Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Article pubs.acs.org/IC

Linking Low-Coordinate Ge(II) Centers via Bridging Anionic N-Heterocyclic Olefin Ligands

Emanuel Hupf,^{†,§} Felix Kaiser,^{‡,§} Paul A. Lummis,^{†,§} Matthew M. D. Roy,[†] Robert McDonald,[†] Michael J. Ferguson,[†][©] Fritz E. Kühn,[‡][©] and Eric Rivard^{*,†}[©]

[†]Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta T6G 2G2, Canada [‡]Catalysis Research Center and Department of Chemistry, Technische Universität München, Lichtenbergstra β e 4, 85748 Garching bei München, Germany

Supporting Information

ABSTRACT: We introduce a large-scale synthesis of a sterically encumbered N-heterocyclic olefin (NHO) and illustrate the ability of its deprotonated form to act as an anionic four-electron bridging ligand. The resulting multicenter donating ability has been used to link two low oxidation state Ge(II) centers in close proximity, leading to bridging Ge-Cl-Ge and Ge-H-Ge bonding environments supported by Ge₂C₂ heterocyclic manifolds. Reduction of a dimeric [RGeCl]₂ species (R = anionic NHO, [(MeCNDipp)₂C= CH]⁻; Dipp = 2,6-ⁱPr₂C₆H₃) did not give the expected acyclic



RGeGeR analogue of an alkyne, but rather ligand migration/disproportionation transpired to yield the known diorganogermylene R₂Ge and Ge metal. This process was examined computationally, and the ability of the reported anionic NHO to undergo atom migration chemistry contrasts with what is typically found with bulky monoanionic ligands (such as terphenyl ligands).

INTRODUCTION

Ligand design remains a lynchpin of modern inorganic chemistry, with the use of bulky ligands to access reactive low coordinate bonding environments being a particularly active field of study.¹ Recently, main group compounds have been shown to exhibit "transition-metal like" reactivity, and this concept relies on the presence of low coordination numbers for small molecule activation² leading to nonmetal mediated catalysis.³ The development of bridging ligands that retain a high degree of steric bulk^{4,5} adds a new dimension of reactivity, including the cooperative binding of substrates (cf. H^{-} and F^{-} encapsulation by bis(boranes)).⁶ Chart 1 outlines recently prepared low valent main group species supported by bulky bridging ligands,^{4,5} wherein heterocycle formation allows the placement of two electron-deficient/reactive centers in close proximity.

In this article, we demonstrate the ability of a sterically hindered vinylic ligand (R) [MeIPrCH]⁻ (MeIPr = [(MeCN-Dipp)₂C; Dipp = $2,6^{-i}Pr_2C_6H_3$],^{7,8} to link two low oxidation state Ge(II) centers via a terminal carbon atom acting as a four-electron donor (Scheme 1). Computational studies also explain our inability to access an inorganic alkyne RGeGeR upon reduction of the Ge(II) chloride precursor [(MeIPrCH)-GeCl]₂; this observation can be linked to the high propensity of the reported anionic NHO ligand to form bridging isomers leading to the eventual extrusion of Ge via the isomer $R_2Ge=Ge.$ ⁹ While the bridging of two Ge(II) centers via anionic heteroatom-based ligands to yield dimeric [(μ -R')GeCl]₂ species (e.g., $R' = -NR_2$, $-PR_2$, -OR, or -SR) is

Chart 1. Selected Examples of Sterically Hindered Bridging Ligands and Their Use to Link Electron-Deficient Main Group Centers^a



^aMes = 2,4,6-Me₃C₆H₂; Trip = 2,4,6-ⁱPr₃C₆H₂.

known,¹⁰ herein we show that added interactions between the linked Ge(II) centers in the form of bridging Ge-Cl-Ge and Ge-H-Ge interactions are possible, opening the door for possible cooperative activation of substrates in catalysis.

