Structure Elucidation

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Using N-Heterocyclic Vinyl Ligands to Access Stable Divinylgermylenes and a Germylium Cation

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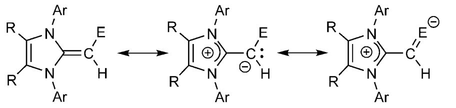
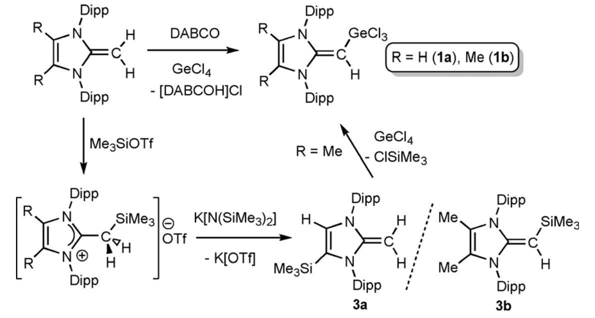
Abstract: *Two efficient methods are presented to install σ- and π-electron-donating N-heterocyclic vinyl groups onto main-group elements (E): halosilane elimination and base-induced E−C bond formation. Placement of two NHC=CH$^-$ ligands (NHC = N-heterocyclic carbene) onto a Ge^{II} center affords a two-coordinate germylene, a heavy congener of the elusive divinyl carbenes. The π-donating ability of this vinylic ligand scaffold was further demonstrated by the synthesis of a three-coordinate germylium cation R$_3$Ge$^+$.*

The synthesis of complexes of low-valent heavy group 14 elements has led to landmark achievements which challenge pre-existing bonding paradigms.[1] Moreover, low-coordinate Si, Ge, or Sn centers can support transition-metal-like reactivity with small molecules (e.g. H_2 and CO_2),[2] thus promoting the growth of main-group element-based catalysis.[3] Herein, we introduce N-heterocyclic vinyl [NHC=CH]$^-$ ligands (NHC = N-heterocyclic carbene unit) as a new method to stabilize low-coordinate species. This ligand class merges the steric tunability of widely used carbene[4] and terphenyl[5] ligands with the benefit of added π-donor properties from the terminal vinylic carbon centers (Scheme 1). Starting from readily available N-heterocyclic olefins (NHOs)[6,7] we are able to transfer [NHC=CH]$^-$ functionalities, thus leading to a π-stabilized two-coordinate, base-free divinylgermylene and a non-arylated germylium cation R$_3$Ge$^+$.



Scheme 1. Suggested resonance forms depicting the donor capability of N-heterocyclic vinyl ligands (R = H, Me; Ar = aryl groups; E = low-coordinate main group element).



Scheme 2. Accessing the divinylgermanes **1a** and **1b** by two pathways. DABCO = 1,4-diazabicyclo[2.2.2]octane, Tf = trifluoromethanesulfonyl.

Rapid access to Ge^{IV} complexes of N-heterocyclic vinylenes was accomplished by combining the known NHOs IPr=CH$_2$ (IPr = (HCNDipp)$_2$C, Dipp = 2,6-iPr$_2$C$_6$H$_3$)[6f] and ^{Me}IPr=CH$_2$ [^{Me}IPr = (MeCNDipp)$_2$C][6f] with equimolar amounts of DABCO[8] and GeCl$_4$ (Scheme 2). The resulting pale-yellow vinyl-substituted chlorogermanes (IPr=CH)GeCl$_3$ (**1a**) and (^{Me}IPr=CH)GeCl$_3$ (**1b**) were obtained in good yields (73 and 69%) and each characterized by X-ray crystallography (see Figures S1 and S2 in the Supporting Information).[9] The C$_{IPr}$−C$_{vinyl}$ bond lengths (C2−C1) in **1a** and **1b** are consistent with double-bond character [1.380(2) and 1.377(4) Å, respectively], while short covalent C–Ge distances are found to result from the formal sp^2 hybridization at the carbon center (C1−Ge1: **1a** 1.8418(17), **1b** 1.836(3) Å).

