Germanium Double Bonds

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Exploiting Electrostatics To Generate Unsaturation: Oxidative Ge=E Bond Formation Using a Non π-Donor Stabilized $[R(L)Ge:]^+$ Cation

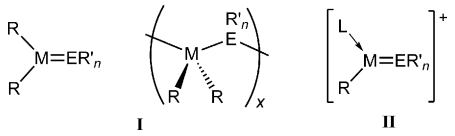
Arnab Rit, Rémi Tirfoin, and Simon Aldridge**

Abstract: *The two-coordinate germanium cation $[(IDipp)\{(Me_3Si)_2CH\}Ge:]^+$ has been synthesized, which lacks π-donor stabilization of the metal center and consequently has a very small HOMO–LUMO gap (187 kJ mol^{-1}). It undergoes a variety of facile oxidative bond-forming reactions, most notably allowing access to the first examples of Group 14 metal cations containing M=E multiple bonds (E = C, N). The use of an electrostatic (rather than purely steric) strategy to discourage aggregation means that less bulky systems (for example, containing a primary alkylidene fragment, =CHR) are accessible.*

The chemistry of multiply bonded species featuring the heavier Group 14 elements silicon–lead has attracted significant attention in recent years,[1] reflecting fundamental differences in their electronic/geometric structure compared to their carbon congeners, and their associated potential for exploitation in bond activation, and ultimately in catalysis.[1,2] While the existence of such compounds for many years appeared contrary to the so-called "double bond rule",[3] the synthesis in the early 1980s of landmark compounds featuring Si=C and Si=Si bonds,[4] initiated investigations across a broad field spanning synthetic, catalytic, and materials science.[2,5]

One of the intrinsic challenges associated with the isolation of systems containing M=E double bonds (where E = C, N, O, for example) is the thermodynamic incentive for aggregation presented by the formation of strong M−E single (sigma) bonds.[6] A highly successful approach to circumvent this problem makes use of extremely bulky peripheral substituents and the increase in coordination number implicit in aggregation.[7,8] Another strategy, which to our knowledge has been explored only in transition metal functionalized systems, involves the use of a net cationic charge at the Group 14 center to provide an electrostatic disincentive to oligomerization (Scheme 1)).[9]

In the case of germanium, the synthesis of Ge=E bonds (E = C, N, O) typically relies on the use of a germylene precursor ($R_2Ge:$) and labile sources of the ER'_n fragment (for example, R_2CN_2, RN_3, N_2O).[8g,10] Syntheses of related cationic systems can therefore be conceived from similar reagents and $[R(L)Ge:]^+$, provided that R and L are sufficiently strongly σ-donating to facilitate oxidation of the cationic metal center. Cationic germyliumylidene systems of this type are relatively rare, however,[11a] having mainly been isolated within an N-heterocyclic scaffold employing a neutral or monoanionic (bidentate) ligand.[11b–f] Acyclic systems featuring a wide angle at the metal center might be expected to offer enhanced possibilities for oxidative reactivity, but are very rare indeed, and all known examples are stabilized by π-donor ancillary substituents.[12] The use of such substituents delivers enhanced stability, but the associated widening of the HOMO–LUMO energy gap, typically results in systems less labile towards oxidative addition.



I II

Scheme 1. Generic neutral (**I**) and cationic (**II**) heavier Group 14 systems featuring alkylidene, imido, or oxo functional groups ($ER'_n = CR_2$, NR, O).

In attempting to access multiply-bonded Ge^{IV} complexes of type $[R(L)Ge{=}ER'_n]^+$, we therefore targeted highly reactive $[R(L)Ge:]^+$ cations featuring minimal π-stabilization and a relatively small HOMO–LUMO gap. Accordingly, we present here the synthesis of a two-coordinate system of the type $[alkyl(NHC)Ge:]^+$ (NHC = N-heterocyclic carbene) and its use in the synthesis of Group 14 cations of type **II** featuring M=E multiple bonds (E = C, N; Scheme 1). In contrast to approaches based on purely steric strategies, this method allows access to less encumbered systems, for example, a Ge=C bond featuring a primary (CH-containing) alkylidene fragment.

Chlorogermylene **1** was synthesized from $IDipp{\cdot}GeCl_2$ [IDipp = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] and $LiCH(SiMe_3)_2$ by salt metathesis, and isolated as a white solid in 69% yield (see the Supporting Information for characterizing data).[13] Moreover, **1** proves to be a suitable precursor for the synthesis of acyclic monocationic Ge^{II} species by chloride abstraction using a salt of a very weakly coordinating anion such as $[BAr^f_4]^-$ [$Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$]. Thus, reaction with $Na[BAr^f_4]$ in fluorobenzene immediately generates a dark orange solution, from which $[(IDipp)\{(Me_3Si)_2CH\}Ge][BAr^f_4]$ (**2-BAr$^f_4$**) could be isolated as orange crystals in 63% yield (Scheme 2).

