

A stable heavier group 14 analogue of vinylidene

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Abstract

Vinylidene ($\text{H}_2\text{C}=\text{C}$) is a member of the family of compounds of composition CH , (and isomeric with ethyne, $\text{HC}\equiv\text{CH}$) but has been observed only transiently—having a lifetime in the region of 0.1 ns. Indeed, no simple (non base-stabilised) compounds of the type $\text{R}_2\text{E}=\text{E}$ have been structurally characterized for any of the group 14 elements. Here we show that by employing the bulky and strongly electron-donating boryl ligand $(\text{HCDippN})_2\text{B}$ ($\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$), a simple monomeric digermavinylidene compound $(\text{boryl})_2\text{GeGe}$ can be synthesized, which is stable at room temperature. Both its formation via the two-electron chemical oxidation of the symmetrical Ge^0 compound $\text{K}_2[(\text{boryl})\text{GeGe}(\text{boryl})]$, and its subsequent reaction chemistry (e.g. with H_2), are consistent with high substituent lability and the accessibility of both 1,1 and 1,2-substitution patterns. Structural and computational studies of $\{(\text{HCDippN})_2\text{B}\}_2\text{GeGe}$ reveal a weak GeGe double bond—the π component of which contributes to the highest occupied molecular orbital (HOMO)—with a Ge-centred lone-pair as the HOMO-1.

Main Text

Compounds of empirical composition CH have played key roles in establishing theories of chemical bonding central to our understanding of structure and reactivity.¹ These include ethyne (HC≡CH) containing archetypal C-C σ and π bonds,² and the prototype aromatic system benzene,³ as well as pseudo Jahn-Teller distorted cyclobutadiene,⁴ and the highly strained, but kinetically inert cubane, C₈H₈.⁵ Analogues of a number of these systems featuring other group 14 elements have also proved to be synthetically accessible,⁶⁻⁹ with the contrasting geometric and electronic structures adopted by the heavier analogues of alkynes, for example, providing a rationale for their unusual ‘transition metal like’ reactivity.¹⁰ While the alkyne form of C₂H₂ is thus well established, the alternative methyldiene carbene (vinylidene) isomer, H₂CC, has not been isolated and structurally characterized, being known to exist only as a transient species under high vacuum and/or high temperature conditions.¹¹⁻¹³ The 1,2-migration of a hydrogen atom to generate ethyne is calculated to be highly exothermic and to occur via a very low energetic barrier (ca. 10 kJ mol⁻¹); as such the lifetime of H₂CC is very short (ca. 10⁻¹⁰ s).¹⁴⁻¹⁷ Formal replacement of H with F yields difluorovinylidene, F₂CC for which the calculated kinetic barrier to isomerization is significantly higher (ca. 150 kJ mol⁻¹), and which can therefore be generated and spectroscopically investigated in an argon matrix at temperatures up to 15 K.¹⁸ ‘Free’ vinylidene systems which are stable at temperatures close to ambient are, however, unknown, with structural characterization of H₂CC systems relying instead on coordination to a transition metal as a trapping strategy.¹²

In the case of heavier analogues of ethyne, E₂H₂ (E = Si-Pb), the linear alkyne-like structure (isomer **A**, Figure 1) is calculated to lie relatively high in energy, reflecting the reduced strength

of E-E π bonds (and increased doublet-quartet separation for the EH ‘monomer’ unit) on descending Group 14. Alternative *trans*-bent (**B**), vinylidene (**E**), and other isomers incorporating bridging hydrogen atoms (**C** and **D**) are predicted to be closer to the energetic minimum.¹⁹⁻²³ Consistently, vinylidene structures have been suggested by high resolution laser spectroscopy/*ab initio* calculations for the transient species $\text{H}_2\text{C}=\text{E}$ (E = Si, Ge), while a hydride-bridged structure has been proposed for Si_2H_2 based on rotational spectra obtained at 73 K.^{24,25} Incorporation of highly sterically demanding substituents, rather than H, however, distorts the potential energy landscape to the extent that only the relatively unhindered 1,2-disubstituted *trans*-bent geometry (**B**) has been realized among structurally characterized derivatives.^{6,7,26-29} The alternative 1,1 (vinylidene) isomer **E** features a highly electronically and sterically unsaturated Group 14 center in the 2-position which is prone to reaction with Lewis bases, and this strategy has recently been exploited by Scheschkewitz,^{30,31} and by Fillipou to generate N-heterocyclic carbene stabilized heavier vinylidenes.^{32,33} To our knowledge, however, no simple structurally characterized systems of the type R_2EE have been reported for any of the Group 14 elements.

