$), 0.82 (t, 9H, $^3J_{HH}$ = 7.7 Hz, $SiCH_2C$**H**$_3$, $SiEt_3$), 1.73 (s, 6H, C**H**$_3$, Mes), 1.91 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.17 (s, 6H, C**H**$_3$, Mes), 2.39 (s, 6H, C**H**$_3$, Mes), 2.77 (br. s, 3H, NC**H**$_3$, NHC), 3.13 (br. s, 3H, NC**H**$_3$, NHC), 5.03 (s, 1H, Ge**H**), 6.79 (s, 2H, *m*-Ph, Mes), 6.97 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *m*-Ph, C_6H_3), 7.00 (s, 2H, *m*-Ph, Mes), 7.49 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *p*-Ph, C_6H_3) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_5Br, 298K): 4.1 (Si**C**H_2CH_3, $SiEt_3$), 7.8 ($SiCH_2$**C**H_3, $SiEt_3$), 8.2 (C4/5-**C**H_3, NHC), 20.8, 20.9, 21.0 (**C**H_3, Mes), 34.4 (N**C**H_3, NHC), 79.5 (br., O**C**$(CF_3)_3$, Al(OR^F)$_4$), 121.9 (q, $^1J_{CF}$ = 292.3 Hz, **C**F_3, Al(OR^F)$_4$), 128.7, 129.6 (*m*-Ph, Mes), 130.4 (*m*-Ph, C_6H_3), 131.3 (*p*-Ph, C_6H_3), [signal for C4/C5-**C**, NHC obscured by those for C_6D_5Br], 135.8 (*o*-Ph, Mes), 137.9 (*p*-Ph, Mes), 139.4 (*i*-Ph, Mes), 148.3 (*o*-Ph, C_6H_3), 151.8 (**C**$_{NHC}$) ppm. [signal for *i*-Ph, C_6H_3 not observed]

^{19}F NMR (376.5 MHz, C_6D_5Br, 298K): −74.6 (C**F**$_3$, Al(OR^F)$_4$) ppm.

^{27}Al NMR (104.3 MHz, C_6D_5Br, 298K): 35.4 (**Al**(OR^F)$_4$) ppm.

^{29}Si NMR (99.3 MHZ, C_6D_5Br, 298K): 11.0 (Ge**Si**Et_3) ppm.

Generation of [(I-Me$_4$)(Ar^{Mes})GeH(SiEt$_3$)][BArF$_{24}$], [(10)H(SiEt$_3$)][BArF$_{24}$]

Et_3SiH (5.9 µL, 0.0366 mmol, 1 equiv.) was added to an *in situ*-generated suspension of **[(10)$_2$][Al(OR^F)$_4$]$_2$** (0.0366 mmol) in C_6D_5Br (0.5 mL) in a J. Young's NMR tube at room temperature. The suspension was sonicated in an ultrasonic bath for 20 min at room temperature, with the colour progressively changing from orange to yellow. After this period, ^{1}H NMR spectroscopy revealed complete conversion to the product.

Spectroscopic data for [(10)H(SiEt$_3$)][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, C_6D_5Br, 298K): 0.18 (m, 3H, $^{2/3}J_{HH}$ = 7.2 Hz, SiC**H**(H)CH_3, $SiEt_3$), 0.38 (m, 3H, $^{2/3}J_{HH}$ = 7.1 Hz, SiCH(**H**)CH_3, $SiEt_3$), 0.78 (t, 9H, $^3J_{HH}$ = 7.2 Hz, $SiCH_2CH_3$, $SiEt_3$), 1.71 (s, 6H, C**H**$_3$, Mes), 1.80 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.14 (s, 6H, C**H**$_3$, Mes), 2.36 (s, 6H, C**H**$_3$, Mes), 2.74 (br. s, 3H, NC**H**$_3$, NHC), 3.05 (br. s, 3H, NC**H**$_3$, NHC), 5.00 (s, 1H, Ge**H**), 6.76 (s, 2H, *m*-Ph, Mes), 6.97 (overlapping d, 2H, $^3J_{HH}$ = 7.5 Hz, *m*-Ph, C_6H_3), 6.97 (s, 2H, *m*-Ph, Mes), 7.49 (overlapping t, 1H, *p*-Ph, C_6H_3), 7.77 (s, 4H, *p*-Ph, $BArF_{24}$), 8.36 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

Generation of [(I-Me$_4$)(Ar^{Mes})GeH(SiH$_2$Ph)][Al(OR^F)$_4$], [(10)H(SiH$_2$Ph)][Al(OR^F)$_4$]

$PhSiH_3$ (4.5 µL, 0.0366 mmol, 1 equiv.) was added to an *in situ*-generated suspension of **[(10)$_2$][Al(OR^F)$_4$]$_2$** (0.0366 mmol) in C_6D_5Br (0.5 mL) in a J. Young's NMR tube at room temperature. The suspension was sonicated in an ultrasonic bath for 20 min at room temperature, with the colour progressively changing from orange to yellow. After this period, ^{1}H NMR spectroscopy revealed complete conversion to the product. Single crystals suitable for X-ray diffraction were obtained by storage of a concentrated C_6D_5Br solution at room temperature for several days.

Spectroscopic data for [(10)H(SiH$_2$Ph)][Al(OR^F)$_4$]:

^{1}H NMR (499.9 MHz, C_6D_5Br, 298K): 1.74 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 1.82 (s, 6H, *o*-C**H**$_3$, Mes), 2.18 (s, 6H, *o*-C**H**$_3$, Mes), 2.35 (s, 6H, *p*-C**H**$_3$, Mes), 2.63 (br. s, 6H, NC**H**$_3$, NHC), 3.57 (dd, 1H, $^3J_{HH}$ = 5.3, 10.7 Hz, Ge**H**), 3.88 (d, 1H, $^3J_{HH}$ = 5.2 Hz, GeSi**H**(H)Ph), 4.91 (d, 1H, $^3J_{HH}$ = 10.7 Hz, GeSiH(**H**)Ph), 6.76 (overlapping m, 2H, *o*-Ph, PhSi), 6.76 (s, 2H, *m*-Ph, Mes), 7.00 (s, 2H, *m*-Ph, Mes), 7.01 (overlapping m, 2H, *m*-Ph, PhSi), 7.10 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph, C_6H_3), 7.19 (overlapping m [with C_6D_5Br], 1H, *p*-Ph, PhSi), 7.57 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-Ph, C_6H_3) ppm.

$^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_5Br, 298K): 7.8 (C4/C5-**C**H_3, NHC), 20.4, 20.8 (*o*-**C**H_3, Mes), 21.0 (*p*-**C**H_3, Mes), 33.7 (N**C**H_3, NHC), 79.5 (br., O**C**$(CF_3)_3$, $Al(OR^F)_4$), 121.9 (q, $^1J_{CF}$ = 291.5 Hz, **C**F_3, $Al(OR^F)_4$), 128.1, 128.2, 128.9, 129.6, 129.95, 130.02, 130.3, 131.5, 131.8 (*i*-, *m*-, *p*-Ph, PhSi, *m*-Ph, Mes, *m*-, *p*-Ph, C_6H_3, and C4/C5-**C**, NHC), 133.9 (*o*-Ph, PhSi), 135.66, 135.73 (*o*-Ph, Mes), 138.1 (*p*-Ph, Mes), 138.5 (*i*-Ph, Mes), 148.0 (*o*-Ph, C_6H_3), 148.9 (**C**$_{NHC}$) ppm. [signal for *i*-Ph, C_6H_3 not observed]

^{19}F NMR (376.5 MHz, C_6D_5Br, 298K): −74.6 (C**F**$_3$, $Al(OR^F)_4$) ppm.

^{27}Al NMR (104.3 MHz, C_6D_5Br, 298K): 35.4 (**Al**$(OR^F)_4$) ppm.

^{29}Si NMR (99.3 MHZ, C_6D_5Br, 298K): −53.3 (Ge**Si**H_2Ph) ppm.

Crystallographic data for [(10)H(SiH$_2$Ph)][Al(OR^F)$_4$]:

$C_{53}H_{45}AlF_{36}GeN_2O_4Si$, M_r = 1585.57, monoclinic, $P2_1/c$, a = 10.9874(2) Å, b = 35.9360(9) Å, c = 16.3608(4) Å, α = 90°, β = 97.997(2)°, γ = 90°, V = 6397.1(3) Å^3, Z = 4, R_1 = 0.0918 (10112, I>2σ{I}), wR_2 = 0.2816 (all 13275 unique reflections).

Generation of [(I-Me$_4$)(Ar^{Mes})GeH(Bpin)][Al(OR^F)$_4$], [(10)H(Bpin)][Al(OR^F)$_4$]

HBpin (5.3 µL, 0.0366 mmol, 1 equiv.) was added to an *in situ*-generated suspension of **[(10)$_2$][Al(OR^F)$_4$]$_2$** (0.0366 mmol) in C_6D_5Br (0.5 mL) in a J. Young's NMR tube at room temperature. The suspension was sonicated in an ultrasonic bath for 20 min at room temperature, with the colour progressively changing from orange to yellow. After this period, ^1H NMR spectroscopy revealed complete conversion to the product.

Spectroscopic data for [(10)H(Bpin)][Al(OR^F)$_4$]:

^1H NMR (400.2 MHz, C_6D_5Br, 298K): 1.16 (s, 6H, C4/C5-C**H**$_3$, Bpin), 1.21 (s, 6H, C4/C5-C**H**$_3$, Bpin), 1.81 (s, 6H, C4/C5-C**H**$_3$, NHC), 1.94 (s, 6H, C**H**$_3$, Mes), 2.09 (s, 6H, C**H**$_3$, Mes), 2.37 (s, 6H, C**H**$_3$, Mes), 3.00 (s, 6H, NC**H**$_3$, NHC), 4.50 (s, 1H, Ge**H**), 6.81 (s, 2H, *m*-Ph, Mes), 6.93 (s, 2H, *m*-Ph, Mes), 7.04 (d, 2H, $^3J_{HH}$ = 8.0 Hz, *m*-Ph, C_6H_3), 7.53 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph, C_6H_3) ppm.

$^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_5Br, 298K): 22 (**B**pin) ppm.

$^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_5Br, 298K): 8.2 (C4/C5-**C**H_3, NHC), 20.77, 20.82, 21.1 (**C**H_3, Mes), 24.4, 24.9 (C4/C5-**C**H_3, Bpin), 34.4 (N**C**H_3, NHC), 79.5 (br., O**C**$(CF_3)_3$, $Al(OR^F)_4$), 86.2 (C4/C5-**C**, Bpin), 121.9 (q, $^1J_{CF}$ = 293.4 Hz, **C**F_3, $Al(OR^F)_4$), 128.5, 128.7, 128.9 (*m*-Ph, Mes and C_6H_3, and C4/C5-**C**, NHC), 131.4 (*p*-Ph,

C_6H_3), 135.7, 135.8 (*o*-Ph, Mes), 137.7 (*p*-Ph, Mes), 138.7 (*i*-Ph, Mes), 148.0 (**C**$_{NHC}$), 148.3 (*o*-Ph, C_6H_3) ppm. [signal for *i*-Ph, C_6H_3 not observed]

^{19}F NMR (376.5 MHz, C_6D_5Br, 298K): −74.6 (C**F**$_3$, Al(OR^F)$_4$) ppm.