The formation of a cationic species is consistent with the large downfield shift of the $CH(SiMe_3)_2$ resonance in the ^{1}H NMR spectrum ($\delta_H = -0.57$ to 3.15 ppm), and X-ray

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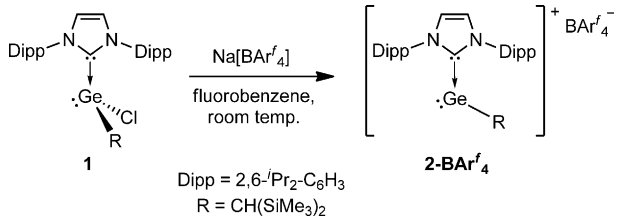
Supporting information for this article, synthetic and spectroscopic data for all new compounds, X-ray crystallographic files for **1**, **2-BAr$^f_4$**·C_6H_5F, **3-BAr$^f_4$**, **4-BAr$^f_4$**, **5-BAr$^f_4$**, **6-BAr$^f_4$**·$0.5C_6H_{14}$, and **7-BAr$^f_4$** in CIF format, are available on the WWW under http://dx.doi.org/10.1002/anie.201508940.



Scheme 2. Synthesis of the acyclic cationic germylene analogue **2-BAr$^f_4$**.

crystallography confirms a monomeric structure in the solid state featuring a two-coordinate acyclic germyliumylidene cation (Figure 1) engaged in no close interactions with the [BAr$^f_4$]$^-$ counter-ion (closest contact 7.33 Å). Cation formation is also reflected in Ge–C$_{NHC}$ and Ge–C$_{alkyl}$ bond lengths [2.082(1) and 1.955(2) Å, respectively] which are markedly shorter than the corresponding distances in **1** [2.118(1) and 2.046(1) Å; see the Supporting Information].

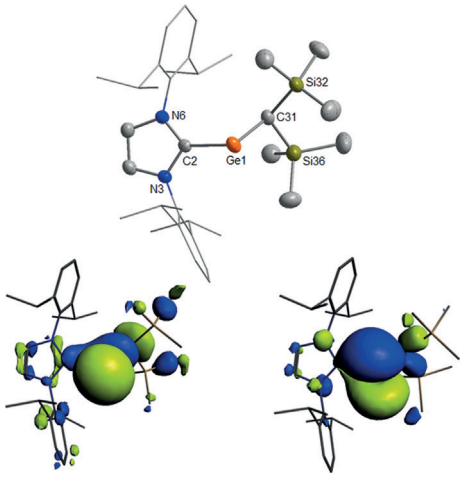
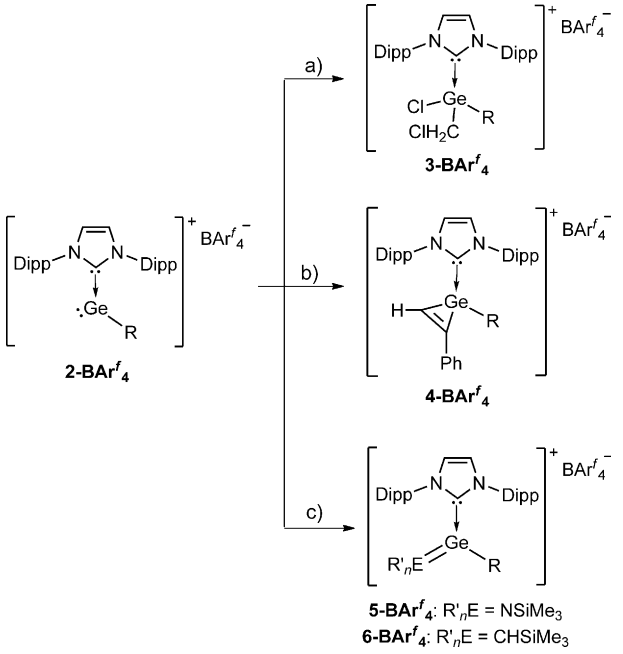


Figure 1. Molecular structure of the cationic component of **2-BAr$^f_4$** as determined by X-ray crystallography (counter-anion and H atoms omitted, and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 50% probability level). Selected bond lengths (Å) and angles (°): Ge1-C2 2.082(1), Ge1-C31 1.955(2), C2-Ge1-C31 102.7(1). DFT calculated HOMO (left, −8.39 eV) and LUMO (right, −6.46 eV) of the cationic component of **2-BAr$^f_4$**. Density isovalue = 0.03.[27]