Attempts to prepare the potential [IPr=CH]$^-$ transfer agent (IPr=CH)SiMe$_3$ invariably led to backbone activation/silyl migration to afford **3a** (Scheme 2; see Figure S6[9]).[10] Fortunately, backbone methylated ^{Me}IPr=CH$_2$ reacted cleanly in a sequential manner with Me$_3$SiOTf and K[N(SiMe$_3$)$_2$] to give the [NHC=CH]$^-$ synthon (^{Me}IPr=CH)SiMe$_3$ (**3b**). The molecular structure of (^{Me}IPr=CH)SiMe$_3$ (**3b**) is shown in Figure S8[9] and the exocyclic C−C bond length (1.361(4) Å) is the same, within experimental error, as in Ghadwal's halosilane complex (IPr=CH)SiCl$_2$H [1.379(2) Å].[7b] The C–Si interaction in **3b** [1.821(3) Å] is, however, substantially elongated relative to the corresponding distance in (IPr=CH)SiCl$_2$H (1.776(2) Å),[7b] thus suggesting that the SiMe$_3$ group in **3b** could be labile. As an initial proof of concept, effective ClSiMe$_3$ elimination occurs between (^{Me}IPr=CH)SiMe$_3$ (**3b**) and GeCl$_4$ to give (^{Me}IPr=CH)GeCl$_3$ (**1b**) in 87% yield without the need of exogenous bases. We anticipate that this route of installing π-donating vinyl ligands will also promote advances in transition-metal chemistry and catalysis.[11]

We then demonstrated the ability of N-heterocyclic vinyl ligands to stabilize low-coordinate centers. First, the requisite dihalogermane precursor [(IPr=CH)$_2$GeCl$_2$] (**4**) was prepared using the procedure outlined in Scheme 3. Compound **4** was characterized by X-ray crystallography (Figure 1) which

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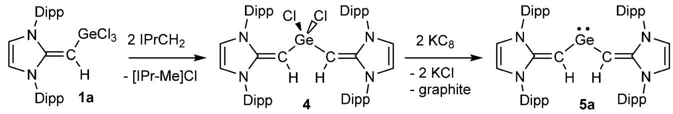


Scheme 3. Synthesis of the divinylgermylene **5a**.

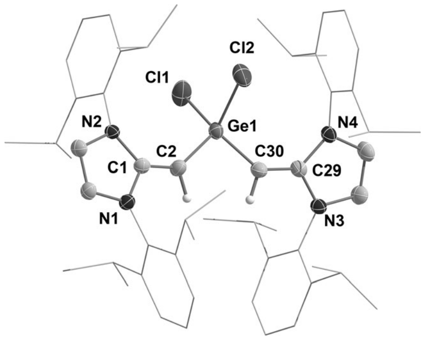


Figure 1. POV-ray depiction of the molecular structure of **4**. Ellipsoids shown at 50% probability. All hydrogen atoms (except those on C2/C30) omitted and flanking Dipp-groups rendered as wireframes. Selected bond lengths (Å) and angles (°): C1–C2 1.371(4), N1–C1 1.396(4), N2–C1 1.391(4), C29–C30 1.359(4), N3–C29 1.400(4), N4–C29 1.393(4), Ge1–C2 1.874(4), Ge1–C30 1.884(4), Ge1–Cl2 2.174(3), Ge1–Cl1 2.204(3), C1–C2 1.371(4), C29–C30 1.359(4); C2-Ge1-C30 104.23(16).[9]

shows that the added bulk at Ge does not alter the vinylic C=C (1.371(4) and 1.359(4) Å) or C–Ge distances (1.884(4) Å avg.) significantly in relation to the mono-ligated precursor (IPr=CH)GeCl$_3$ (**1a**).

With the bis(vinyl)dichlorogermane **4** in hand, we explored its reduction to yield the stable, base-free divinyl germylene [(IPr=CH)$_2$Ge:] (**5a**).[12] Notably, divinyl carbenes are proposed to exist as transition states in the thermal rearrangement of tetrasubstituted cyclopropenes into their corresponding allenes.[13] Stirring **4** with KC$_8$ in THF for 1 hour afforded a new orange crystalline product which was identified as the target monomeric germylene **5a** by X-ray crystallography (Figure 2). Compound **5a** is stable in C$_6$D$_6$ upon heating to 80 °C for 24 hours and decomposes when heated above 190 °C in the solid state. Reduction of (^{Me}IPr=CH)GeCl$_3$ (**1b**) with three molar equivalents of KC$_8$ also yielded the analogous germylene [(^{Me}IPr=CH)$_2$Ge:] (**5b**).[9] This product could arise from ligand redistribution involving a putative digermyne RGeGeR.[5b,14] Attempts to prepare **5a** from IPrCH$_2$·GeCl$_2$[15] and IPrCH$_2$ in the presence of DABCO gave no discernable reaction.