^{27}Al NMR (104.3 MHz, C_6D_5Br, 298K): 35.4 (**Al**(OR^F)$_4$) ppm.

Reaction of [(10)H(Bpin)][Al(OR^F)$_4$] with PhOH

PhOH (31.0 μl, 1.77 M solution in THF, 0.0549 mmol, 1.5 equiv.) was added to a suspension of **[(10)H(Bpin)][Al(OR^F)$_4$]** (0.0366 mmol) in C_6D_5Br (0.5 mL) in a J. Young's NMR tube at room temperature. The suspension was sonicated in an ultrasonic bath for 20 min at room temperature. After this period, ^{1}H NMR spectroscopy revealed complete conversion to **[(10)H$_2$][Al(OR^F)$_4$]** and PhOBpin,[76] which could be identified by comparison of ^{1}H and ^{11}B NMR resonances (reported in C_6D_5Br in **2.3.9**).

4.5.3 Reactivity of [9][BArF$_{24}$] towards trimethylsilylazide and trimethylsilylazidomethane

Generation of [(d$_8$-THF)(IPrMe)(B^{Dipp})Ge(NSiMe$_3$)][BArF$_{24}$], [(d$_8$-THF)9(NSiMe$_3$)][BArF$_{24}$]

Me_3SiN_3 (4.4 μL, 0.0333 mmol, 1 equiv.) was added to a solution of **[9(d$_8$-THF)][BArF$_{24}$]** (0.050 g, 0.0333 mmol) in d$_8$-THF (0.5 mL) in a J. Young's NMR tube at room temperature. The solution slowly changed colour from yellow to colourless, and ^{1}H NMR spectroscopy revealed complete conversion to the product after 2 h at room temperature. No further change was seen upon addition of excess Me_3SiN_3.

Spectroscopic data for [(d$_8$-THF)9(NSiMe$_3$)][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, d$_8$-THF, 298 K): 0.07 (s, 9H, Si(C**H**$_3$)$_3$, NSiMe$_3$), 1.05 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.16 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.18 (overlapping d, 3H, CH(C**H**$_3$)$_2$, NHC), 1.20 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.27 (br. d, 3H, CH(C**H**$_3$)$_2$, NHC), 1.43 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.48 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, NHC), 2.33 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.87 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 3.05 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.49 (br. m, 2H, C**H**(CH$_3$)$_2$, NHC), 6.70 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.30-7.46 (m, 6H, Ph, B^{Dipp}), 7.58 (s, 4H, *p*-Ph, BArF$_{24}$), 7.80 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d$_8$-THF, 298 K): −6 (**B**ArF$_{24}$), 23 (**B**^{Dipp}) ppm.

$^{13}C\{^1H\}$ NMR (100.6 MHz, d_8-THF, 298 K): 0.3 (Si(**C**H_3)$_3$, $NSiMe_3$), 10.9 (C4/C5-**C**H_3, NHC), 21.7, 22.1 (CH(**C**H_3)$_2$, NHC), 23.3, 23.5, 26.4, 27.0 (CH(**C**H_3)$_2$, B^{Dipp}), 30.0, 30.1 (**C**H$(CH_3)_2$, B^{Dipp}), 55.1 (**C**H$(CH_3)_2$, NHC), 118.4 (br. m, $^3J_{CF}$ = 3.6 Hz, *p*-Ph, $BArF_{24}$), 125.2 (*m*-Ph, B^{Dipp}), 125.72 (q, $^1J_{CF}$ = 271.8 Hz, **C**F_3, $BArF_{24}$), 125.72 (C4/C5-**C**, B^{Dipp}), 130.21 (qq, $^3J_{CB}$ = 3.6 Hz, $^2J_{CF}$ = 31.0 Hz, *m*-Ph, $BArF_{24}$), 130.24 (*p*-Ph, B^{Dipp}), 132.6 (C4/C5-**C**, NHC), 135.8 (*o*-Ph, $BArF_{24}$), 138.6 (*i*-Ph, B^{Dipp}), 144.9 (**C**$_{NHC}$), 146.6, 146.9 (*o*-Ph, B^{Dipp}), 163.0 (q, $^1J_{CB}$ = 47.7 Hz, *i*-Ph, $BArF_{24}$) ppm.

$^{19}F\{^1H\}$ NMR (376.5 MHz, d_8-THF, 298 K): −63.4 (BAr**F**$_{24}$) ppm.

Isolation of [(IPrMe)(B^{Dipp})GeN_3{$N(SiMe_3)_2$}][$BArF_{24}$], [(9)N_3{$N(SiMe_3)_2$}][$BArF_{24}$]

Me_3SiN_3 (10.0 µL, 0.0760 mmol, 2.3 equiv.) was added to a solution of **[(9)$_2$][$BArF_{24}$]$_2$** (0.050 g, 0.0333 mmol) in fluorobenzene (1 mL) at room temperature. The solution gradually changed colour from yellow to colourless over 2 h at room temperature. A small number of single crystals (0.010 g, 0.00586 mmol, 17.6%) suitable for X-ray diffraction were obtained by layering this fluorobenzene solution with hexane, followed by storage at room temperature for several days.

Spectroscopic data for [(9)N_3{$N(SiMe_3)_2$}][$BArF_{24}$]:

^1H NMR (400.2 MHz, d_8-THF, 298 K): 0.11 (s, 18H, Si(C**H**$_3$)$_3$, N(SiMe$_3$)$_2$), 1.07-1.68 (overlapping m, 36H, CH(C**H**$_3$)$_2$, B^{Dipp} and NHC), 2.41 (br. s, 6H, C4/C5-C**H**$_3$, NHC), 3.12 (br. sept, 4H, C**H**$(CH_3)_2$, B^{Dipp}), 4.84 (br. m, 1H, C**H**$(CH_3)_2$, NHC), 5.33 (br. m, 1H, C**H**$(CH_3)_2$, NHC), 6.58 (br. s, 2H, C4/C5-**H**, B^{Dipp}), 7.37-7.45 (overlapping m, 6H, Ph, B^{Dipp}), 7.57 (s, 4H, *p*-Ph, $BArF_{24}$), 7.79 (s, 8H, *o*-Ph, $BArF_{24}$) ppm.

ESI-MS (+): Predicted: 843.4891; Found: 843.4938

Crystallographic data for [(9)N_3{$N(SiMe_3)_2$}][$BArF_{24}$]:

$C_{75}H_{86}B_2F_{24}GeN_8Si_2$, M_r = 1705.90, triclinic, P-1, a = 15.1805(3) Å, b = 16.3185(2) Å, c = 17.4996(3) Å, α = 99.7280(10)°, β = 99.556(2)°, γ = 101.4720(10)°, V = 4096.97(12) Å^3, Z = 2, R_1 = 0.0633 (14407, I>2σ{I}), wR_2 = 0.1845 (all 16959 unique reflections).

Generation of [(IPrMe)(B^{Dipp})Ge=CH($SiMe_3$)][$BArF_{24}$], [9{CH($SiMe_3$)}][$BArF_{24}$]

Me_3SiCHN_2 (16.6 µL, 2 M solution in hexanes, 0.0333 mmol, 1 equiv.) was added to a solution of **[9(d_8-THF)][$BArF_{24}$]** (0.050 g, 0.0333 mmol) in d_8-THF (0.5 mL) in a J. Young's NMR tube at room temperature.

The solution immediately changed colour from yellow to colourless, and ^{1}H NMR spectroscopy revealed complete conversion to the product (within ca. 5 min at room temperature).

Spectroscopic data for [9{CH(SiMe$_3$)}][BArF$_{24}$]:

^{1}H NMR (400.2 MHz, d$_8$-THF, 298 K): −0.31 (s, 9H, Si(C**H**$_3$)$_3$, CHSiMe$_3$), 1.14 (d, 6H, $^{3}J_{HH}$ = 7.1 Hz, CH(C**H**$_3$)$_2$, NHC), 1.17 (d, 12H, $^{3}J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.21 (d, 12H, $^{3}J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.46 (d, 6H, $^{3}J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$, NHC), 2.33 (s, 6H, C4/C5-C**H**$_3$, NHC), 2.93 (sept, 4H, $^{3}J_{HH}$ = 6.8 Hz, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.48 (sept, 2H, $^{3}J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$, NHC), 6.04 (s, 1H, GeC**H**), 6.73 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.30-7.45 (m, 6H, Ph, B^{Dipp}), 7.58 (s, 4H, *p*-Ph, BArF$_{24}$), 7.80 (s, 8H, *o*-Ph, BArF$_{24}$) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, d$_8$-THF, 298 K): −6 (**B**ArF$_{24}$), 24 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, d$_8$-THF, 298 K): 0.9 (Si(**C**H$_3$)$_3$, CHSiMe$_3$), 10.4 (C4/C5-**C**H$_3$, NHC), 21.5, 21.8 (CH(**C**H$_3$)$_2$, NHC), 24.0, 25.8 (CH(**C**H$_3$)$_2$, B^{Dipp}), 29.7 (**C**H(CH$_3$)$_2$, B^{Dipp}), 57.8 (**C**H(CH$_3$)$_2$, NHC), 118.4 (br. m, $^{3}J_{CF}$ = 3.6 Hz, *p*-Ph, BArF$_{24}$), 125.2, 125.4 (C4/C5-**C** and *m*-Ph, B^{Dipp}), 125.7 (q, $^{1}J_{CF}$ = 273.0 Hz, **C**F$_3$, BArF$_{24}$), 130.0 (*p*-Ph, B^{Dipp}), 130.2 (qq, $^{3}J_{CB}$ = 3.6 Hz, $^{2}J_{CF}$ = 32.2 Hz, *m*-Ph, BArF$_{24}$), 132.1 (C4/C5-**C**, NHC), 135.8 (*o*-Ph, BArF$_{24}$), 138.6 (*i*-Ph, B^{Dipp}), 146.8 (*o*-Ph, B^{Dipp}), 150.1 (**C**$_{NHC}$), 150.3 (Ge**C**H), 163.0 (q, $^{1}J_{CB}$ = 50.1 Hz, *i*-Ph, BArF$_{24}$) ppm.

^{19}F{^{1}H} NMR (376.5 MHz, d$_8$-THF, 298 K): −63.4 (BAr**F**$_{24}$) ppm.

Isolation of [(IPrMe)(B^{Dipp})Ge(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$], [9(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$]

A small number of single crystals suitable for X-ray diffraction were obtained by layering a concentrated fluorobenzene solution of **[9{CH(SiMe$_3$)}][BArF$_{24}$]** with hexane, followed by storage at −25°C for several days. Due to the low yield and unreproducible nature of this synthesis, full characterising data could not be obtained.

Crystallographic data for [9(OH)(CH$_2$SiMe$_3$)][BArF$_{24}$]:

$C_{73}H_{80}B_2F_{24}GeN_4OSi$, M_r = 1607.71, monoclinic, $P2_1/n$, a = 22.5863(6) Å, b = 13.4829(3) Å, c = 27.6125(8) Å, α = 90°, β = 112.522(3)°, γ = 90°, V = 7767.5(4) Å^3, Z = 4, R_1 = 0.0702 (11404, I>2σ{I}), wR_2 = 0.2194 (all 16087 unique reflections).