RESULTS AND DISCUSSION

This study arose from our exploration of the ligating properties of a recently reported diorganogermylene (MeIPrCH)₂Ge: (1).^{/1} Motivated by our past syntheses of Ge(II) chains, such

Received: May 17, 2019



^{*a*}Herein multiple ligand-element (E) interactions are possible, as shown in red.

as $IPr \cdot GeCl_2GeCl_2$ ($IPr = [(HCNDipp)_2C:])$,^{11a} we combined 1 with $GeCl_2 \cdot dioxane$ in tetrahydrofuran (THF). The resulting highly moisture-sensitive dark yellow-orange solid was shown by X-ray crystallography (Figure 1) to be the halide/ligand



Figure 1. Molecular structure of $[(^{Me}IPrCH)GeCl]_2(2)$ with thermal ellipsoids presented at a 50% probability level. The hydrogen atoms H4 and H4' are shown with an arbitrary radius, and the Dipp groups are depicted in wireframe. Selected bond lengths (Å) and angles (deg): Ge1–Ge2 2.8941(7), Ge–Cl 2.3191(5), Ge–C4 2.0745(14), Ge–C4' 2.1117(15), C1–C4 1.415(2); C4–Ge–C4' 80.78(7), Ge–C4–Ge' 87.47(6), C4–Ge–Cl 95.36(4).



exchange product $[({}^{Me}IPrCH)GeCl]_2$ (2) (eq 1). The key structural feature in 2 is the presence of a puckered Ge_2C_2 ring supported by bridging (${}^{Me}IPrCH$)⁻ ligands; this ring is capped by *syn*-arranged Ge–Cl bonds. The core Ge–C distances [2.0745(14)-2.1117(17) Å] are similar in length as the long Ge–C dative bond in IPr-GeCl₂ [2.112(2) Å],¹² suggesting a lack of Ge–C π -bonding in 2. The transannular Ge…Ge separation in 2 [2.8941(7) Å] is consistent with an absence of Ge–Ge bonding, a finding that has been corroborated by our density functional theory (DFT) computations.¹³ As expected, the presence of bridging interactions involving the (${}^{Me}IPrCH$)⁻ ligands in 2 leads to substantially longer "vinylic" C–C lengths [C1–C4 = 1.415(2) Å] in comparison to those found in the Article

two-coordinate diorganogermylene (^{Me}IPrCH)₂Ge: (1) [1.364(3) Å].^{7f} Furthermore, the computed gas-phase dissociation of **2** into two monomeric ^{Me}IPr=CH-GeCl units has been predicted to be slightly exothermic ($\Delta H_{\text{Diss}} = -1.11 \text{ kcal mol}^{-1}$).

Given that two reactive Ge(II)-halide environments are held in close proximity within 2, we attempted to promote Ge-Ge bond formation via reduction. Combining 2 with the common reducing agents, Na, K, Na/K, KC₈, Rieke Zn or Mg, or the milder reductant $Na[C_{10}H_8]$, consistently afforded the known germylene (^{Me}IPrCH)₂Ge: (1) (Scheme 2; bottom-left reaction). Given that 1 was originally prepared by the reduction of (MeIPrCH)GeCl₃ with 3 equiv of KC₈,^{7f} it is plausible that $[(^{Me}IPrCH)GeCl]_2 2$ is an intermediate in this process. All attempts to isolate 2 by directly reducing (MeIPrCH)GeCl₃ were unsuccessful, and in each case overreduction to yield the germylene 1 and Ge metal transpired; thus, the reduction of 2 is fast. The ease at which the [^{Me}IPrCH]⁻ ligand can bridge two Ge centers and eventually yield the observed disproportionation products will be revisited later.