Trans-bent dimetallyne systems REER (E = Si-Pb) are unique in being the only isolable heavier group 14 compounds of composition E_2R_2 ;^{6,7} such systems also constitute a landmark in small molecule activation chemistry as the first main group molecules capable of the ambient temperature activation of H_2 (for E = Ge).³⁴ To date, dimetallyne compounds have been reported in conjunction with bulky aryl, silyl and amido R substituents.^{26-29,35-39} We have recently been utilizing sterically encumbered boryl ligands (predominantly $(\text{HCDippN})_2\text{B}$, where Dipp = 2,6-*i*-Pr₂C₆H₃) to support main group compounds featuring unusual coordination numbers and/or

oxidation states.^{40,41} The extremely strong σ -donor capabilities of this ligand class dictate much of the chemistry of its complexes: elevated HOMO (highest occupied molecular orbital) energies and enhanced reactivity towards small molecule activation are features of low-valent boryl-substituted main group compounds.^{40,42} As such, we set out to explore the synthetic and reaction chemistry of dimetallyne systems with R = boryl; in doing so we reveal the potential for labile metal-to-metal transfer of the boryl group and the synthesis of first stable group 14 vinylidene compound, (boryl)₂Ge=Ge.

Results and Discussion

Syntheses. The N-heterocyclic carbene (NHC) stabilized (boryl)germanium(II) chloride, (IPr₂Me₂)GeCl{B(NDippCH)₂} (**1**, where I^{Pr₂Me₂} = 1,3-diisopropyl-4,5-dimethylimidazolylidene; see Supplementary Figure 14) is readily synthesized from (I^{Pr₂Me₂})GeCl₂ and (thf)₂Li{B(NDippCH)₂}^{43,44} and is susceptible to reduction chemistry leading to the formation of Ge-Ge bonds (Figure 2). Thus, the reaction of **1** with the Mg^I dimer [{HC(MeCMesN)₂}Mg]₂ (Mes = 2,4,6-Me₃C₆H₂)⁴⁵ yields the unsymmetrical mono NHC-stabilized digermine (I^{Pr₂Me₂}){(HCDippN)₂B}GeGe{B(NDippCH)₂} (**2**; see Supplementary Figure 15), while the corresponding reaction under forcing conditions with excess potassium metal (or potassium graphite) generates the more highly reduced, formally Ge⁰ compound K₂[(HCDippN)₂B}GeGe{B(NDippCH)₂}] (**3**; Figure 3). Each of these compound types finds precedent in the corresponding chemistry of terphenyl-substituted Ge₂ systems,^{46,47} and descriptions of both **2** and **3** as featuring formal Ge=Ge double bonds are consistent with the Ge-Ge distances measured by X-ray crystallography (2.275(1), 2.392(1) Å, respectively). Thus, similar bond lengths have been found for ('BuNC)Ar'GeGeAr' (2.343(1) Å)⁴⁶ and

$K_2[Ar^*GeGeAr^*]$ (2.391(1) Å),⁴⁶ while the product of the reaction of **2** with dihydrogen, $(I^{Pr_2Me_2})\{(HCDippN)_2B\}GeGe(H)_2\{B(NDippCH)_2\}$ (**4**; see Supplementary Figure 16), features a Ge-Ge single bond and a correspondingly longer separation (2.453(4) Å)³³ [$Ar' = C_6H_3-2,6-(C_6H_3^iPr_2-2,6)$; $Ar^* = C_6H_3-2,6-(C_6H_2^iPr_3-2,4,6)$].