Isolation of [(IPrMe)(B^{Dipp})Ge(μ_2-O)$_2$Ge(B^{Dipp})(IPrMe)][$BArF_{24}$]$_2$, [9(μ_2-O)$_2$9][$BArF_{24}$]$_2$

A small number of single crystals suitable for X-ray diffraction were obtained by layering a concentrated THF solution of **[(THF)9(NSiMe$_3$)][$BArF_{24}$]** with hexane, followed by storage at room temperature for several days. Due to the low yield and unreproducible nature of this synthesis, full characterising data could not be obtained.

Crystallographic data for [9(μ_2-O)$_2$9][$BArF_{24}$]$_2$:

$C_{147}H_{148}B_4F_{49}Ge_2N_8O_2$, M_r = 3178.15, triclinic, P-1, a = 17.0627(4) Å, b = 17.6442(6) Å, c = 28.9146(7) Å, α = 95.590(2)°, β = 103.783(2)°, γ = 106.679(3)°, V = 7969.0(4) Å^3, Z = 2, R_1 = 0.0734 (22847, I>2σ{I}), wR_2 = 0.2298 (all 32907 unique reflections).

4.6 References

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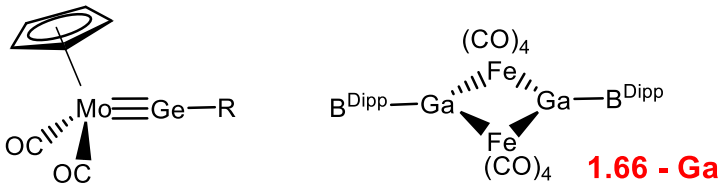
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Chapter V

Boryl-Substituted Germanium-Metal Bonds

5.1 Introduction

Inspired by the widespread use of metal-carbon multiply-bonded systems in catalysis,[1] recent interest in multiple bonds between germanium and transition metals[2,3] has led to the synthesis of germylynes featuring M≡Ge triple bonds involving metals such as* chromium,[4] molybdenum,[4–11] tungsten,[4,6–10,12–16] rhenium,[17] and niobium.[18] These have primarily been supported by terphenyl ligands,[4,5,8,9,18] with examples supported by Cp*,[6,13,14] amido,[11] trisyl ($C(SiMe_3)_3$)[10,12,15] and silyl[19] ligands also known. The two major synthetic routes to such germylynes (salt metathesis and addition/elimination)[2,3] both utilise two-coordinate Ge^{II} chlorogermylenes as the source of the [RGe] fragment (with dehydrogenation of Ge^{IV} hydrides a less frequently used strategy).[12,15]



R = Ar^{Mes}, Ar^{Tripp}, $N(SiMe_3)(Ar^*)$, $C(SiMe_3)_3$, SiR_3

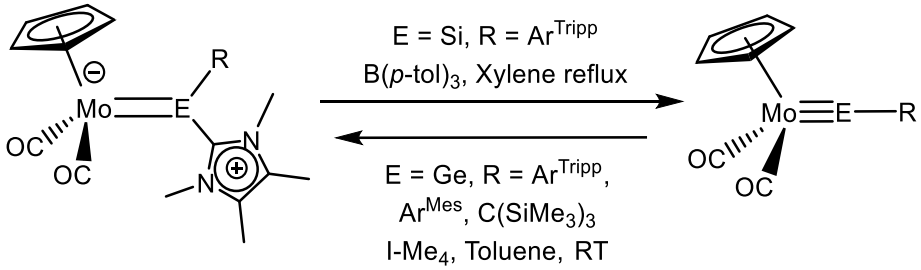
Figure 5.1: Examples of molybdenum germylynes (left) and a rare example of a boryl-substituted main group-transition metal bond (right)

Boryl groups, despite their increasing use in other areas of group 14 chemistry, have yet to be applied to the stabilisation of group 14-transition metal bonds.† Within main group chemistry more generally, there is only one study by Jones regarding the synthesis of compounds featuring boryl-substituted bonds between aluminium/gallium and iron (**1.66**).[20] This in turn is due to a lack of boryl-substituted low-valent main group halides (with no (B^{Dipp})EX species being known for group 14 elements).

*Theses[19,25] and publications[18] from the Filippou group refer to germylynes involving metals including titanium, tantalum, nickel, iron, and ruthenium, however all of these compounds are unpublished (and only "private communication" or theses not available electronically[58,59] are provided as reference).

†A search of the Cambridge Structural Database reveals the only M-Ge-B linkages [M = transition metal] to be in complexes featuring germaborate cluster ligands.[60–67]

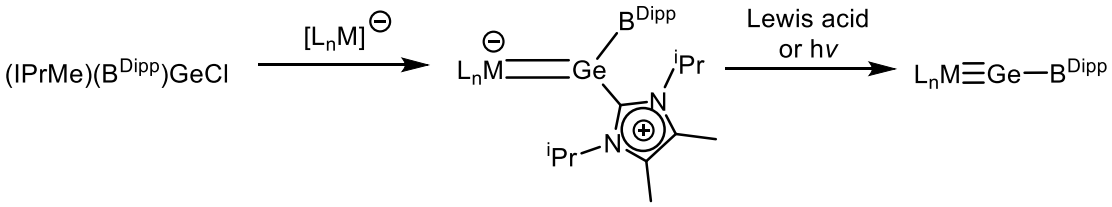
In silicon chemistry, a similar paucity of Si^{II} precursors (with any ligand) initially hindered the synthesis of triply-bonded systems. However, an innovative solution to this problem was developed by Filippou, who utilised an NHC-coordinated terphenyl chlorosilylene to synthesise a zwitterionic molybdenum silylene, from which the NHC could be abstracted using a Lewis acidic borane to generate the first example of a silylyne complex.[21] Such a route has subsequently been applied to synthesise a silyl-substituted germylyne,[19] while analogous zwitterionic germylenes have been synthesised in the reverse sense by the addition of NHCs to germylynes featuring trisyl and terphenyl ligands.[10]



Scheme 5.1: Abstraction of an NHC to generate a silylyne, and NHC addition to germylynes

5.2 Project aims

The boryl-substituted chlorogermylene **2.31** utilised in the synthesis of a germylium-ylidene in Chapter 3 represents a possible entry point to the first boryl-substituted germanium-transition metal bonds. Through reaction with anionic transition metal fragments, the [(IPrMe)(B^{Dipp})Ge] moiety could then be assimilated through M-Ge bond formation.



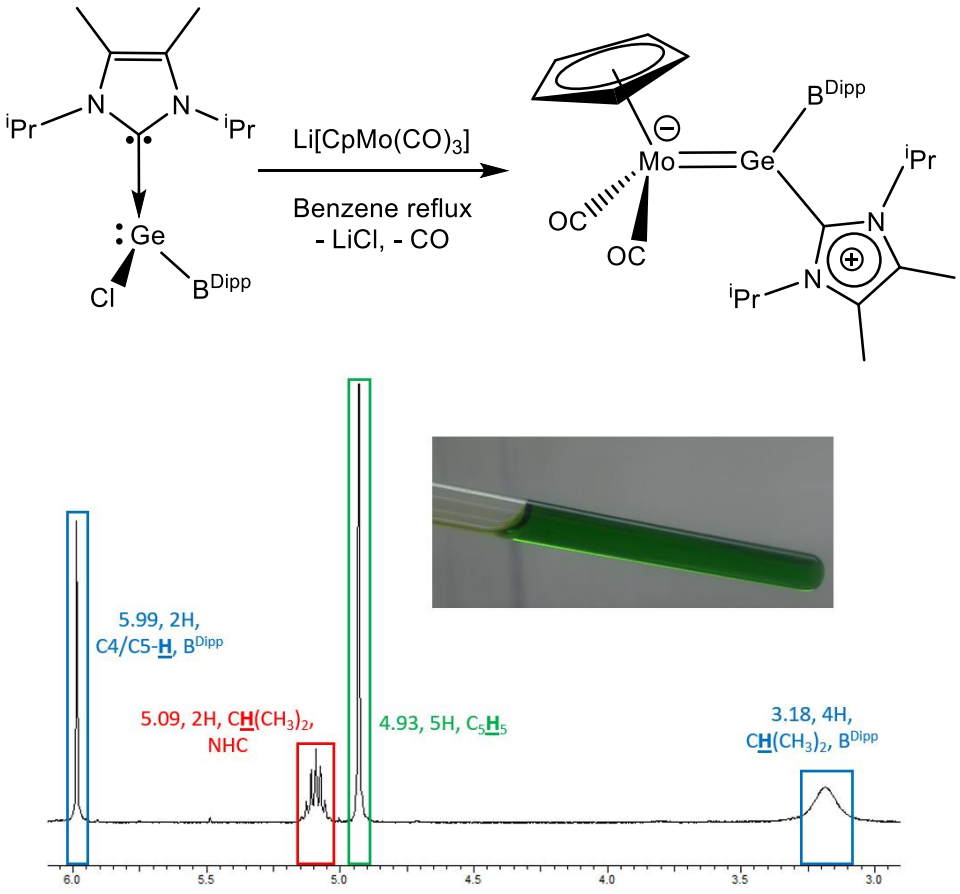
Scheme 5.2: Proposed synthetic route to boryl-substituted germylynes

A variety of interesting reactivities could then be envisaged; for example, following the method of Filippou, the NHC could then be abstracted by a borane or other Lewis acid to generate a germylyne; alternatively, photolysis/thermolysis or removal otherwise of a carbonyl ligand from the metal could potentially trigger migration of the NHC from germanium to M.

Group 6 is a logical starting point given the widespread previous use of these elements in compounds featuring multiple bonds to germanium, thereby enabling comparison with other ligand systems. Subsequently, it would be of interest to investigate the synthesis of germylynes involving metals for which previous attempts (with other supporting ligands) have failed;* for example, efforts to synthesise compounds featuring iron-germanium multiple bonds from the corresponding ferrio-germylenes have proven unsuccessful when using Mes*,[22] $CH(SiMe_3)_2$,[23] Ar^{Mes},[24] or Ar^{Tripp} [24,25] substituents at germanium.

5.3 Results and discussion

5.3.1 Boryl-substituted germanium-molybdenum complexes



*Scheme 5.3: Synthesis of (green) germylene complex **16**, and an excerpt from its ^{1}H NMR spectrum. Chemical shifts in ppm. Resonances due to Ph of B^{Dipp}, C4/5-C**H**$_3$ of NHC, and CH(C**H**$_3$)$_2$ of NHC and B^{Dipp} are not shown.*

Upon combination of Li[CpMo(CO)$_3$] and **2.31** in THF, toluene or benzene, the suspension turns green. This change occurs slowly at room temperature, but more rapidly on heating, with the optimal conditions being found to be refluxing in benzene for 2 h. Removal of the solvent *in vacuo* and extraction of the resulting residue with hexane, followed by concentration and storage overnight at

−25°C, allowed the isolation of striking green crystals (albeit in extremely poor yield, 11.8%). Although these were not suitable for X-ray crystallography, large green single crystals suitable for structural analysis could be grown by slow evaporation of a concentrated Et_2O solution at room temperature. These were revealed to contain the complex {$CpMo(CO)_2$}Ge(B^{Dipp})(IPrMe) (**16**), featuring the first example of a structurally characterised boryl-substituted bond between germanium and molybdenum.