Motivated by the presence of long Ge-Cl bonds in [(^{Me}IPrCH)GeCl]₂ (2) [2.3191(5) Å], this complex was combined with Na[BAr^F₄] in Et₂O (Ar^F = 3,5-(F₃C)₂C₆H₃). The resulting orange-red solid was identified by single-crystal X-ray diffraction as [{(^{Me}IPrCH)Ge}₂(μ -Cl)][BAr^F₄] ([3]- $[BAr_{4}]$; $[3]^{+}$ contains a butterfly-shaped $Ge_{2}C_{2}$ ring (Figure 2) capped by a bridging chloride to form a propellane structure¹⁴ with Ge–Cl distances of 2.457(1) and 2.507(1) Å. Attempts to synthesize a dicationic species $[Ge{\mu}]$ $(^{Me}IPrCH)_{2}$ Ge]²⁺ by reacting $[(^{Me}IPrCH)GeCl]_{2}$ (2) with 2 equiv of $AlCl_3$ gave the monocationic $[3]^+$ as major product in ca. 70% spectroscopic yield, according to ¹H NMR analysis of the crude reaction mixture. However, the intended dication $[Ge{\mu-(MeIPrCH)_2}Ge]^{2+}$ was examined computationally and was found to be a minimum structure on the potential energy surface. Notably, the computed Ge-Ge separation of the dication is predicted to be 2.9466 Å (Figure S24)¹³ and no sign of Ge-Ge bonding was found, either by Natural Bond Order (NBO)¹⁵ or Atoms-in-Molecules (AIM)¹⁶ analyses (Figure S36c in the Supporting Information).¹³ Moreover, this bonding scenario was complemented by our Non-Covalent Index (NCI)¹⁷ study, which revealed weakly repulsive Ge…Ge interactions (Figure S37c in the Supporting Information).¹³

As Ge(II) hydrides have played important roles in main group catalysis^{3a,d} and as precursors to Ge nanomaterials,¹⁸ we attempted the synthesis of the hydride dimer [(MeIPrCH)-GeH]₂. Addition of 2 equiv of Li[HBEt₃] to 2 in THF eventually gave X-ray quality single crystals of the hydridebridged salt $[{(^{Me}IPrCH)Ge}_2(\mu-H)][BEt_4] [4][BEt_4]$ (Scheme 2 and Figure 3). The Ge---Ge separation of 2.584(1) Å in [4][BEt₄] is in the range expected for a single bond, and is significantly shorter than the Ge…Ge distance of 2.8247(8) Å in Fässler's $[Ph_2ZrGe_4(\mu-H)]^{3-}$ cluster,¹⁹ which is the only other reported species with a structurally authenticated Ge-H-Ge unit. The Ge-H distances in $[4][BEt_4]$ of 1.71(4) and 1.70(5) Å were the same within error as those [1.74(3) Å average (avg)] found in $[Ph_2ZrGe_4(\mu-H)]^{3-.19}$ Intrigued by the short Ge…Ge distance in $[4][BEt_4]$, we performed a series of DFT computations on the cation $[4]^+$.¹³ The geometrical parameters of the computed optimized structure of $[4]^+$ were in good agreement with the crystallographically determined molecular structure. The

Scheme 2. Formation of the Cationic Halide- and Hydride-Bridged Ge(II) Cations $[3]^+$ and $[4]^+$, as well as the Low-Coordinate Germylenes 1 and 5 from the Ge(II) Precursor 2





Figure 2. Molecular structure of $[\{(^{Me}IPrCH)Ge\}_2(\mu-Cl)][BAr^F_4]$ ([3][BAr^F_4]) with thermal ellipsoids presented at a 50% probability level. The hydrogen atoms H4 and H54 are shown with an arbitrary radius, and the Dipp groups are depicted in wireframe; the $[BAr^F_4]^$ anion was omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–Ge2 2.7547(6), Ge1–Cl 2.457(1), Ge2–Cl 2.507(1), Ge1–C4 2.087(3), Ge2–C54 2.068(4), C1–C4 1.434(4), C51–C54 1.436(4); Cl–Ge1–C4 88.44(8), Cl–Ge1–C54 88.19(8), Cl–Ge2– C4 87.54(8), Cl–Ge2–C54 87.15(8), C4–Ge1–C54 78.3(1), C4– Ge2–C54 79.0(1), Ge1–Cl–Ge2 67.41(3).