Attempted removal of the remaining carbene donor from **2** by the use of strong Lewis acids (such as $B(C_6H_5)_3$ and $B(C_6F_5)_3$) proved unsuccessful, so attempts were made to synthesize a neutral, donor-free system of stoichiometry $Ge_2(boryl)_2$ by the oxidation of the dianionic component of **3**. Accordingly, reaction with two equivalents of $[Cp_2Fe][BAr^f_4]$ ($Ar^f = C_6H_3(CF_3)_{2-3,5}$) in benzene- d_6 solution proceeds quantitatively (as determined by *in situ* multinuclear NMR measurements) generating a species featuring a single boryl ligand environment. Similar chemistry can be effected using the triphenylcarbenium (trityl) oxidant, $[Ph_3C][B(C_6F_5)_4]$, and in this case the product $\{(HCDippN)_2B\}_2GeGe$ (**5**) can be crystallized from pentane solution (in 60-70% yield) and characterized by X-ray crystallography (Figure 3) in addition to standard spectroscopic and analytical methods.

Structural characterization of digermavinylidene 5. In contrast to the corresponding aryl-substituted systems, **5** is shown crystallographically to feature a unique 1,1-disubstitution pattern about the Ge_2 fragment, with Ge(2) being covalently linked only to the other germanium center, Ge(1). No evidence is obtained from either crystallography (difference Fourier map) or 1H NMR spectroscopy for the presence of any hydrogen atoms attached to Ge(2). Moreover, in contrast to the geometry observed for digermene systems, X_2GeGeX_2 ,⁶ the four atoms defining the X_2GeGe

unit in **5** (i.e. Ge(1), Ge(2), B(1) and B(2)) lie within a single plane (largest out-of-plane deviation = 0.03 Å). The Ge(1)-B distances (2.033(2) Å) are consistent with those measured for other boryl complexes featuring three-coordinate germanium (e.g. 2.057(4) Å for **2**); as with **2** and **3**, the Ge-Ge distance (2.312(1) Å) is within the range expected for a Ge=Ge double bond.⁶ Of additional note regarding the solid state structure of **5** is the relatively close approach of one of the flanking aryl rings of each of the boryl ligands to the one-coordinate germanium centre, Ge(2). These are characterized by contacts of 2.904(2) and 2.917(2) Å, and a marked ‘canting’ of the boryl ligand heterocycle in each case to one side of the Ge-B bond (leading, for example, to disparate Ge(1)-B(1)-N angles of 116.3(1) and 139.9(1)°). These structural observations are thought to be linked to the presence of weak stabilizing interactions involving the flanking arene π systems and the formally vacant in-plane p orbital at Ge(2) (vide infra).

Evidence for the retention of these weak π interactions in solution is obtained from variable temperature ¹H NMR measurements. At room temperature only one signal corresponding to the boryl heterocycle backbone CH of **5** is observed, together with one ⁱPr CH and two ⁱPr CH₃ resonances for the C₆H₃ⁱPr_{2-2,6} groups. Cooling a solution in toluene-d₈ to below 213 K, however, results in splitting of each of these signals (see Supplementary Figure 8), consistent with a lower symmetry structure akin to that observed in the solid state (and slow fluxional interconversion on the NMR timescale). From these measurements a value for ΔG^\ddagger can be obtained which defines an upper limit for the energy associated with the Ge(2)-arene π interactions (43 kJ mol⁻¹).⁴⁸ From a mechanistic perspective, this barrier is closely comparable to the energy calculated by DFT methods for a mono-bridged Ge(μ -boryl)Ge(boryl) transition state (akin to structure **C**, Figure 1) describing the transfer of one boryl ligand between the germanium

centres (40 kJ mol^{-1} ; Supplementary Figure 21). As such, a plausible mechanism for the observed fluxionality involves shuttling of a boryl ligand along the Ge_2 vector.