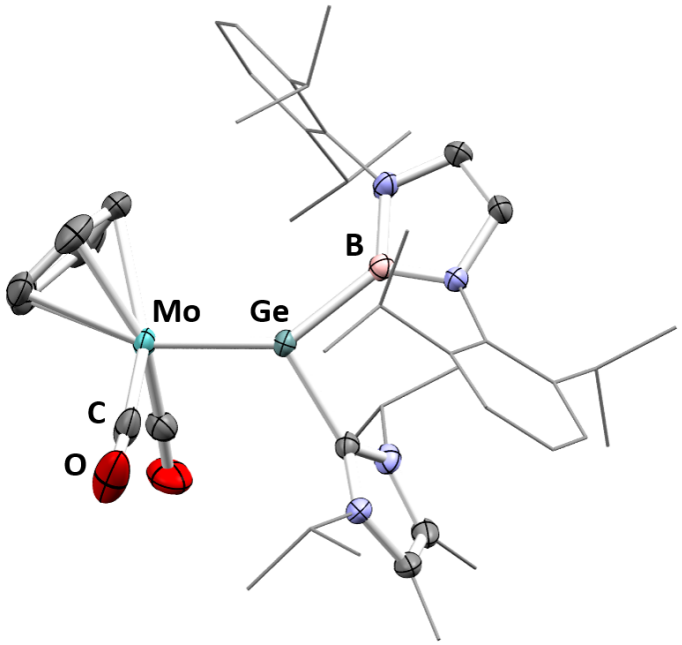


*Figure 5.2: Structure of **16**. For clarity, B^{Dipp} Dipp and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Mo-Ge: 2.4020(4), Ge-B: 2.098(3), Ge-C_{NHC}: 2.069(3), Mo-C_{CO}: 1.942(3) (L), 1.924(3) (R), C-O: 1.160(3) (L), 1.174(4) (R), Mo-C_{Cp}: 2.342(2), 2.343(4), 2.352(4), 2.361(3), 2.367(4) (mean: 2.353, Mo-$Cp_{centroid}$: 2.031), Mo-Ge-B: 141.97(8), Mo-Ge-C_{NHC}: 118.96(8), B-Ge-C_{NHC}: 98.2(1), C_{CO}-Mo-Ge: 92.92(9) (L), 87.00(9) (R), Mo-C_{CO}-O: 175.2(3) (L), 177.4(3) (R)*

The depiction of **16** in Scheme 5.3, with a double bond and a zwitterionic structure, can be justified by (i) the planar geometry at germanium (sum of angles = 359.1°), and (ii) the alignment of the [Ge(B^{Dipp})(IPrMe)] fragment and the [$CpMo(CO)_2$] unit (displacement of $Cp_{centroid}$ from the B-Ge-Mo plane: 0.083 Å).[26] This description is also consistent with an expected formally 18 valence electron molybdenum centre. Alternatively, compound **16** could be represented as a metallo-germylene with a Mo-Ge single bond, with donation of the germanium lone pair to the molybdenum centre. The Mo-Ge bond length of 2.4020(4) Å and Mo-Ge-B angle of 141.97(8)° can be compared to a series of analogous molybdenum complexes synthesised by Filippou,[10] featuring terphenyl and trisyl ligands in combination with the I-Me_4 NHC (see Table 5.1). The slightly longer Mo-Ge bond and more acute Mo-

Ge-R angle in this example can be explained by the bulkier NHC N-substituent (though this Mo-Ge bond is shorter than those in several other complexes featuring N-heterocyclic[27–29] or bis(alkyl) germylenes).[30] The NMR spectra of **16** are similar to those for {CpMo(CO)$_2$}Ge{C(SiMe$_3$)$_3$}(I-Me$_4$) (**5.1**), in terms of the signal due to the Cp ligand in the ^{1}H (4.93 vs. 5.34 ppm for **5.1**) and ^{13}C spectra (88.0 vs. 89.6 ppm), and that for the CO ligands in the ^{13}C spectrum (244.5 vs. 243.7 ppm).[10]

[for {CpMo(CO)$_2$}Ge(R)(NHC)]			Mo-Ge (Å)	Mo-Ge-R (°)	*ν*(CO) (solid state)	*ν*(CO) (toluene)
R		NHC			(cm^{-1})	(cm^{-1})
16	B^{Dipp}	IPrMe	2.4020(4)	141.97(8)	1863, 1777	1942, 1858, 1803, 1735
5.1	C(SiMe$_3$)$_3$	I-Me$_4$	2.4004(5)	142.8(1)	1847, 1770	1861, 1785
5.2	Ar^{Mes}	I-Me$_4$	2.3924(2)	142.28(4)	N/A	1854, 1783
5.3	Ar^{Tripp}	I-Me$_4$	2.4015(5)	148.76(9)	N/A	1862, 1786
1.39	C(SiMe$_3$)$_3$	(none)	2.2805(2)	169.60(3)	1916, 1865	1930, 1868

*Table 5.1: Structural metrics and IR data for **16** as compared to other germylene complexes, and a trisyl-substituted germylyne (**1.39**) for comparison*

The solid state IR (ATR) spectrum of **16** features sharp carbonyl stretching peaks at 1863 and 1777 cm^{-1}, which are similar to those measured for **5.1** (1847 and 1770 cm^{-1})[10] and consistent with the solid state structure determined by X-ray crystallography. Intriguingly, however, the IR spectrum measured for **16** in toluene solution is very different from that measured in the solid state, featuring four broad signals at 1942, 1858, 1803 and 1735 cm^{-1}. By contrast, the spectra for **5.1** show only a slight shift in the two (still sharp) bands for solution phase samples, as compared to the solid state (peaks at 1861 and 1785 cm^{-1} in toluene). The terphenyl-containing compounds **5.2** and **5.3** (for which IR data is unfortunately not reported in the solid state) give rise to IR absorptions in toluene at 1854 and 1783 cm^{-1}, and 1862 and 1786 cm^{-1}, respectively.[10]

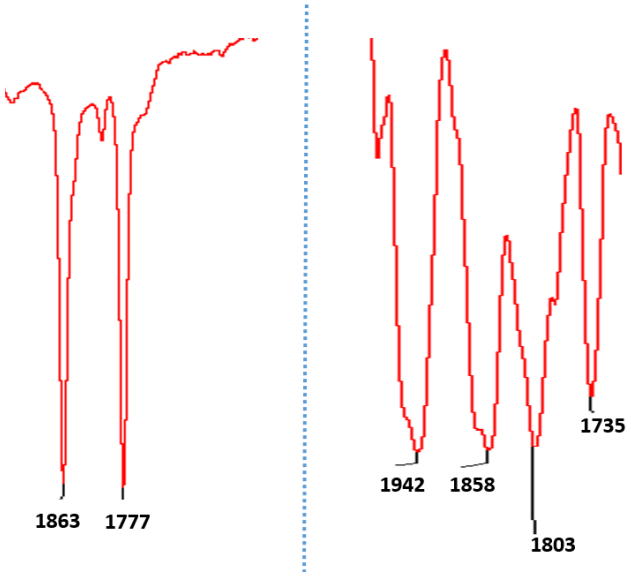
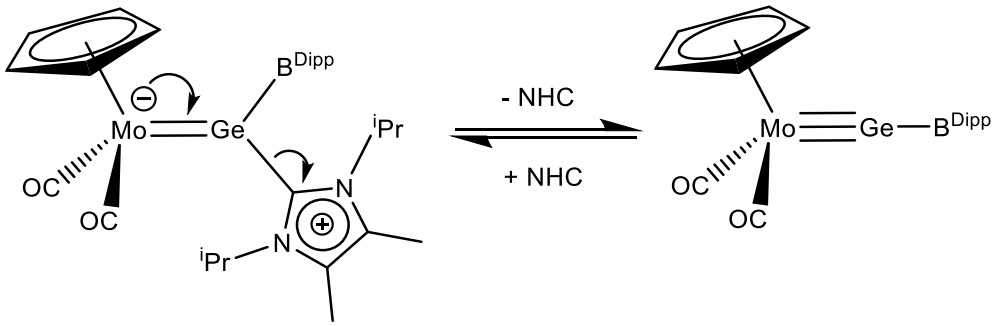


*Figure 5.3: The carbonyl stretching region of the IR spectra of **16** in the solid state (left) and in toluene (right)*

This differing pattern of bands in solution and the solid state implies that the structure of **16** in solution is different from that in the solid state, and, given the number of bands observed, suggests that more than one species is present in solution. The peak at 1942 cm^{-1} is in a region similar to the highest wavenumber absorption measured for germylyne species featuring Mo≡Ge triple bonds (e.g. for $Cp(CO)_2Mo{\equiv}GeR$: 1930 cm^{-1} for R = $C(SiMe_3)_3$; 1939 cm^{-1} for R = Ar^{Tripp}, both in toluene).[10] In such cases, the lack of an additional neutral donor at germanium results in more π-donation from molybdenum to germanium, so correspondingly less to the carbonyl ligands and a higher measured carbonyl stretching frequency. Thus, it is proposed in the case of compound **16** that there is reversible dissociation of the NHC in solution, and an equilibrium with an *in situ*-formed germylyne at room temperature (Scheme 5.4).

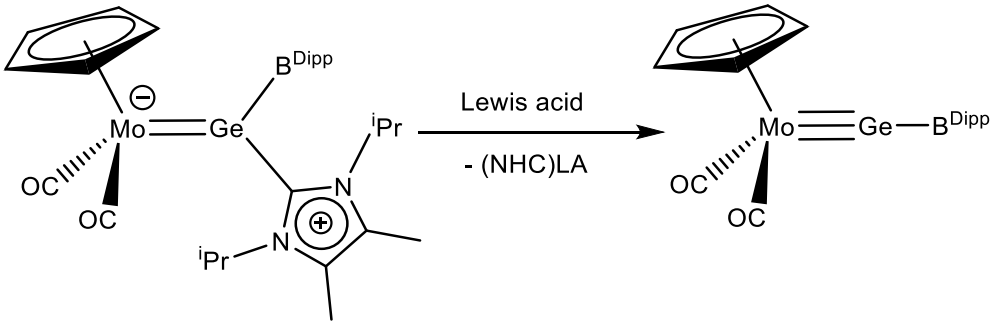


*Scheme 5.4: Proposed equilibrium between **16** and in situ-formed germylyne*

Presumably the stronger donor boryl substituent favours this loss of the NHC donor to a greater extent than for the related terphenyl and trisyl containing systems. Intriguingly, calculations by Filippou

suggest a relatively small dissociation energy for the NHC from {CpMo(CO)$_2$}Si(Ar^{Tripp})(I-Me$_4$), such that dissociation might be observed at elevated temperature.[21] There is also the additional effect of the bulkier NHC here as compared to Filippou's examples, which may relatively favour dissociation in this case. Consistent with this idea, Scheschkewitz has recently reported that I-Me$_4$ is able to replace IPrMe in (CO)$_4$Fe{SiMe$_2$(IPrMe)} and (CO)$_4$Fe{GeMe$_2$(IPrMe)}.[31]

In the case of **16**, this dissociation is presumably a very rapid process, such that only one species is observed by NMR while a mixture is seen by IR, reflecting the relative timescales of these spectroscopic techniques. Variable temperature NMR studies in d_8-toluene (from 173 K to 375 K) do not appear to evidence the presence of free NHC at either low or high temperature. From a kinetic perspective, lowering the temperature might be expected to "freeze out" the dynamic process, however thermodynamically this disfavours dissociation on entropic grounds, while conversely at high temperature dissociation would be more thermodynamically favourable but exchange might be too rapid to allow observation of distinct sets of NMR resonances for the two species. However, the shift in certain resonances on changing the temperature is indicative of a potential change in the position of equilibrium; for instance, the signal arising from the Cp ligand shifts from 4.99 ppm at 173 K to 4.77 ppm at 375 K.