To better understand the electronic structure of **2**$^+$, DFT calculations were carried out at the BP86/TZP level using the ADF software suite (Supporting Information). These accurately reproduce the key geometric parameters, and reveal the ambiphilic nature of the germanium center: the HOMO, essentially a germanium-centered lone pair, features significant metal 4s (13.6%) and 4p character (29.5%), while the LUMO is dominated by Ge 4p$_z$ character (70.4%; Figure 1). Most interestingly, the calculated HOMO–LUMO gap (187 kJ mol^{-1}) is small, being in the range of other Main Group compounds capable of small molecule activation,[14] and consistent with the lack of π-donor substituents α to the metal center. Thus, despite its cationic nature, the lability of **2**$^+$ in oxidative bond activation processes can be foreseen.[15]

These predictions are borne out by initial experimental observations: orange crystals of **2-BAr$^f_4$** dissolve immediately in CH_2Cl_2 at ambient temperature to give a colorless solution. NMR studies reveal the quantitative formation of [(IDipp)-{(Me$_3$Si)$_2$CH}Ge(CH$_2$Cl)Cl][BAr$^f_4$] (**3-BAr$^f_4$**) by oxidative addition of a single C–Cl bond [Scheme 3 and Figure 2(a)].



Scheme 3. Oxidative reactivity of **2-BAr$^f_4$**. Key reagents and conditions: a) CH_2Cl_2, 25 °C, 5 min; b) PhCCH, fluorobenzene, 25 °C, 5 min; c) R′$_n$EN$_2$, fluorobenzene, 25 °C.

This facile insertion reactivity contrasts with other two-coordinate germylene-type cations (which can be synthesized and manipulated unchanged in CH_2Cl_2 solution).[11a–c,12a,b] Further evidence of the capability of **2**$^+$ to undergo formal oxidation is obtained from its reaction with PhCCH, although rather than C–X bond cleavage, this chemistry proceeds through [2+1] cycloaddition to give the germacyclopropene complex [(IDipp){(Me$_3$Si)$_2$CH}Ge(HCCPh)][BAr$^f_4$] (**4-BAr$^f_4$**). Similar reactivity has previously been observed for neutral germylenes with related alkyne substrates, although not for cationic systems.[16] The presence of the vinylidine fragment is signaled by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, which reveal a characteristic **HC**=CPh resonance at δ_H = 8.34 ppm with an accompanying ^{13}C{^{1}H} NMR signal at δ_C = 137.7 ppm.[17] The structure of **4-BAr$^f_4$** was unambiguously confirmed by X-ray crystallography [Figure 2(b)], with the C31-C32, Ge1-C31, and Ge1-C32 bond lengths [1.330(5), 1.903(3), and 1.913(3) Å, respectively] and the C31-Ge1-C32 angle [40.8(2)°] further corroborating the presence of a germacyclopropene unit.[16]

The propensity of **2-BAr$^f_4$** to readily and cleanly undergo oxidation to Ge^{IV} species therefore prompted us to probe its suitability in the synthesis of cationic complexes featuring Ge=E multiple bonds, on the basis that the net positive charge would discourage the sorts of di- or oligomerization processes