Electronic structure of **5.** The 1,1-disubstituted structure of **5** observed both in the solid state and in hydrocarbon solution is in line with the results of Density Functional Theory calculations (including dispersion) which reveal that the digermavinylene isomer is ca. 10 kJ mol^{-1} more stable than the alternative (*trans*-bent) 1,2 system. While these data imply that the energetic difference between the two substitution patterns is small, this idea is consistent with the observed reactivity of **5** (vide infra), and it is noteworthy that our calculations carried out using the same method, for related terphenyl systems, $\text{Ge}_2\text{Ar}'_2$, show that the corresponding *trans*-bent isomer is more stable by $>100 \text{ kJ mol}^{-1}$.⁴⁹ The molecular orbital occupancy for **5** is consistent with a singlet (1A_1) ground state, in line with its observed diamagnetism, and with predictions made for both the parent vinylidene $\text{H}_2\text{C}=\text{C}$ and its digermanium analogue $\text{H}_2\text{Ge}=\text{Ge}$ (Figure 4).^{15,19,21,22} However, the ordering of key molecular orbitals for **5** differs from that found in $\text{H}_2\text{C}=\text{C}$ (for which the highest occupied molecular orbital, HOMO, is the C-centered lone pair).⁵⁰ The HOMO for **5** (at -3.79 eV) is the GeGe π bond, with the HOMO-1 (at -4.70 eV) possessing the predominant $\text{Ge}(2)$ -centered lone pair character. These differences are in line with expectations of E-E π bond strengths on descending group 14, i.e. with the much more weakly stabilized (higher lying) nature of the Ge-Ge π -bonding molecular orbital than its C-C counterpart.⁶ In common with $\text{H}_2\text{C}=\text{C}$, however, the lowest unoccupied molecular orbital (LUMO; -2.24 eV) is the formally vacant $\text{Ge}(2)$ $p\pi$ orbital which lies in the B_2GeGe plane (and points towards the flanking aryl π systems), with the Ge-Ge π^* orbital (the LUMO+1) being a further 0.27 eV higher in energy. Accordingly, the electronic spectrum of **5** (Supplementary Figure 13) contains

a very strong band at 460 nm which features significant a contribution from the Ge=Ge π to π^* transition. Finally, in line with the notion of stabilization of the in-plane p orbital at Ge(2) via a weak arene π interaction, it is possible to identify a low-lying orbital (HOMO-11, -6.37 eV) which features an in-phase interaction between the Ge p_x orbital and the respective flanking arene π -systems, albeit with a relatively small germanium contribution (ca. 3%; Supplementary Figure 22).

Reactivity. The synthesis of **5** from **3** illustrates the lability of the boryl ancillary ligands about the Ge₂ unit, a factor which is additionally reflected in the reaction chemistry of **5** (Figure 2). Thus, the 1,2-disubstitution pattern can be re-established by the addition of potassium graphite, KC₈ (which regenerates **3**), or by the addition of I^{Pr²Me₂} (which yields mono-NHC adduct **2**). The highly unsaturated nature of **5**, and its relatively small HOMO-LUMO gap (ca. 150 kJ mol⁻¹) also suggest that it should activate dihydrogen under mild conditions.³³ This hypothesis is borne out by experiment: **5** takes up two equivalents of H₂ at 4 atm pressure and 318 K. The product so generated, however, is shown by both ¹H NMR and X-ray crystallography to be the symmetrical 1,2-diboryl-digermane {(HCDippN)₂B}(H)₂GeGe(H)₂{B(NDippCH)₂} (**6**; Figure 5 and Supplementary Figure 17). Consistent with the idea of ready boryl migration under such conditions, the presumed intermediate of composition (boryl)₂Ge₂(H)₂ (that is, the product of uptake of the first equivalent of H₂) is calculated to prefer a 1,2-diboryl-digermane geometry over other less symmetrical alternatives by > 20 kJ mol⁻¹ (Supplementary Figure 20).