*Scheme 5.5: Proposed NHC-abstraction from **16** to give a germylyne*

The logical next step was to try to isolate this potential germylyne, by abstraction of the NHC. Addition of the frequently used Lewis acid B(C$_6$F$_5$)$_3$ to a sample of **16** in C$_6$D$_6$ at room temperature resulted in an immediate colour change to red, however this red species could unfortunately not be isolated and characterised. Filippou has reported that addition of B(C$_6$F$_5$)$_3$ to a similar silicon complex resulted in

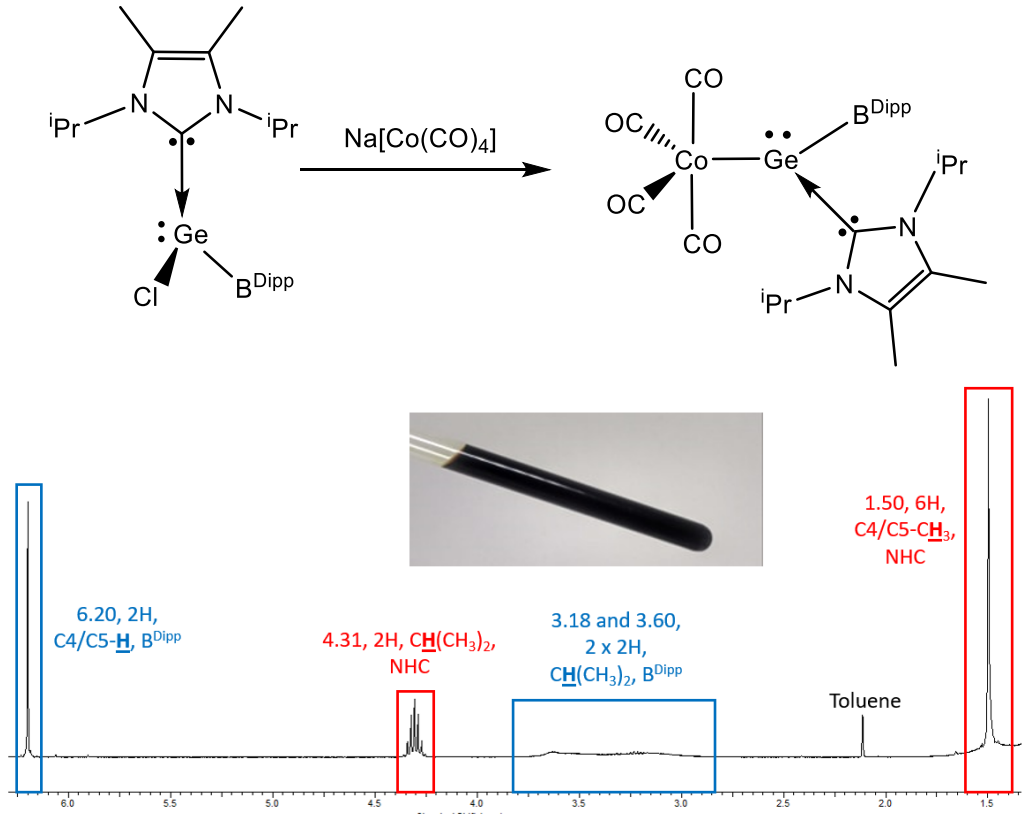
electrophilic attack of the borane at the electron-rich Cp ring, also resulting in a red compound,[25] suggesting alternative reaction pathways may be a problem for this borane. Furthermore, Braunschweig has reported that boron reagents can react with metal carbonyl complexes at the oxygen of the carbonyl group.[32,33] In addition, it may be this borane is too bulky to form an adduct with this NHC. Hence, a less electrophilic and less bulky borane was chosen. Upon addition of BPh_3 to a sample of **16** in C_6D_6 at room temperature, the solution turned a lighter green. In NMR measurements acquired as quickly as possible after mixing, the new resonances for the NHC ligand, and a sharp new peak at ca. −8 ppm in the ^{11}B NMR spectrum, are consistent with formation of the known adduct (IPrMe)BPh_3.[34] New resonances also appear in the ^{1}H NMR spectrum corresponding to the boryl and Cp ligands. Interestingly, analogous NHC abstraction by B(*p*-tol)$_3$ from {CpMo(CO)$_2$}Si(Ar^{Tripp})(I-Me$_4$) is reported to require heating at ca. 145°C, giving credence to the idea of more facile NHC-dissociation in this case.[21]

Intriguingly, the singular new Cp signal at 4.16 ppm gradually disappears over the course of 3 d at room temperature, with the concomitant appearance of two new Cp resonances at 4.08 and 4.22 ppm (each integrating as 2 protons with respect to the boryl/NHC peaks); no apparent resonance corresponding to the fifth Cp proton could be identified. Corresponding ^{13}C NMR resonances can be identified at 83.6 and 88.6 ppm. Synchronously, the new signals corresponding to the boryl ligand also reduce in intensity, with fresh resonances growing in (e.g. a broad C4/5-**H** backbone signal at 6.30 ppm being replaced by a sharp one at 6.37 ppm). Given the low barrier to rotation of Cp rings coordinated to transition metals,[35,36] the desymmetrisation of the Cp signals observed here is potentially indicative of some kind of onward reaction of the putative transient germylyne involving the Cp ring. Although there is an example from Filippou of an *in situ*-generated silyl-substituted germylyne undergoing dimerisation,[19] in that case the Cp* NMR resonances remained equivalent, suggesting that something more complex is occurring in this case. Unfortunately, however, the very similar solubilities of this product and (IPrMe)BPh_3 precluded its isolation and crystallographic characterisation.

The use of alternative Lewis acids was thus attempted. The addition of $GaCl_3$ to a sample of **16** in C_6D_6 resulted in the immediate appearance of a new major NHC-containing species in the ^1H NMR spectrum; this is presumably (IPrMe)$GaCl_3$, which is known, though its ^1H NMR spectrum is not reported in C_6D_6.[37] However, the multitude of resonances for the other ligands, as well as the purple colour of the solution, implied further reaction with $GaCl_3$, though such a product could not be isolated. CO_2 has previously been employed to remove NHCs,[38] as the formed adducts tend to have conveniently low solubility. Treatment of a toluene solution of **16** with CO_2 resulted in the formation of precipitate, which could be removed by filtration. However, ^1H NMR analysis of the filtrate revealed only the presence of $B^{Dipp}OH$. $(B^{Dipp})Li(thf)_2$ is reported to form $B^{Dipp}OH$ upon reaction with CO_2,[39] and there is precedent for CO_2 inserting into bonds between tin and boryl groups.[40] An alternative strategy towards the isolation of a germylyne was photolysis of **16**, which could potentially lead to loss of a carbonyl group and migration of the NHC from germanium to molybdenum; however, following irradiation of a solution of **16** in C_6D_6 with 254 nm UV radiation, the only observed boryl-containing product was $B^{Dipp}H$.

Attempts to synthesise the corresponding tungsten complex for comparison proved unsuccessful, with the attempted reaction of **2.31** and $Na[CpW(CO)_3]$ only leading to minor conversion to a new product even after prolonged heating, consistent with the general observation that molybdenum carbonyls are usually more reactive than those of tungsten[4,41] (and indeed chromium, hence it was not thought worthwhile to synthesise the corresponding chromium metallate).

5.3.2 Boryl-substituted germanium-cobalt complexes



*Scheme 5.6: Synthesis of cobalt germylene complex **17**, and excerpt from its ^{1}H NMR spectrum. Chemical shifts in ppm. Resonances due to Ph of B^{Dipp}, and $CH(C\underline{\mathbf{H}}_3)_2$ of NHC and B^{Dipp} are not shown.*

Following the chemistry outlined above with group 6 metal carbonylate anions, analogous chemistry was explored with other d-block nucleophiles. Reaction of $Na[Co(CO)_4]$ and **2.31** in toluene led to a slow darkening of the colour of the solution at room temperature (to a deep red) and the concomitant production of precipitate. After 2 d, this solution could be filtered and concentrated, with storage at −25°C overnight yielding a crop of deep red crystals. X-ray diffraction analysis revealed these to contain $(CO)_4CoGe(B^{Dipp})$(IPrMe) (**17**), featuring the first example of a structurally characterised boryl-substituted bond between germanium and cobalt (Figure 5.4). Compound **17** crystallised with two independent molecules in the unit cell; one of these molecules is displayed in Figure 5.4, and the structural metrics for both molecules are given below.

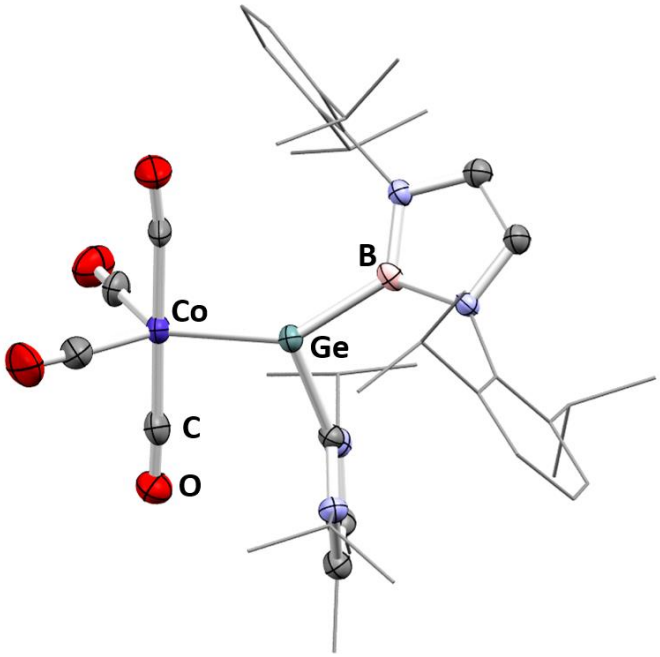


*Figure 5.4: Structure of **17**. For clarity, B^{Dipp} Dipp and NHC ^{i}Pr and Me groups shown in wireframe format. Key bond lengths (Å) and angles (°): Co-Ge: 2.269(2)/2.2666(9), Ge-B: 2.058(6)/2.070(5), Ge-C_{NHC}: 2.054(4)/2.048(4), Co-C_{CO}: 1.831(6)/1.824(4) (ax., top), 1.839(6)/1.824(6) (ax., bottom), 1.822(7)/1.807(5) (eq., left), 1.820(6)/1.801(8) (eq., right), C-O: 1.153(7)/1.159(5) (ax., top), 1.131(7)/1.155(7) (ax., bottom), 1.14(1)/1.143(6) (eq., left), 1.129(6)/1.16(1) (eq., right), Co-Ge-B: 143.6(1)/145.3(1), Co-Ge-C_{NHC}: 110.5(1)/109.9(1), B-Ge-C_{NHC}: 104.7(2)/102.7(2), C_{CO}-Co-Ge: 90.7(2)/90.3(2) (ax., top), 88.9(2)/88.2(2) (ax., bottom), 133.7(2)/133.3(2) (eq., left), 119.1(2)/120.4(2) (eq., right), Co-C_{CO}-O: 172.4(6)/172.3(5) (ax., top), 177.2(6)/177.2(6) (ax., bottom), 177.5(7)/177.7(6) (eq., left), 176.1(6)/174.3(6) (eq., right)*