computed Ge…Ge separation was 2.620 Å, and interestingly, as was also found for the dicationic $[Ge{\mu-(^{Me}IPrCH)_2}Ge]^{2+}$, no sign of Ge–Ge bonding could be located by either NBO or AIM¹⁶ analyses (Figure S36b in the Supporting Information) despite the significantly shorter Ge–Ge distance in $[4]^{+,13}$ Moreover, a weakly repulsive Ge…Ge interaction was located by a NCI study (Figure S37b in the Supporting Information).¹³ Thus, one needs to be careful in assigning bonding



Figure 3. Molecular structure of $[\{(^{Me}IPrCH)Ge\}_2(\mu-H)][BEt_4]$ ([4][BEt_4]) with thermal ellipsoids presented at a 50% probability level. The hydrogen atoms H1, H4, and H54 are shown with an arbitrary radius, and the Dipp groups are depicted in wireframe; the [BEt_4]⁻ anion was omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-Ge2 2.584(1), Ge1-H1 1.71(4), Ge2-H 1.70(5), Ge1-C4 2.088(4), Ge2-C34 2.077(4), C1-C4 1.425(6), C31-C34 1.422(6); H1-Ge1-C4 79(2), H1-Ge1-C34 81(3), H1-Ge2-C4 80(3), H1-Ge2-C34 80(2), C4-Ge1-C34 78.1(2), C4-Ge2-C34 78.3(2), Ge1-H1-Ge2 98(3).

schemes on the basis of short interatomic distances alone, especially when the elements are hydride-bridged. The central Ge–H–Ge unit in [4]⁺ can best be described as a 3-center-2-electron bond with an average computed Ge–H Wiberg Bond Index (WBI) of 0.45.²⁰ Pronounced hydridic character was also found by both Natural Population Analysis (NPA) and AIM (computed charges of -0.19 and -0.45 e, respectively). Despite numerous attempts, we were only able to obtain bulk quantities of [4]⁺ as its analytically pure [BEt₄]⁻ salt a single

time. In all other attempts, $[4][BEt_4]$ was obtained with various quantities of cocrystallized mixed hydridoalkylborate salts $[4][BH_xEt_v]$.

The formation of the perethylated $[BEt_4]^-$ anion likely proceeds via a known H/Et scrambling reaction between BEt₃ (a byproduct in the synthesis of $[4]^+$) and $[HBEt_3]^{-21}$ Fortunately in each preparation, the cationic portion of the cocrystallized salts remained as $[4]^+$. While a pure sample of $[4][BEt_4]$ was stable at room temperature in THF, the mixed salts $[4][BH_xEt_y]$ slowly decomposed in THF to give the Nheterocyclic olefin ^{Me}IPrCH₂,²² (^{Me}IPrCH)₂Ge: (1),^{7f} and various unidentified products, likely via anion (B–H hydride) mediated decomposition of $[4]^{+.23}$

The hydrogen-bridged cation $[4]^+$ affords two shielded second-order multiplet ¹H NMR resonances spanning from -1.13 to -1.27 ppm (d_8 -THF), assigned to ligand -CH-Ge and bridging hydride Ge-H-Ge environments, respectively (Figure 4). As anticipated, the deuterium analogue $[4^D]^+$



Figure 4. Superposition of ligand –CH-Ge and Ge-H-Ge/Ge-D-Ge resonances in the ¹H NMR spectra (d_8 -THF) of [4][BEt₄] (blue), [4^D][BH_xEt_y] (red), and the ²H{¹H} NMR spectrum of [4^D]-[BH_xEt_y] (black).