Digermavinylidene **5** is thus uniquely stable as a compound of the type E₂R₂ featuring a 1,1-

disubstitution pattern. Steric influences on the relative stabilities of germanium systems of this type have been probed computationally: H_2GeGe is calculated to be 36 kJ mol^{-1} more stable than HGeGeH , while related bulky aryl derivatives favour the ArGeGeAr isomer by $>70 \text{ kJ mol}^{-1}$.⁴⁹ Although the boryl substituent employed in **5** is undoubtedly bulky, the use of a five-membered heterocycle (rather than a six-membered aryl substituent) reduces the steric pressure exerted by the *ortho* Dipp groups in comparison, for example, with Power's Ar'GeGeAr' system,²⁸ particularly given the greater length of Ge-B (vs. Ge-C) bonds in such systems ($2.057(4) \text{ \AA}$ and $2.033(2) \text{ \AA}$ for **2** and **5**, respectively, vs. $1.996(3) \text{ \AA}$ for Ar'GeGeAr'). Moreover, the conversion of a digermine to a digermavinylidene is effectively an intramolecular disproportionation reaction, converting two formally Ge^{I} centers to Ge^{II} and Ge^0 . Similar net processes have been reported for group 13 metals in the presence of boryl ligands, with the generation of $(\text{boryl})_2\text{M}^{\text{II}}$ radicals ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) and elemental metal from M^{I} precursors being driven, at least in part, by the stabilization of the higher oxidation state by the strongly σ -donating boryl group.⁴¹ The observation of the digermavinylidene structure for **5**, conceivably relies on similar electronic effects promoting the formation of Ge^{II} , allied to (weak) arene π -stabilization of the Ge^0 center by the flanking Dipp groups.

Methods

Manipulations were carried out under a dry, oxygen-free argon or dinitrogen atmosphere, with reagents dissolved or suspended in aprotic solvents, and combined or isolated using cannula and glove box techniques. $(\text{I}^{\text{Pr}2\text{Me}2})\text{GeCl}\{\text{B}(\text{NDippCH})_2\}$ (**1**) was synthesized from $(\text{I}^{\text{Pr}2\text{Me}2})\text{GeCl}_2$ and $(\text{thf})_2\text{Li}\{\text{B}(\text{NDippCH})_2\}$ in diethyl ether. $(\text{I}^{\text{Pr}2\text{Me}2})\{(\text{HCDippN})_2\text{B}\}\text{GeGe}\{\text{B}(\text{NDippCH})_2\}$ (**2**) and $\text{K}_2[\{(\text{HCDippN})_2\text{B}\}\text{GeGe}\{\text{B}(\text{NDippCH})_2\}]$ (**3**) were synthesized from **1** via reduction chemistry

in toluene solution using $[\{\text{HC}(\text{MeCMesN})_2\}\text{Mg}]_2$ (Mes = 2,4,6-Me₃C₆H₂) and potassium graphite, respectively. **2** was recrystallized from hexane, **3** from a *ca.* 2:1 mixture of hexane and toluene. $\{(\text{HCDippN})_2\text{B}\}_2\text{GeGe}$ (**5**) was synthesized by adding a solution of **3** in benzene to two equivalents of either $[\text{Cp}_2\text{Fe}][\text{BAr}^f_4]$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, and recrystallized from pentane. The germanium hydrides $(\text{I}^{\text{Pr}^2\text{Me}^2})\{(\text{HCDippN})_2\text{B}\}\text{GeGe}(\text{H})_2\{\text{B}(\text{NDippCH})_2\}$ (**4**) and $\{(\text{HCDippN})_2\text{B}\}(\text{H})_2\text{GeGe}(\text{H})_2\{\text{B}(\text{NDippCH})_2\}$ (**6**) were synthesized from solutions of **2** and **5**, respectively (in hexane or pentane), by exposure to H₂. Reaction of **5** with potassium graphite led to the regeneration of **3**, while reaction of **5** with I^{Pr²Me²} was shown to give rise to mono-carbene adduct **2**. We characterized new compounds by elemental analysis, UV/Visible spectroscopy (for compounds **2**, **3** and **5** which contain Ge=Ge double bonds), cyclic voltammetry (for **2** and **5**), and multinuclear NMR spectroscopy; the structures of all new compounds **1** – **6** in the solid state were determined by single-crystal X-ray diffraction studies. Density Functional Theory (DFT), as implemented in the Amsterdam Density Functional code, has been employed to calculate molecular geometries, orbital energies and compositions, and electronic transition energies.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Contributions A.R. synthesized and characterized the compounds. J.C. collected the single-crystal X-ray crystallographic data and solved the crystal structures. A.R. and H.N. carried out the DFT calculations. S.A. generated and managed the project and wrote the manuscript. All authors discussed the results and commented on the manuscript.