The geometry at the cobalt centre in **17** is trigonal bipyramidal as expected (τ = 0.76/0.73),[‡] with germanium occupying an equatorial site. The depiction in terms of a singly-bonded metallo-germylene structure as per Scheme 5.6 is consistent with an expected formally 18 valence electron cobalt centre. The Co-Ge bond length (2.269(2)/2.2666(9) Å) is shorter than the majority of bonds between germanium and cobalt, though shorter bonds are known (see comparison in Table 5.2). Noticeable in the structure of **17** are the distortions arising due to the proximity of the bulky Dipp groups of the boryl group to the bulky cobalt carbonyl fragment; thus, there is a marked deviation from linearity in both the C4/5 centroid-C_{NHC}-Ge angle of the NHC (163.9°/163.9°) and in the Co-C_{CO}-O angle of the carbonyl moiety adjacent to the boryl group (172.4(6)°/172.3(5)°, whereas other such angles are in the range 176.1(6)°-177.5(7)°/174.3(6)°-177.7(6)°). Furthermore, the M-Ge-B angle is larger than for the molybdenum case (143.6(1)°/145.3(1)° vs. 141.97(8)°). This greater steric congestion is also reflected

[‡]τ (geometry index/structural parameter) is a means of quantifying the geometry of five-coordinate centres, from 0 (perfectly square pyramidal) to 1 (perfectly trigonal bipyramidal).[68,69]

in the ^{1}H NMR spectrum, which, for example, features two resonances corresponding to the boryl C**H**$(CH_3)_2$ isopropyl environment, as opposed to one in **16**. The IR spectrum of **17** features four peaks in the carbonyl stretching region (1996, 1922, 1880, 1851 cm^{-1}), as expected given the approximate C_{2v} symmetry.[42]

$\{(CO)_4Co\}_2GePh_2$ [43]	2.4674(5)	$(CO)_7Co_2\{\kappa^1Ge\text{-}Ge(PhC(N^tBu)_2)(HMDS)\}$[44]	2.2938(8)
$[NEt_4]_2[(CO)_{24}Co_{10}Ge_2]$[45]	2.3463(13)	**17**	**2.269(2)/ 2.2666(9)**
$(CO)_5(\mu_2\text{-}CO)Co_2\{\mu_2\text{-}\kappa^2Ge,N\text{-}Ge(PhC(N^iPr)_2)(HMDS)\}$[46]	2.2983(4)	$\{(CO)_3CoGe[N(SiMe_2{}^iPr)_2]_2\}_2$[47]	2.262(1)
$(CO)_6Co_2\{\kappa^1Ge\text{-}Ge(PhC(N^tBu)_2)(HMDS)\}_2$[44]	2.2959(6)	$CpCo\{\kappa^2Ge\text{-}Ge(PhC(N^tBu)_2)\{(C_5H_4)_2Fe\}Ge(PhC(N^tBu)_2)\}$[48]	2.1967(6)

*Table 5.2: Exemplar Co-Ge bond lengths (Å) as compared to **17** (shortest given if the compound features more than one) {HMDS = $N(SiMe_3)_2$}*

5.3.3 Boryl-substituted germanium-iron complexes

Combination of one equivalent of the nucleophilic iron carbonylate $Na[CpFe(CO)_2]$ and **2.31** in C_6D_6 leads to the slow formation of a new product at room temperature, as revealed by new ligand resonances in the ^{1}H NMR spectrum. Ca. 60% conversion was achieved after 2 weeks at room temperature, with concomitant colour change to purple. Interestingly, a potentially analogous complex $\{CpFe(CO)_2\}Ge(Ar^{Tripp})(I\text{-}Me_4)$ is also reported to be purple.[25] However, this product could not be isolated, primarily because larger-scale preparation was frustrated by significant amounts of decomposition (to $B^{Dipp}H$), to an extent that increased with temperature. Attempts to use the more nucleophilic iron compound $Na[Cp^*Fe(CO)_2]$ also failed, with product formation proving to be considerably slower, presumably due to steric factors.

Given the slow rate of reaction with stoichiometric $Na[CpFe(CO)_2]$, the use of an excess was investigated. Addition of 3 equivalents to a solution of **2.31** in C_6D_6 resulted in a broad, uninterpretable ^{1}H NMR spectrum (possibly due to the presence of paramagnetic impurities), with a change of colour to dark red. Following removal of the solvent *in vacuo*, extraction with hexane and storage at −25°C produced a small crop of deep red crystals suitable for X-ray diffraction. These were revealed to contain

the complex {CpFe(CO)$_2$}$_2$(B^{Dipp})GeH (**18**), featuring the first example of a structurally characterised boryl-substituted bond between germanium and iron (Figure 5.5).

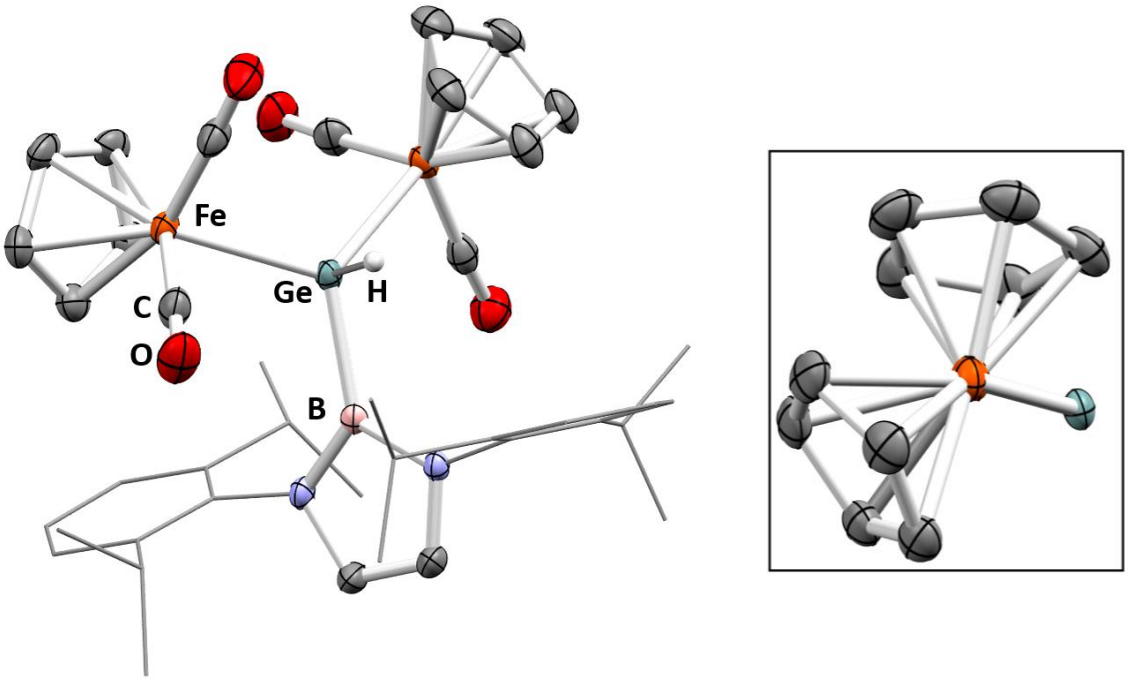
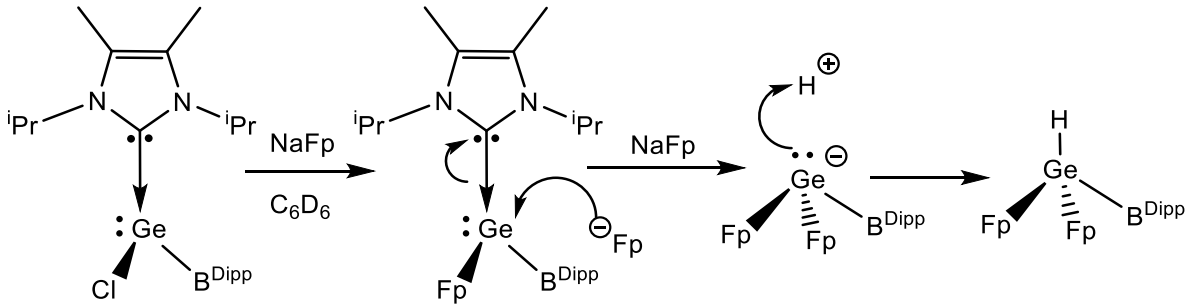


*Figure 5.5: Structure of **18** (L) and view along the Fe-Fe vector illustrating the relative disposition of Cp groups (R). For clarity, hydrogen atoms (other than Ge**H**) omitted, and B^{Dipp} Dipp groups shown in wireframe format (L), and all groups other than Cp omitted (R). Key bond lengths (Å) and angles (°): Fe-Ge: 2.4724(5) (L), 2.4877(6) (R), Ge-B: 2.095(2), Fe-C$_{CO}$: 1.753(4) (L,L), 1.748(2) (L,R), 1.748(3) (R,L), 1.744(2) (R,R), C-O: 1.148(4) (L,L), 1.156(3) (L,R), 1.155(4) (R,L), 1.160(3) (R,R), Fe-C$_{Cp}$: 2.108(3), 2.105(4), 2.115(3), 2.120(3), 2.115(2) (mean: 2.113) (L), 2.119(3), 2.117(2), 2.111(3), 2.101(3), 2.106(3) (mean: 2.111) (R), Fe-Ge-B: 116.86(6) (L), 117.25(6) (R), C$_{CO}$-Fe-Ge: 82.7(1) (L,L), 84.86(9) (L,R), 94.2(1) (R,L), 90.2(1) (R,R), Fe-C$_{CO}$-O: 176.7(3) (L,L), 177.3(2) (L,R), 174.9(3) (R,L), 174.6(3) (R,R) [where, for example, (L,R) indicates the right carbonyl group on the left iron atom, as depicted above]*

Potentially, the formation of this product proceeds via initial salt metathesis to generate {CpFe(CO)$_2$}Ge(B^{Dipp})(IPrMe), followed by attack of another [CpFe(CO)$_2$]$^-$ moiety (with concomitant loss of the NHC), to give Na[{CpFe(CO)$_2$}$_2$(B^{Dipp})Ge]. The resulting germanium-centred anion, substituted by three strongly donating moieties, would be expected to be extremely basic,[49] and so be capable of deprotonating, for instance, the solvent or liberated NHC, to form the observed hydride product. The attack of [CpFe(CO)$_2$]$^-$ (or indeed other anionic nucleophiles) at a germylene with bulky substituents in a non-salt metathesis reaction is quite unusual,[50,51] and is likely favoured in this case by the entropic offset of the loss of the NHC as an independently stable leaving group. In a related example, Rivard reported the isolation of a small amount of [IDippH][Na{Ge(OSiMe$_3$)$_3$}$_2$] from the reaction of NaOSiMe$_3$ and (IDipp)GeCl$_2$, potentially also proceeding via nucleophile-induced NHC-ejection.[52]



*Scheme 5.7: Formation of compound **18** (Fp = {CpFe(CO)$_2$})*

The structure of **18** features an almost planar arrangement of the boryl and {CpFe(CO)$_2$} groups about the germanium centre (sum of angles at germanium between these ligands = 349.5°), due to the extreme steric demands of these ligands and the much smaller profile of the hydride ligand. The Fe-Ge distances (2.4724(5) Å and 2.4877(6) Å, mean = 2.480 Å) are predictably longer than in other examples of Ge^{IV} centres coordinated by two {CpFe(CO)$_2$} substituents, and even longer than those in the majority of ferrio-germylenes, with the exception of a bulky 6-membered NacNac-supported example (see Table 5.3). Compared with the two other known bis-{CpFe(CO)$_2$} complexes,[53,54] which have a cis-orientation of the Cp rings on the same side of the Fe-Ge bonds relative to one another, the Cp rings in this case are trans-orientated (dihedral angle between the Cp least squares planes: 45.6°), presumably due to the sterically demanding ancillary ligand at germanium.