The C-Ge-C angle in (**5a**) (96.76(2)°) is considerably narrower than in **4** (104.23(16)°) and suggests a high degree of p-character within the vinylic C–Ge bonds in **5a**. For comparison, Power's bis(amido)germylene [(Ar*NH)$_2$Ge:] (Ar* = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Me$_3$)) has an acute N-Ge-N angle of 88.6(2)°,[16] with intra-ligand dispersion forces leading to bond angle narrowing. The IPr=CH units in **5a** adopt symmetric arrangements which enable two Dipp groups to form a protective steric pocket about the Ge center.

The bonding situation in **5a** has been investigated by DFT methods.[9] A natural population analysis (NPA) reveals a rather large negative charge on the vinylic carbon atoms C4 and C4′ in **5a** ($q = -0.88$ e), whereas the Ge atom carries a charge of +0.61 e. The exocyclic C1–C4 (C1′–C4′) bonds have considerable double-bond character (Wiberg bond indices; WBI = 1.52) with bonding density in the σ- and π-regions. As expected with the narrow C-Ge-C bond angle, the corresponding bonds are derived from orbitals of predominantly p-character at Ge. A second-order perturbation analysis revealed donation of π-electron density from the terminal carbon atoms in the IPr=CH$^-$ ligands to a p orbital on Ge ($E = 19.2$ kcal mol^{-1}), which is also nicely illustrated in the computed HOMO−2 (Figure 3, left). The LUMO in **5a** has a large contribution at Ge with overall C–Ge π*-character, while the HOMO and HOMO−1 display exocyclic C–C π-bonding and a germanium lone pair, respectively (Figure 3). The presence of Ge–C π-interactions is also reflected in the vinylic ^{1}H NMR resonance of **5a** (5.10 ppm; C$_6$D$_6$), which is considerably downfield shifted from its dichlorogermane precursor **4** (3.09 ppm; C$_6$D$_6$), thus implying a substantial degree of π-delocalization in the C-Ge-C manifold.

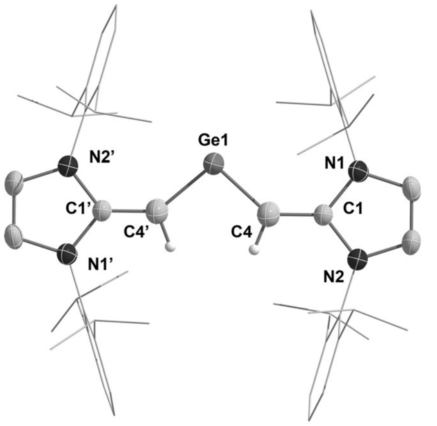


Figure 2. POV-ray depiction of the molecular structure of **5a**. Ellipsoids shown at 50% probability. All hydrogen atoms (except those on C4/C4′) omitted and flanking Dipp-groups rendered as wireframes. Selected bond lengths (Å) and angles (°): Ge1–C4 1.849(4), C1–C4 1.361(4); C4-Ge1-C4′ 96.76(2).

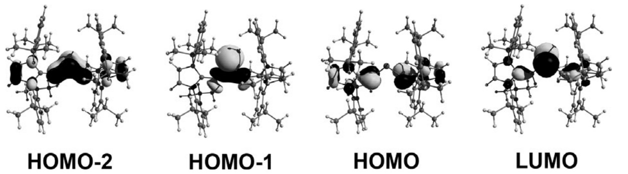
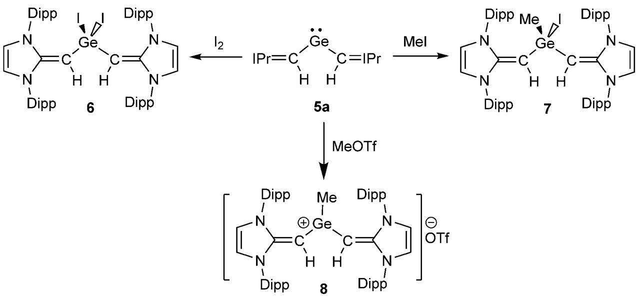


Figure 3. POV-ray depiction of the Kohn–Sham orbitals of **5a** at the B3LYP/6-31G(d,p) level of theory.