Author Information X-ray crystallographic data for compounds **1**, **2**, **3**, **4**, **5** and **6** are freely available from the Cambridge Crystallographic Data Centre (CCDC 1447808-1447813). Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to S.A. (simon.aldridge@chem.ox.ac.uk).

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Supplementary Information

General considerations and starting material preparations; synthetic, spectroscopic and analytical data for new compounds; X-ray crystallographic studies; computational details (including TD-DFT); CIFs for all crystal structures.

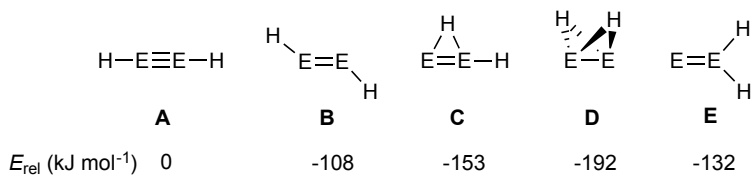


Figure 1. Isomeric forms of E_2H_2 . Depicted are alkyne-like (**A**), *trans*-bent (**B**), mono- and bis(hydride) bridged (**C**, **D**) and vinylidene isomers (**E**), with calculated relative energies taken from the literature for $\text{E} = \text{Ge}$.²⁰

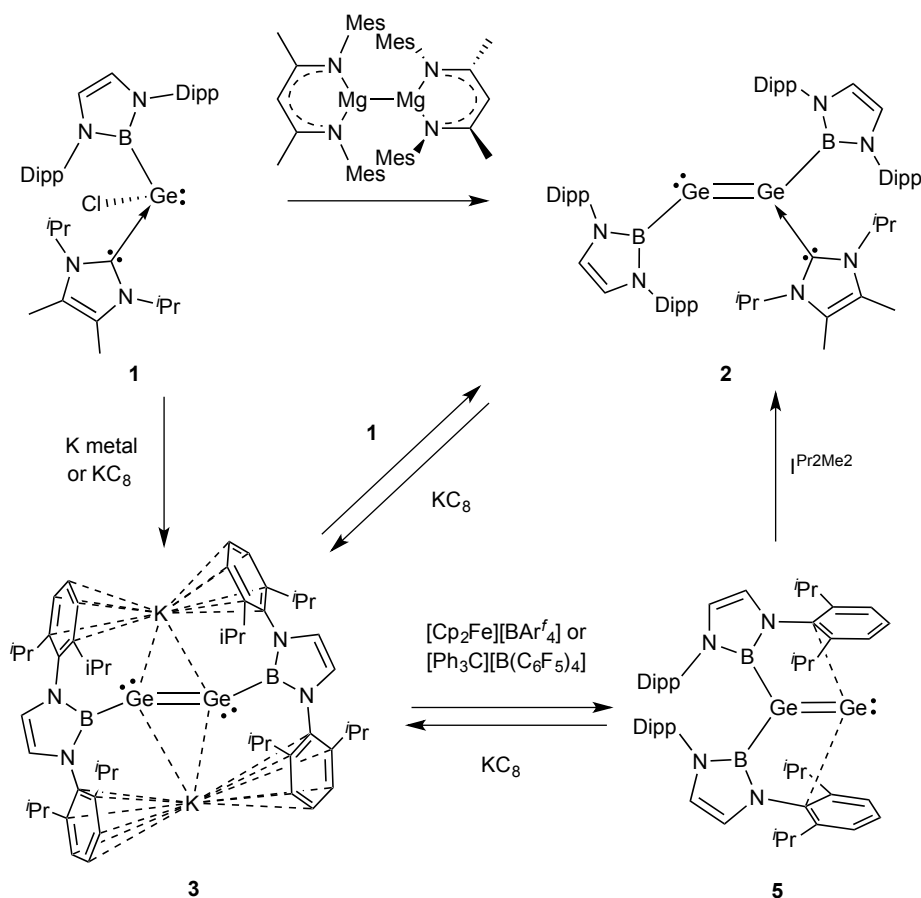


Figure 2. Synthesis of digermavinylidene **5** and related digermanium systems **2** and **3**. Reduction of NHC-stabilized chlorogermylene **1** yields either the singly base-stabilized Ge_2 dimer **2** (using a Mg^{I} reductant), or the more highly reduced base-free Ge_2^0 dianion **3** (using a more powerful