(prepared from Li[DBEt₃] and **2**) yielded a triplet ¹H NMR resonance at -1.28 ppm due to coupling of the ligand *CH* proton with the deuterium atom in the Ge-*D*-Ge bridge (³*J*_{HD} = 1.9 Hz; Figure 4), while a Ge-*D*-Ge resonance was located at -1.08 ppm in the ²H{¹H} spectrum for [4^D]⁺ (Figure 4).¹³

Our synthetic investigations of $[(^{Me}IPrCH)GeCl]_2$ (2) concluded with an attempt to induce HCl loss by treatment with Li(THF)₄[CPh₃] as a possible Brønsted base. However, direct Cl/CPh₃ exchange transpired to yield the monomeric germylene ($^{Me}IPrCH$)Ge(CPh₃) (5) (Scheme 2) as an orangered solid (see Figure S1 in the Supporting Information for the X-ray structure).¹³ The metrical parameters of 5 were in line with what is expected for an anionic NHO-supported diorganogermylene.^{7f}

To gain a better understanding of the reduction pathway from $[(^{Me}IPrCH)GeCl]_2$ (2) to $(^{Me}IPrCH)_2Ge:$ (1) and bulk Ge metal, we investigated possible intermediates by DFT computations at the B3LYP/cc-pVDZ level.¹³ We started with the assumption that reduction of 2 would initially yield the cyclic Ge(I) dimer cyclic-Ge(μ -R)₂Ge [R = (^{Me}IPrCH)⁻] (Figure 5); as expected this species features a Ge-Ge single bond [2.4538 Å]. Moreover, cyclic-Ge(μ -R), Ge is a local minimum on the potential energy surface and is isostructural to $Ge(\mu-H)_2Ge$, which has been predicted to be the most stable isomer within the parent Ge₂H₂ structural series.²⁴ Interestingly, the Ge–Ge bond in *cyclic*-Ge(μ -R)₂Ge is derived from the canted overlap of Ge(p) orbitals to yield a "bent" σ bond (Figure 5) as determined by real-space bonding analysis according to the AIM and Electron-Localizability Indicator (ELI-D) space-partitioning schemes (Figures 5, S35, S36d, and S38d).¹³ This Ge-Ge unit in cyclic-Ge(μ -R)₂Ge has been computed to readily accept a proton [$\Delta H = -296.4$ kcal mol^{-1} ; Eqn 2] to yield the hydrogen-bridged cation [4]⁺. For reference, a similar proton affinity has been computed for the N-heterocyclic carbene ITr (ITr = $[(HCNCPh_3)_2C:)^{25}$

A plausible isomer of *cyclic*-**Ge**(μ -**R**)₂**Ge** would be the open digermylene form, *acyclic*-**RGeGeR**, which was computed to be only +3.8 kcal mol⁻¹ higher in energy (Figure 5). Thus, one sees a minimal energy difference between doubly bridging and nonbridging [^{Me}IPrCH]⁻ coordination. *acyclic*-**RGeGeR** contains a typical Ge–Ge single bond (Figures S35 and S36e in



Figure 5. Computed relative enthalpies for the formation of the diorganogermylene 1 from the *cyclic*-Ge(μ -R)₂Ge. The enthalpy of sublimation of germanium is included in the final step, decomposition of R₂Ge=Ge into R₂Ge and Ge(s) ($\Delta_{sub}H = 89.5$ kcal mol⁻¹).²⁷ (inset) The highest occupied molecular orbital of the *cyclic*-LGe(μ -R)₂Ge representing the overlap of the Ge(p) orbitals and the geometry of the monobridged RGe(μ -R)Ge intermediate.



the Supporting Information)¹³ and is structurally similar to related 1,2-diaminodigermylenes reported by Jones and coworkers.²⁶