{CpFe(CO)$_2$}$_2$Ge(N$_3$)$_2$[54]	2.342(1)	{CpFe(CO)$_2$}$_6$Ge$_6$[55]	2.3998(6)
{CpFe(CO)$_2$}$_2$GeCl$_2$[53]	2.357(4)	{CpFe(CO)$_2$}Ge{^{t}BuC(NDipp)$_2$}[56]	2.4415(11)
{CpFe(CO)$_2$}Ge(Ar^{Tripp})[24]	2.3747(8)	**18**	**2.480 (mean)**
{CpFe(CO)$_2$}Ge(Ar^{Dipp})[24]	2.3790(4)	{CpFe(CO)$_2$}Ge[CH{CMe(NDipp)}$_2$][57]	2.4961(17)

*Table 5.3: Exemplar Fe-Ge bond lengths (Å) in compounds containing the {CpFe(CO)$_2$} moiety as compared to **18** (longest given if the compound features more than one)*

5.4 Conclusions

In this chapter, efforts to use (IPrMe)(B^{Dipp})GeCl (**2.31**) as a precursor for the formation of the first complexes featuring boryl-substituted germanium-metal bonds have been described. Thus, the green complex {$CpMo(CO)_2$}Ge(B^{Dipp})(IPrMe) (**16**) could be made as the first such molybdenum example, with IR data indicating a potentially unique equilibrium with the corresponding NHC-free germylyne in solution, as a result of the strongly electron-donating boryl group. Unfortunately, various attempts to remove the NHC in a preparative sense did not result in the isolation of the free germylyne. The deep red complex $(CO)_4$CoGe(B^{Dipp})(IPrMe) (**17**) could be synthesised using a similar protocol as the first cobalt example, with its structure exhibiting distortions due to the bulk of the boryl group. Though the putative iron complex {$CpFe(CO)_2$}Ge(B^{Dipp})(IPrMe) eluded isolation, the red diiron system {$CpFe(CO)_2$}$_2$(B^{Dipp})GeH (**18**) could be made as the first boryl-substituted Fe-Ge containing compound. These compounds evidence the general principle of this synthetic route, which could in the future be applied towards the synthesis of further group 14-metal bonds featuring boryl or other ligands. However, given the sluggish pace of these reactions, which led to unsuccessful reactions at worst and poor yields at best, further modification is necessary to optimise synthetic viability. Unpublished work by Filippou[25] suggests the replacement of carbonyls by phosphines in anionic transition metal fragments (e.g. use of Li[$CpMo(CO)_2(PMe_3)$]) increases the yield of such reactions due to both an enhanced nucleophilicity and also because of the more facile elimination of PMe_3 compared to CO, and hence such a strategy seems sensible (as does use of a less bulky germanium precursor).

5.5 Synthesis and characterisation of novel compounds

Synthesis of {$CpMo(CO)_2$}GeB^{Dipp}(IPrMe), 16

Li[$CpMo(CO)_3$] (0.075 g, 0.296 mmol) and (IPrMe)(B^{Dipp})GeCl (0.200 g, 0.296 mmol) were combined in benzene (40 mL) at room temperature, and the solution was heated to reflux for 2 h, quickly turning green in colour. The solvent was then removed *in vacuo*, and the resulting green residue extracted with hexane (2 x 15 mL); the filtrate was concentrated to incipient crystallisation, and stored at −25°C overnight, to yield 0.030 g (0.0350 mmol, 11.8%) of a green crystalline solid that could be isolated by

filtration. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated Et_2O solution in a λ-tube at room temperature.

Spectroscopic data for 16:

^{1}H NMR (400.2 MHz, C_6D_6, 298 K): 0.79 (br. d, 6H, CH(C**H**$_3$)$_2$, NHC), 1.16 (br. d, 15H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.27 (v. br. m, 9H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.58 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, NHC), 1.63 (s, 6H, C4/C5-C**H**$_3$, NHC), 3.18 (br. m, 4H, C**H**(CH$_3$)$_2$, B^{Dipp}), 4.93 (s, 5H, C$_5$**H**$_5$), 5.09 (sept, 2H, $^3J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$, NHC), 5.99 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.10-7.22 (overlapping m, 6H, Ph, B^{Dipp}) ppm.

^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6, 298 K): 35 (**B**^{Dipp}) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): 10.5 (C4/C5-**C**H$_3$, NHC), 21.2, 22.6 (CH(**C**H$_3$)$_2$, NHC), 24.5, 24.8, 26.1 (CH(**C**H$_3$)$_2$, B^{Dipp}), 29.0 (**C**H(CH$_3$)$_2$, B^{Dipp}), 53.2 (**C**H(CH$_3$)$_2$, NHC), 88.0 (**C**$_5$H$_5$), 122.2 (C4/C5-**C**, B^{Dipp}), 124.1 (*m*-Ph, B^{Dipp}), 126.0 (C4/C5-**C**, NHC), 127.9 (*p*-Ph, B^{Dipp}), 141.1 (*i*-Ph, B^{Dipp}), 147.6 (*o*-Ph, B^{Dipp}), 174.6 (**C**$_{NHC}$), 244.5 (**C**O) ppm.

Elemental microanalysis: found (calc. for $C_{44}H_{61}BGeMoN_4O_2$): C 62.06 (61.64)%, H 7.35 (7.17)%, N 6.37 (6.53)%

Crystallographic data for 16:

$C_{44}H_{61}BGeMoN_4O_2$, M_r = 857.30, triclinic, P-1, a = 9.8942(4) Å, b = 12.6373 (6) Å, c = 18.4205 (8) Å, α = 85.073 (4)°, β = 88.397 (4)°, γ = 69.207(4)°, V = 2145.25(17) Å^3, Z = 2, R_1 = 0.0324 (7100, I>2σ{I}), wR_2 = 0.0816 (all 8849 unique data).

Synthesis of (CO)$_4$CoGe(B^{Dipp})(IPrMe), 17

Na[Co(CO)$_4$] (0.057 g, 0.296 mmol) and (IPrMe)(B^{Dipp})GeCl (0.200 g, 0.296 mmol) were combined in toluene (20 mL), and stirred at room temperature for 2 d. The resulting deep red solution was filtered from a small amount of precipitate, and the filtrate then concentrated to incipient crystallisation; storage at −25°C overnight resulted in a crop of deep red crystals, which could be isolated by filtration for a yield of 0.147 g (0.181 mmol, 61.2%). These crystals were suitable for X-ray diffraction.

Spectroscopic data for 17:

^{1}H NMR (400.2 MHz, C_6D_6, 298 K): 0.72 (d, 6H, $^3J_{HH}$ = 7.1 Hz, CH(C**H**$_3$)$_2$, NHC), 1.09 (v. br. m, 6H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.20 (v. br. m, 18H, CH(C**H**$_3$)$_2$, B^{Dipp}), 1.23 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$, NHC), 1.50 (s, 6H, C4/C5-

C**H**$_3$, NHC), 3.18 (br. m, 2H, C**H**$(CH_3)_2$, B^{Dipp}), 3.60 (br. m, 2H, C**H**$(CH_3)_2$, B^{Dipp}), 4.31 (sept, 2H, $^3J_{HH}$ = 7.0 Hz, C**H**$(CH_3)_2$, NHC), 6.20 (s, 2H, C4/C5-**H**, B^{Dipp}), 7.11-7.21 (overlapping m, 6H, Ph, B^{Dipp}) ppm.

$^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6, 298 K): 34 (**B**^{Dipp}) ppm.

$^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 298 K): 10.4 (C4/C5-**C**H_3, NHC), 20.8, 21.7 (CH(**C**$H_3)_2$, NHC), 24.0, 26.4 (CH(**C**$H_3)_2$, B^{Dipp}), 29.1 (**C**$H(CH_3)_2$, B^{Dipp}), 54.2 (**C**$H(CH_3)_2$, NHC), 122.8 (C4/C5-**C**, B^{Dipp}), 124.0, 124.2, 124.9 (br., *m*-Ph, B^{Dipp}), 127.0 (C4/C5-**C**, NHC), [signal for *p*-Ph, B^{Dipp} obscured by that for C_6D_6], 140.4 (*i*-Ph, B^{Dipp}), 145.5, 147.6 (*o*-Ph, B^{Dipp}), 171.9 (**C**$_{NHC}$), 231.3 (br., **C**O), 239.6 (**C**O) ppm.

Crystallographic data for 17:

$C_{41}H_{56}BCoGeN_4O_4$, M_r = 811.22, monoclinic, $P2_1/c$, a = 22.9495(7) Å, b = 18.6975(3) Å, c = 22.3065(7) Å, α = 90°, β = 119.057(4)°, γ = 90°, V = 8367.0(5) Å^3, Z = 8, R_1 = 0.0515 (13684, I>2σ{I}), wR_2 = 0.1338 (all 17277 unique data).

Isolation of {CpFe(CO)$_2$}$_2$(B^{Dipp})GeH, 18

Na[$CpFe(CO)_2$] (0.044 g, 0.222 mmol, 3 equiv.) and (IPrMe)(B^{Dipp})GeCl (0.050 g, 0.0740 mmol) were combined in C_6D_6 (0.5 mL) in a J. Young's NMR tube at room temperature, resulting in a slow colour change to red. After storage for 1 week at room temperature, the solvent was removed *in vacuo*, and the resulting residue extracted with hexane (2 x 5 mL); following concentration, the filtrate was stored at −25°C for several months to yield a small number of red crystals suitable for X-ray diffraction. Due to the low yield and unreproducible nature of this synthesis, full characterising data could not be obtained.

Crystallographic data for 18:

$C_{40}H_{47}BFe_2GeN_2O_4$, M_r = 814.89, triclinic, P-1, a = 10.5738(3) Å, b = 10.7749(3) Å, c = 19.0458(4) Å, α = 98.781(2)°, β = 100.188(2)°, γ = 113.948(3)°, V = 1890.11(10) Å^3, Z = 2, R_1 = 0.0355 (7461, I>2σ{I}), wR_2 = 0.0970 (all 7910 unique data).