Compound **5a** exhibits an intense absorption at $\lambda = 493$ nm ($\varepsilon = 30600$ L mol^{-1} cm^{-1}), and is significantly blue-shifted in comparison to Power's diarylgermylene Ar*$_2$Ge ($\lambda_{max} = 578$ nm)[17] which contains similar C(sp$_2$)–Ge(p) linkages as in **5a**. Thus the added C–Ge π interactions in **5a** effectively raise the LUMO level (which has Ge–C π* character). This postulate is supported by TD-DFT computations which afford an absorption maximum at $\lambda = 465$ nm for **5a** in the gas phase arising from a HOMO–LUMO ($\pi \rightarrow n/\pi^*$, $\Delta E_{\text{HOMO–LUMO}} = 61.5$ kcal mol^{-1}) transition. As expected for such a large energy gap, **5a** is unreactive towards H_2. Notably, Aldridge's arylsilylgermylene Ar*GeSi(SiMe$_3$)$_3$ has an estimated $\Delta E_{\text{HOMO–LUMO}}$ of 32 kcal mol^{-1} and can readily activate H_2.[18]

Despite the steric bulk about Ge in [(IPr=CH)$_2$Ge:] (**5a**), smooth oxidative addition transpired with I_2 and MeI to give [(IPr=CH)$_2$GeI$_2$] (**6**) and [(IPr=CH)$_2$GeMe(I)] (**7**), respectively (Scheme 4). Of much greater interest was the reaction of **5a** with MeOTf, which gave an orange-colored product later identified as the three-coordinate germylium salt [(IPr=CH)$_2$GeMe]OTf (**8**; Scheme 4). As expected, **8** afforded symmetric IPr=CH$^-$ environments (by ^{1}H and ^{13}C{^{1}H} NMR data) as well as a ^{19}F NMR resonance at $\delta = -78.9$ ppm in CD$_2$Cl$_2$, assigned as free OTf$^-$.[19] The Me group attached to the Ge center in **8** resonates at $\delta = -1.06$ ppm (^{1}H NMR; C$_6$D$_6$), which is considerably shielded in comparison to the cation [Trip$_2$GeMe]$^+$ (Trip = 2,4,6-iPr$_3$C$_6$H$_2$) (1.53 ppm; C$_6$D$_6$),[20] thus suggesting the possible stabilization of the positive charge at Ge through added C–Ge π interactions.



Scheme 4. Reactivity of the divinylgermylene **5a** with I_2, MeI, and MeOTf.

The molecular structure of **8** (Figure 4) displays a planar three-coordinate Ge center ($\Sigma°$(Ge) = 360.0(4)°) with no interactions between Ge and OTf$^-$, thus making it the first isolable germylium cation (R$_3$Ge$^+$) without bulky aryl or silyl groups.[20,21] The Ge–C$_{\text{vinyl}}$ distances are nearly equivalent (Ge1–C8 1.815(4), Ge1–C4 1.820(4) Å), while a longer Ge–C$_{\text{Me}}$ distance (Ge1–C9) of 1.926(4) Å is present. The C–C$_{\text{vinyl}}$ separations in [**8**]$^+$ (C1–C4 1.401(5), C5–C8 1.393(5)) are elongated compared to those in **5a**, and are in line with delocalization of the cationic charge onto the flanking imidazole rings.[22] Upon Me$^+$ addition the C4-Ge1-C8 angle widens (106.19(17)°) compared to that of **5a**. The molecular structure of **8** nicely illustrates how the N-heterocyclic vinyl ligands effectively shield the adjacent Ge atom to allow formation of an ion-separated germylium salt. Thus we expect the isolation of additional low-coordinate bonding environments using this novel ligand construct.