Both the cyclic-Ge(μ -R)₂Ge and acyclic-RGeGeR isomers can potentially yield the digermavinylidene R₂Ge=Ge: via 1,2ligand migration (Figure 5).²⁸ A monobridged intermediate for this process, $RGe(\mu - R)Ge$, was also located and found to be similar in relative energy as $R_2Ge=Ge$; notably $RGe(\mu-R)Ge$ has considerable Ge=Ge multiple bond character (short Ge-Ge distance 2.294 Å), which is slightly shorter than the corresponding distance of 2.391 Å in R₂Ge=Ge. The latter species is similar to Aldridge's digermavinylidene ^BR₂Ge=Ge $({}^{B}R = (HCNDipp)_{2}B^{-}).{}^{9}$ Conversion of either cyclic-Ge(μ -R)₂Ge or acyclic-RGeGeR into RGe(μ -R)Ge and R₂Ge=Ge was computed to be thermodynamically feasible $\left[\Delta H = +14.3\right]$ to 18.1 kcal mol⁻¹], while decomposition of $R_2Ge=Ge$ into R_2 Ge (1) and Ge_(s) was predicted to be an exothermic process $\left[\Delta H = -33.9 \text{ kcal mol}^{-1}\right]$, once the energetics associated with the formation of bulk germanium metal were considered (Figure 5).⁹ Comparative Non-Covalent Index (NCI) analyses were performed to gain insight into the different stabilities of R₂Ge=Ge and the isolable boryl-stabilized digermavinyldene ${}^{B}\bar{R}_{2}Ge=Ge$ (Figure S39).¹³ This study revealed additional dispersive interactions between the terminal Ge=Ge unit and the flanking boryl ligands ^BR₂Ge=Ge,²⁹ leading to a more enclosed Ge=Ge vicinity when compared to its anionic-NHO counterpart $R_2Ge=Ge$. Thus, ${}^BR_2Ge=Ge$ represents another example of how ligand-derived dispersion forces can stabilize unusual bonding environments.³⁰

CONCLUSION

The synthesis of the dimeric Ge(II) species $[(^{Me}IPrCH)-GeCl]_2(2)$ is reported, wherein with two Ge centers are linked by a bulky anionic N-heterocyclic olefin ligand. In addition, the ability of related Ge₂C₂ cyclic scaffolds to support bridging μ chloride and μ -hydride units between low-valent Ge(II) centers was shown. Accompanying computational studies revealed the ease at which the $[^{Me}IPrCH]^-$ ligand can form bridged species en route to final 1,2-migration. We hope that the ligand binding mode introduced in this study will encourage the future construction of linked bimetallic species for use in cooperative catalysis.

EXPERIMENTAL SECTION

General. All reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen or argon or in a nitrogen/argon-filled glovebox (Innovative Technology, Inc./ MBraun). Solvents were dried using a Grubbs-type solvent purification system manufactured by Innovative Technology, Inc. or MBraun, degassed, and stored under an atmosphere of nitrogen or argon prior to use.³¹ Fluorobenzene was dried by refluxing over calcium hydride, followed by distillation, degassing (freeze–pump–thaw method), and storage over molecular sieves prior to use. 1,4-Diazabicyclo[2.2.2]octane (DABCO), germanium(II) chloride–dioxane (1:1 complex), paraformaldehyde, methyl iodide, potassium *tert*-butoxide, HCl (4.0 M in dioxane), LiD, triethylborane (1.0 M solution in hexanes), and SuperHydride (1.0 M solution of Li[HBEt₃]