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Chapter VI

Conclusions and future work

6.1 Conclusions and future work

This thesis has explored the use of boryl, terphenyl and amido ligands in a variety of interesting areas of low-valent germanium chemistry.

In Chapter 3, several chlorogermylenes, and from these germanium cations, could be synthesised. The first isolable germylium-ylidenes featuring boryl, terphenyl, primary amido, and borylamido ligands were all structurally characterised. This breadth of ligands utilised in stabilising such low-valent, electrophilic species inevitably led to a wide variety of interesting structures. For instance, concerning terphenyl-substituted cations, subtle variation in ligand steric bulk resulted in either dimeric or monomeric structures, and in the latter case aryl or anagostic interactions could be observed. Though attempts in this work to vary the ligand steric bulk (of the NHC) in the case of boryl systems was less successful, this could be attempted in future work by increasing the steric bulk of the boryl group (a boryllithium incorporating Tripp groups has been synthesised within the Aldridge group).[1]

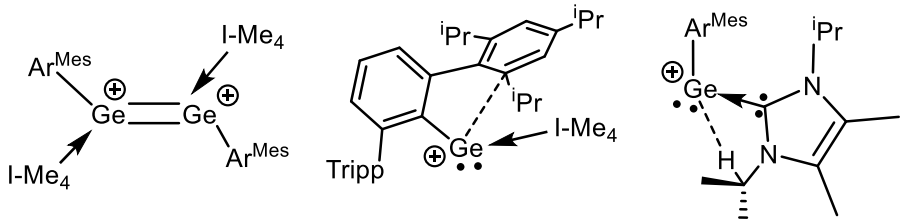


Figure 6.1: Novel structural features of the germylium-ylidenes ***[(10)$_2$][BArF$_{24}$]$_2$, [11][BArF$_{24}$]*** *and* ***[12][BArF$_{24}$]*** *(counteranions omitted)*

Some minor forays were made into the use of further ligand types; though no novel germanium compounds could be isolated featuring these, they are nevertheless interesting enough to merit future work (Figure 6.2). Bulkier, alkyl-substituted silyl ligands[2] would be more appropriate choices than $Si(SiMe_3)_3$ given the presumed migration that complicated the attempted synthesis of silyl-substituted cations in this study (**6.1**). NHCs featuring backbone-appended WCAs have been previously investigated within the Aldridge group (albeit only in transition metal chemistry),[3–5] and offer the possibility of expanding the small current number of zwitterionic germanium cations (**6.2**).[6–10] An

aluminyl system has led to fascinating results within the Aldridge group,[11–13] and its use as a ligand in germanium chemistry would be a natural evolution in increasing electropositivity from reactive boron-[14] and zinc-substituted[15] germylenes (**6.3**). A related project in the group is currently exploring germylium-ylidenes stabilised by NHC-tethered amido and alkoxide ligands,[16,17] with the idea that the tether might encourage reductive elimination; the use of other anionic donors as part of such tethered systems would also be fascinating (**6.4**).

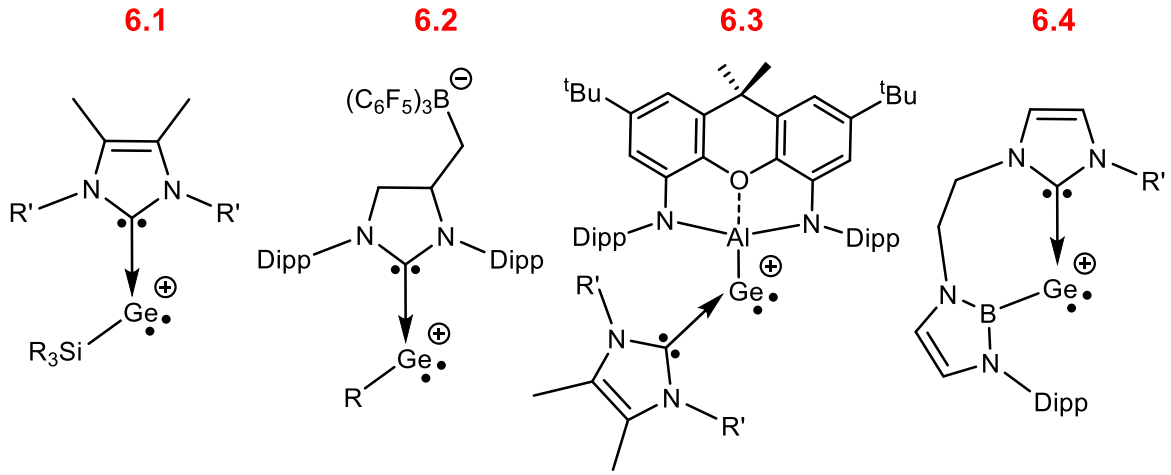


*Figure 6.2: Suggested germylium-ylidenes for future synthesis (counteranion omitted for **6.1**, **6.3** and **6.4**)*

The extension of this chemistry to other members of group 14 would also be of interest; though terphenyl-substituted cations have been explored for the cases of silicon,[18–22] tin[23–25] and lead,[26] boryl-substituted examples featuring these elements would be extremely novel (**6.5,** Figure 6.3). Furthermore, isoelectronic group 13 (Ar^{Tripp})E (E = Ga, In, Tl) species have been made featuring terphenyl ligands[27–29] (though not boryl groups),[30] however little reactivity was reported;[31] potentially, combination with NHCs may foster a greater propensity towards small molecule activation and multiple bond formation (**6.6**).[32–36]

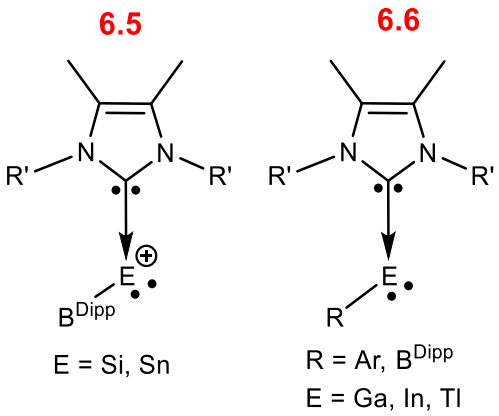


*Figure 6.3: Suggested synthetic targets featuring other main group elements (counteranion omitted for **6.5**)*

In Chapter 4, the reactivity of germylium-ylidenes was explored. The ready activation of protic, hydridic and apolar E-H bonds was demonstrated, primarily by a boryl-substituted cation, though those with terphenyl substituents provided comparison. As well as this aptitude for oxidative addition, cationic systems demonstrated novel onward reactivity following small molecule activation as a result of their charge, namely elimination in the case of ammonia, and reaction with water/alcohols/THF in the case of silanes and boranes. Attempts towards the formation of multiple bonds led to novel boryl-substituted germylium hydroxide, azide and μ-oxo dimer species. Attempted reactions with unsaturated substrates (e.g. CO, N_2O, alkynes etc.) were mainly frustrated by the extreme moisture-sensitivity of the cationic species; hence, a somehow more robust system would be desirable to enable the exploration of this facet of potential reactivity, in which interesting, but limited, results have been seen for germylene systems.[37–39] With a view to utilising the novel reactivity observed here in catalysis, a less sensitive system whose synthesis was more scalable would also be desirable. In an alternative strategy for multiple bond formation, metathesis with (IPrMe)(B^{Dipp})GeCl (**2.31**) was attempted, mainly unsuccessfully with NaPCO towards analogues of various systems featuring germanium-phosphorus bonds,[10,40–42] and this and other possibilities would be interesting for further exploration.

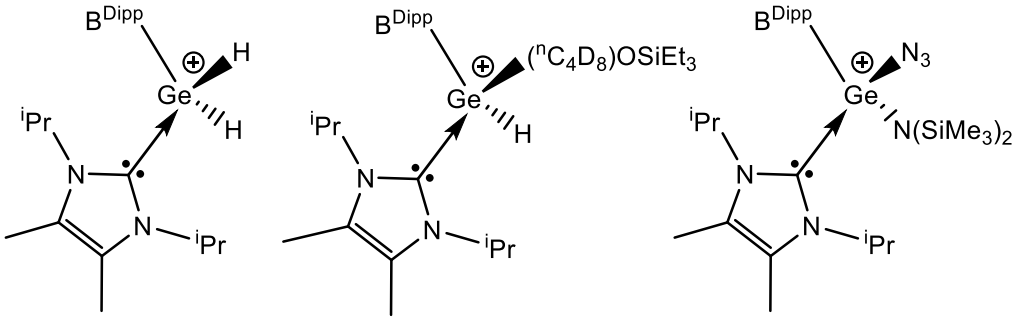


*Figure 6.4: Ge^{IV} products accessed via reactions of the germylium-ylidene **[9][BArF$_{24}$]** (counteranion omitted)*

In Chapter 5, the use of **2.31** to synthesise the first examples of compounds featuring metal-germanium bonds substituted by boryl groups was explored, and success was achieved in the case of molybdenum, cobalt, and iron, though unfortunately the first example of a boryl-substituted germylyne could not be isolated. Silylene/stannylene transfer to $Ni(COD)_2$ has previously been demonstrated,[43,44] but with no analogous reports for germylenes, and hence attempts were made here (unsuccessfully). This and other metals would be interesting for future exploration (box, Figure 6.5). In general, the studies in this area were hindered by low yields, suggesting a modification in approach is necessary; unpublished work by Filippou suggests increased yields can be achieved in metathesis reactions through the use of phosphine-substituted transition metal precursors (e.g. $Li[CpMo(CO)_2(PMe_3)]$ rather than $Li[CpMo(CO)_3]$),[45] and so such a strategy in future work would be sensible.

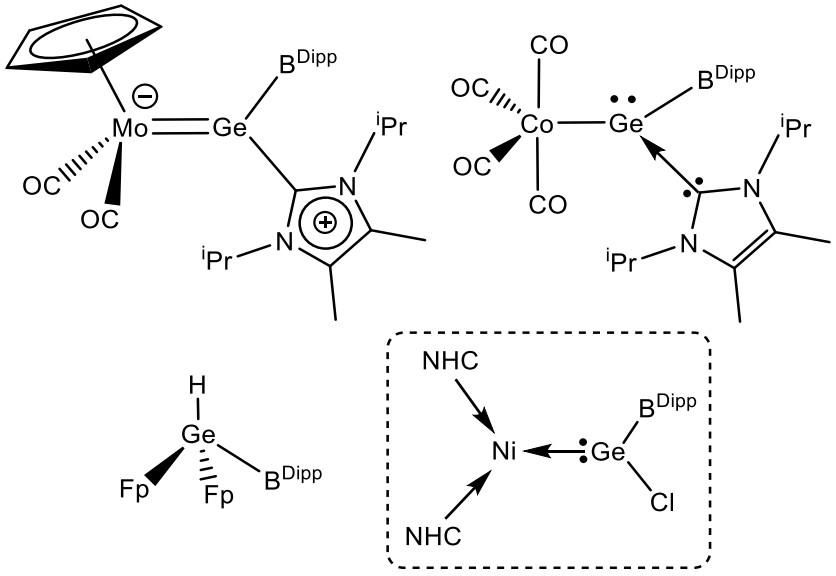


Figure 6.5: Metal-germanium complexes synthesised in this work (Fp = {$CpFe(CO)_2$}), and a targeted system involving nickel (box)

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