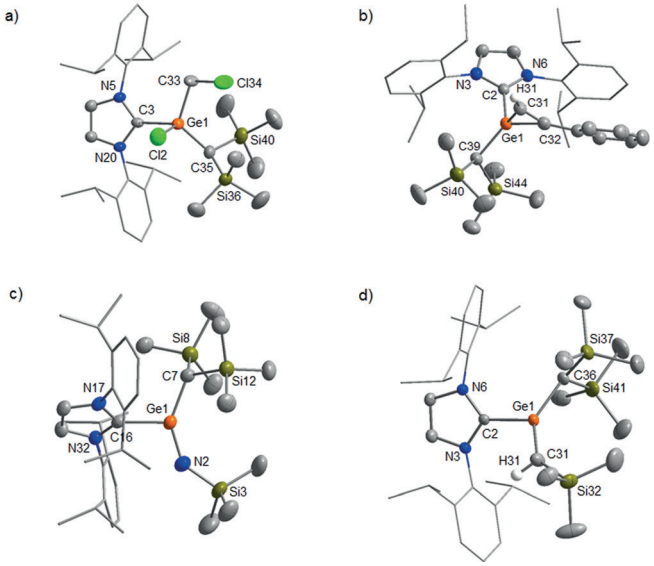


Figure 2. Molecular structures of the cationic components of a) **3-BAr$^f_4$**, b) **4-BAr$^f_4$**, c) **5-BAr$^f_4$**, and d) **6-BAr$^f_4$** as determined by X-ray crystallography (counter-anions and most H atoms omitted, and Dipp groups shown in wireframe format for clarity; thermal ellipsoids set at the 50% probability level). Selected bond lengths (Å) and angles (°): (for **3-BAr$^f_4$**) Ge1-C3 2.021(4), Ge1-C35 1.937(5), C3-Ge1-C35 118.0(1); (for **4-BAr$^f_4$**) Ge1-C2 1.992(3), Ge1-C39 1.941(3), C31-C32 1.330(5), C31-Ge1-C32 40.8(2); (for **5-BAr$^f_4$**) Ge1-C16 1.992(4), Ge1-C7 1.930(4), Ge1-N2 1.669(4), C16-Ge1-C7 109.7(1), C16-Ge1-N2 107.5(1); (for **6-BAr$^f_4$**) Ge1-C2 1.996(3), Ge1-C36 1.939(3), Ge1-C31 1.761(3), C2-Ge1-C31 109.0(1), C2-Ge1-C36 112.3(1).[27]

seen for neutral analogues.[18,19] Accordingly, the reaction of **2-BAr$^f_4$** with Me_3SiN_3 at ambient temperature yields N_2 and the pale yellow imido complex [(IDipp){$(Me_3Si)_2$CH}Ge(NSiMe_3)][BAr$^f_4$] (**5-BAr$^f_4$**) in 57% yield (Scheme 3). The formation of a Ge^{IV} imido complex is signaled (i) by the appearance of the NHC C(2) signal at $\delta_C = 155.2$ ppm, that is, in a range similar to other Ge^{IV} complexes (for example, **3/4-BAr$^f_4$**, $\delta_C = 152.1/155.1$ ppm; see the Supporting Information), and (ii) by the presence of two $SiMe_3$ signals (at $\delta_H = -0.19$ and 0.06 ppm) in a 1:2 ratio (in CD_2Cl_2), for the $NSiMe_3$ and $CH(SiMe_3)_2$ units, respectively. The monomeric nature of **5-BAr$^f_4$** is confirmed crystallographically (Figure 2c), and is in contrast to the observation that smaller N-substituents (and even $SiMe_3$) are known to give rise to dimeric charge-neutral germa-imines, despite the presence of bulky supporting ligands.[20] The Ge=N bond and pendant substituents (C7, C16, and Si3) lie within a single plane (largest deviation from the least-squares plane = 0.04 Å), to which the planar NHC heterocycle is inclined at an angle of 49.7°. Moreover, the Ge1–N2 bond length [1.669(4) Å] is very short in comparison to those reported previously for Ge=N double bonds [1.688(9)–1.704(5) Å],[10a,21] and, indeed, is even shorter than that calculated for the parent unsubstituted system $H_2Ge{=}NH$ [1.695 Å],[22] presumably reflecting the orbital contraction engendered by the large partial positive charge borne by the germanium center (Mulliken charge, ca. +1.07; see the Supporting Information).

DFT calculations also recreate the important metric parameters of $\mathbf{5}^+$, and allow evaluation of key molecular orbitals defining the Ge=N interaction. Thus, while the HOMO is essentially an N-centered lone pair (Supporting Information), the HOMO−1 is shown to possess Ge–N π-bonding character (N 27.7%, Ge 11.0% pπ contribution; Figure 3). There appears to be no significant contribution to HOMO-1 from the NHC π-system, thereby supporting a description of $\mathbf{5}^+$ as featuring a discrete Ge=N double bond.

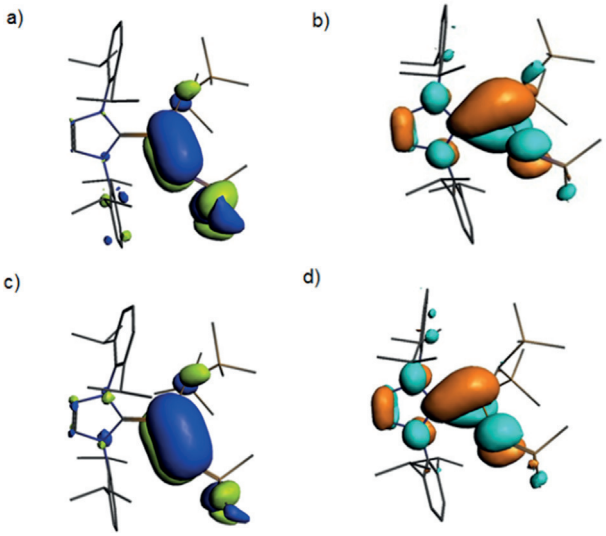


Figure 3. DFT calculated MOs of the cationic components of **5-BAr$^f_4$** [a) HOMO-1 (−8.38 eV) and b) LUMO (−5.71 eV)] and **6-BAr$^f_4$** [c) HOMO (−7.81 eV) and d) LUMO (−5.40 eV)]. Density isovalue = 0.03.