in THF) were purchased from Aldrich and used as received. Germanium tetrachloride was obtained from Gelest and used as received. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na- $[BAr_{4}^{F}]$) was purchased from Ark Pharmaceuticals and heated under vacuum at 110 °C for 48 h prior to use, after which it was stored inside a glovebox at room temperature. (^{Me}IPrCH)₂Ge (^{Me}IPr = $[(MeCNDipp)_2C; Dipp = 2,6^{-1}Pr_2C_6H_3)$,^{7f} [Li(THF)₄][CPh₃],³² KC₈,³³ and (DippN=CMe)₂³⁴ were prepared according to literature procedures. ¹H, ¹³C{¹H}, ¹¹B{¹H}, and ¹⁹F{¹H} NMR spectra were recorded on a Varian Inova-400, Varian Inova-500, Bruker AVHD500 cryo, Bruker AV400, or Varian Inova-700 spectrometer and referenced externally to SiMe₄ (¹H, ¹³C{¹H}), F₃B·OEt₂ (¹¹B), and CFCl₃ (¹⁹F{¹H}), respectively. ²H{¹H} NMR was referenced internally to THF (1.73 ppm downfield shifted to SiMe₄). Because all NMR samples were prepared in a glovebox containing solvent, minor contamination of NMR solvent is sometimes observed. Where applicable, these minor impurities are noted on the spectra provided in the Supporting Information. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI MS) measurements were conducted on a Waters LCT, liquid injection field desorption ionization special ionization cell obtained from Linden CMS GmbH. Elemental analyses and UV-visible spectroscopic measurements were performed by the Analytical and Instrumentation Laboratory at the University of Alberta or the Mikroanalytisches Labor der Technischen Universität München. Infrared spectra were recorded using a Nic-Plan FTIR microscope. Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp apparatus.

Synthesis of Li[DBEt₃]. SuperDeuteride was prepared by a slightly modified procedure as described by Brown and co-workers,³⁵ adding BEt₃ (7.0 mmol, 1.0 M solution in hexanes) to a suspension of LiD (126 mg, 14.0 mmol) in 6 mL of THF. The resulting reaction mixture was stirred at room temperature for 12 h and filtered to give a clear solution of Li[DBEt₃] (0.53 M in THF/hexanes).

Large-Scale Synthesis of [^{Me}IPrH]Cl. N_iN' -Bis-(2,6-diisopropylphenyl)-butane-2,3-diimine (72.4 g, 179 mmol) was dissolved in 1.2 L of THF in an oven-dried Schlenk flask and cooled in an ice bath. Paraformaldehyde (8.06 g, 268 mmol) was suspended in a 4.0 M solution of HCl in 1,4-dioxane (80.5 mL, 320 mmol), and this suspension was added to the yellow solution of diamine via cannula over a period of 20 min. The resulting suspension was warmed to room temperature and stirred for 18 h. The solvent was removed to final residual volume of ca. 200 mL, 600 mL of Et₂O was added, and the mixture was stored at -18 °C for 2 h. The crude product was then isolated by vacuum filtration and recrystallized from a mixture of 120 mL of MeOH and 700 mL of Et₂O. [^{Me}IPrH]Cl was isolated as a colorless crystalline solid (40.5 g, 50%). ¹H NMR analysis revealed the formation of pure [^{Me}IPrH]Cl with resonances that matched literature values.³⁶

Large-Scale Synthesis of ^{Me}IPrCH₂.³⁷ [^{Me}IPrH]Cl (35.5 g, 78.4 mmol) was suspended in 1 L of THF in an oven-dried Schlenk flask. KO^tBu (17.2 g, 154 mmol) was quickly added, and the slightly turbid mixture was stirred for 40 min. MeI (4.78 mL, 10.9 g, 76.8 mmol) was added, and the resulting yellow slurry was stirred for 40 h. The slurry was suction filtered through diatomaceous earth, the remaining filter cake was washed with 200 mL of THF, and the filtrate was evaporated to dryness. ^{Me}IPrCH₂ was isolated from the filtrate as a colorless solid (24.3 g, 72%) with ¹H NMR data consistent with the literature.²²

Large-Scale Synthesis of (^{Me}IPrCH)GeCl₃. ^{Me}IPrCH₂ (24.3 g, 56.5 mmol) and 1,4-diazabicyclo[2.2.2]octane (6.39 g, 56.5 mmol) were dissolved in 500 mL of toluene. GeCl₄ (6.44 mL, 12.1 g, 56.5 mmol) was added, and the suspension was stirred for 18 h. The suspension was filtered, the remaining filter cake was washed with 500 mL of THF, and the volatiles were removed from the filtrate in vacuo leaving a thick slurry behind. Addition of 300 mL of pentane caused further precipitation of the product that was isolated by filtration, washed with pentane (2 × 50 mL), and dried in vacuo. This procedure afforded (^{Me}IPrCH)GeCl₃ as a colorless solid (31.0 g, 91%) with spectroscopic data that matched those found in the literature.^{7f}