potassium reducing agent). Subsequent oxidation of **3** using two equivalents of a one-electron chemical oxidant (ferrocenium or trityl salts) yields digermavinylidene **5**, via a 1,2-boryl migration. [$\text{I}^{\text{Pr}2\text{Me}2}$ = 1,3-diisopropyl-4,5-dimethyl-imidazolylidene; Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl]

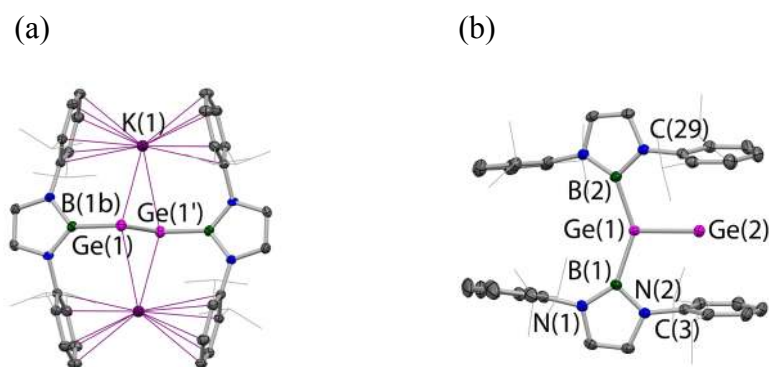


Figure 3. Molecular structures (a) of **3**, and (b) of **5** as determined by X-ray crystallography.

Displacement ellipsoids are set at the 40% level; hydrogen atoms have been omitted and isopropyl groups drawn in wireframe format for clarity. Selected bond distances and angles are as follows: (for **3**): Ge(1)-Ge(1') 2.392(1) Å, Ge(1)-B(1b) 2.097(8) Å, B(1b)-Ge(1)-Ge(1') 102.5(2) $^{\circ}$; (for **5**): Ge(1)-Ge(2) 2.312(1) Å; Ge(1)-B(1) 2.033(2) Å; Ge(1)-B(2) 2.033(2) Å; Ge(2)-C(3) 2.904(2) Å; Ge(2)-C(29) 2.917(2) Å, B(1)-Ge(1)-Ge(2) 108.5(1) $^{\circ}$, B(1)-Ge(1)-B(2) 142.6(1) $^{\circ}$, B(2)-Ge(1)-Ge(2) 108.9(1) $^{\circ}$, Ge(1)-B(1)-N(1) 116.3(1) $^{\circ}$, Ge(1)-B(1)-N(2) 139.9(1) $^{\circ}$.