Previously reported germene complexes have been stabilized by electronic effects (for example, by resonance stabilization through an ylide form/charge transfer to an aromatic π system, or by conjugation with an alkyne moiety) in conjunction with comprehensive steric shielding of both the germanium and carbon atoms by bulky substituents.[23] Given its use in Ge=N bond formation, we hypothesized that **2-BAr$^f_4$** might be utilized to synthesize a cationic species containing a discrete Ge=C double bond, potentially even one containing a less sterically protected primary alkylidene fragment, CH(R).[24] Accordingly, **2-BAr$^f_4$** reacts readily with Me_3SiCHN_2 by N_2 elimination to generate the system [(IDipp){$(Me_3Si)_2$CH}Ge{CH(SiMe_3)}][BAr$^f_4$] (**6-BAr$^f_4$**) as a colorless crystalline material in excellent yield (90%; Scheme 3). The presence of the **CH**$SiMe_3$ fragment in the product is demonstrated by characteristic resonances at $\delta_H = 5.02$ ppm and $\delta_C = 131.5$ ppm (in CD_2Cl_2),[25] and the monomeric nature of the complex established by X-ray crystallography (Figure 2d). At a superficial level, **6-BAr$^f_4$** is of interest in containing three different types of C-donor, that is, alkyl, alkylidene, and N-heterocyclic carbene ligands, with associated Ge–C bond lengths of 1.939(3) (Ge1–C36), 1.761(3) (Ge1–C31), and 1.996(3) Å (Ge1–C2), respectively. With respect to the alkylidene ligand, the sums of bond angles around Ge1 and C31 are 359.9 and 360.0°, respectively, and the "twist" angle at the Ge=C double bond (that is, between the C2–Ge1–C36 and Si32–C31–H31 planes) is close to zero

(7.2°). The Ge1–C31 bond length is very short, shorter even than that calculated for the parent germaethene $H_2Ge{=}CH_2$ (1.773 Å),[26] while the Ge=C bonds determined for charge transfer stabilized systems (those featuring significant contributions from $R_2Ge^{+}{-}CR'_2{}^{-}$ resonance forms) are significantly longer (> 1.80 Å).[23a,c] The presence of a localized Ge=C double bond in **6-BAr$^f_4$** is also supported by DFT calculations, with the HOMO shown to constitute a Ge–C π-bonding orbital, and the LUMO the corresponding π*-orbital (Figure 3c,d). As with **5-BAr$^f_4$** there is little discernible delocalization of the Ge–C π-bonding MO into the NHC framework, reflecting a torsion angle of 40.3° between the N-heterocycle and C31-Ge1-C36 planes. Thus, while the Ge1–C2 bond length [1.996(3) Å] and the corresponding distance in **5-BAr$^f_4$** [1.992(4) Å] are significantly shortened from the corresponding distance in **2-BAr$^f_4$** [2.082(1) Å], this is thought to be due to the smaller size of the Ge^{IV} (rather than Ge^{II}) center instead of any significant π-bonding interaction with the NHC heterocycle.

In conclusion, we have isolated an acyclic two-coordinate monocationic germylene **2-BAr$^f_4$**, which features essentially no π-donor stabilization of the metal center and hence has a very small HOMO–LUMO gap (187 kJ mol^{-1}). This facilitates versatile oxidative reaction chemistry including C-Cl bond insertion and [2+1] cycloaddition. Most interestingly, it allows for the synthesis of the first examples of heavier Group 14 element cations containing M=E multiple bonds (E = C, N). These systems (for M = Ge) feature the shortest M–C and M–N bonds reported for simple germanium alkylidene and imido derivatives, presumably owing (at least in part) to the orbital contraction brought about by the large partial positive charge at the metal center. From a synthetic viewpoint, the use of an electrostatic (rather than wholly steric) approach to discourage aggregation allows access to a system containing a primary (that is, CH-containing) alkylidene fragment.

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[27] CCDC 1426694-1426700 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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