Gas-phase DFT calculations[9] reproduced the experimentally observed metrical parameters within [**8**]$^+$ nicely and the bonding situation was assessed by NBO analysis. The

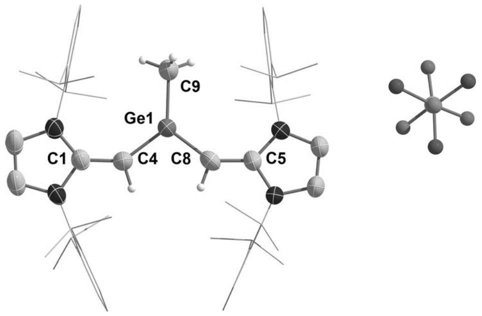


Figure 4. POV-ray depiction of the molecular structure of **8**. Ellipsoids shown at 50% probability. All hydrogen atoms (except those on C4/C8/C9) omitted, flanking Dipp-groups rendered as wireframes and the triflate counteranion with a ball-and-stick model. Selected bond lengths (Å) and angles (°): Ge1–C8 1.815(4), Ge1–C4 1.820(4), Ge–C9 1.926(4), C1–C4 1.401(5), C5–C8 1.393(5); C8-Ge-C4 106.19(17), C8-Ge-C9 125.98(18), C4-Ge-C9 127.83(18), C1-C4-Ge 141.5(3), C5-C8-Ge 142.3(3); C8-Ge-C4-C1 torsion angle 174.3(5).

computed NPA charge on Ge1 increases substantially from 0.61 e in the divinylgermylene **5a** to a value of 1.50 e in [**8**]$^+$, and is consistent with a Ge-centered cation in the latter species. However, delocalization of π-electron density from the IPr=CH$^-$ units to Ge was also found in [**8**]$^+$ as evidenced by HOMO-13 and HOMO-1 (Figure 5). The HOMO and LUMO in [**8**]$^+$ (C=C π and Ge–C π*, respectively) remain nearly unaltered in relation to the corresponding orbitals in the precursor **5a**. The Ge–C bonds in [**8**]$^+$ are highly polarized (WBI: Ge1–C4 1.09; Ge1–C8 1.09; Ge1–C9 0.84) with about 70% of the electron density located at the carbon atoms. The increase in Ge–C$_{\text{IPrCH}}$ bond order in relation to the Ge–C$_{\text{Me}}$ linkage is a reflection of added stabilizing Ge–C interactions. The orange color of [**8**]$^+$ is due to the longest wavelength absorption in the UV/vis at $\lambda_{\max} = 486$ nm ($\varepsilon = 15\,600$ L mol^{-1} cm^{-1}), which is linked to a HOMO–LUMO ($\pi \rightarrow \pi^*$) transition, as confirmed by TD-DFT.[9]

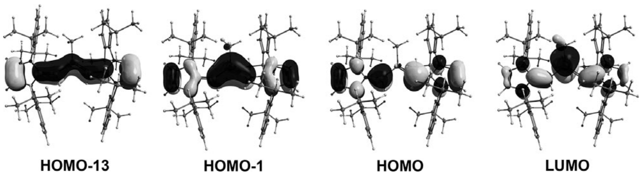


Figure 5. POV-ray depiction of the Kohn–Sham orbitals of [**8**]$^+$ obtained at the B3LYP/6-31G(d,p) level of theory.

In conclusion we present the first isolable base-free divinyl germylenes, heavy-element homologues of the elusive divinyl carbenes. The viability of using σ- and π-donating N-heterocyclic vinyl ligands to stabilize electron-deficient low-coordinate centers was demonstrated by the isolation of the stable three-coordinate germylium cation [(IPrCH)$_2$GeMe]$^+$. This new ligand archetype should facilitate the discovery of additional new inorganic bonding modes,[1,5] and enable high oxidation-state metal environments to be obtained for possible catalytic applications.

Acknowledgments

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Keywords: carbenes · density functional calculations · germanium · structure elucidation · X-ray diffraction

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Communications

Structure Elucidation

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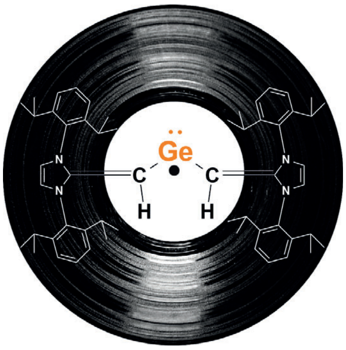
Using N-Heterocyclic Vinyl Ligands to Access Stable Divinylgermylenes and a Germylium Cation



Germylenes go vinyl: N-heterocyclic vinyl ligands pave the way for the isolation of the first base-free divinylgermylene, a heavy congener of divinyl carbenes. The π-donating ability of this vinylic ligand scaffold was further demonstrated by the synthesis of a three-coordinate germylium cation R_3Ge^+.