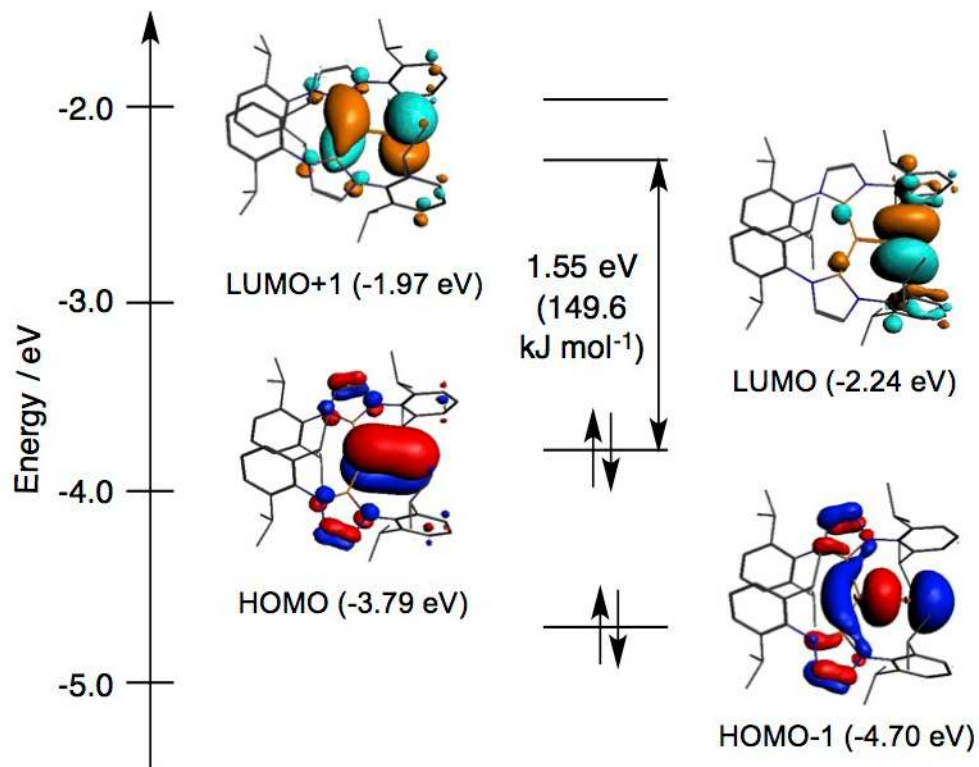


Figure 4. Electron density surfaces and energies for key molecular orbitals of **5**. Of the occupied orbitals (which have the phases of the wavefunction depicted in red/dark blue), the HOMO constitutes the GeGe π -bond, with the lower-lying HOMO-1 possessing lone pair character at the terminal germanium centre. The virtual orbitals depicted (phases shown in brown/pale blue) feature π -type contributions from the terminal germanium atom either in the GeB₂ plane (LUMO) or perpendicular to it (LUMO+1). The latter orbital possesses GeGe π^* character. [HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital]

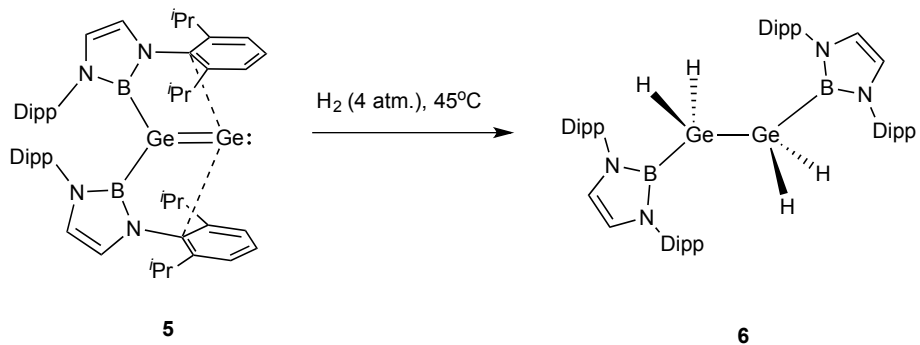


Figure 5. Uptake of dihydrogen by digermavinylidene **5**. Reaction of **5** with H₂ at ca. 4 atm pressure and 45°C goes to completion over a period of 6 hours, and occurs via the uptake of two equivalents of dihydrogen, with accompanying 1,2-migration of one of the boryl substituents. The symmetrical structure of the resulting diboryldigermene has been confirmed by spectroscopic and crystallographic measurements.