Large-Scale Synthesis of (^{Me}IPrCH)₂Ge (1). (^{Me}IPrCH)GeCl₃ (22.1 g, 36.3 mmol) and KC₈ (14.7 g, 109 mmol) were placed in an oven-dried Schlenk flask and cooled in an ice-bath, and 350 mL of Et₂O was quickly added. The resulting suspension was stirred for 18 h and filtered through diatomaceous earth, and the filter cake was washed with Et₂O (2×100 mL). The filtrate was then evaporated to dryness, and 100 mL of pentane was added, followed by stirring for 1 h. The resulting suspension was then stored at -30 °C for 18 h, and the red precipitate was isolated by filtration and washed with 5 mL of cold (-30 °C) pentane. The solid was dried in vacuo to give 1 as a red solid (8.75 g, 52%). The ¹H NMR spectrum of 1 is identical to that reported in the literature.^{7f}

Synthesis of [(MelPrCH)GeCl]₂ (2). (MelPrCH)₂Ge (0.251 g, 0.269 mmol) was dissolved in 10 mL of THF in a 20 mL scintillation vial to afford a deep red solution. To this solution was added Cl₂Ge· dioxane (0.062 g, 0.27 mmol) as a powder, and the resulting mixture was allowed to stir for 1 h, leading to an immediate color change to yellow. Removal of the volatiles in vacuo afforded a dark yelloworange solid that was washed with 2×3 mL of cold (-30 °C) hexanes to yield the desired product 2 (0.235 g, 81%). Crystals suitable for X-ray crystallographic analysis were obtained by adding 2 mL of toluene to the product, filtering this solution through a 1 cm plug of diatomaceous earth, and layering the filtered solution with an equal volume of hexanes. This mixture was then stored at -30 °C for 48 h, yielding yellow-orange crystals of 2. ¹H NMR (C₆D₆, 700 **MHz**): δ 1.01 (d, 12H, ${}^{3}J_{HH} = 7.0$ Hz, CH(CH₃)₂), 1.06 (d, 12H, ${}^{3}J_{\text{HH}} = 7.0 \text{ Hz}, \text{CH}(\text{CH}_{3})_{2}), 1.30 \text{ (d, 12H, } {}^{3}J_{\text{HH}} = 7.0 \text{ Hz}, \text{CH}(\text{CH}_{3})_{2}),$ 1.39 (s, 6H, ImCH₃), 1.45 (s, 6H, ImCH₃), 1.49 (d, 12H, ${}^{3}J_{HH} = 7.0$ Hz, CH(CH₃)₂), 2.78 (br, 4H, CH(CH₃)₂), 3.02 (sept, 4H, ${}^{3}J_{HH} =$ 7.0 Hz, $CH(CH_3)_2$), 3.03 (s, 2H, ^{Me}IPrCHGe), 7.12 (br d, 4H, ³ J_{HH} = 7.7 Hz, Dipp-*m*-H), 7.15 (d, 4H, ${}^{3}J_{HH} = 7.7$ Hz, Dipp-*m*-H), 7.21 (t, 2H, ${}^{3}J_{HH}$ = 7.7 Hz, Dipp-*p*-H), 7.25 (t, 2H, ${}^{3}J_{HH}$ = 7.7 Hz, Dipp-*p*-H). ¹³C{¹H} NMR (C₆D₆, 176 MHz): δ 9.1 (ImCH₃), 10.2 (ImCH₃), 24.0 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 25.1 $(CH(CH_3)_2)$, 28.9 $(CH(CH_3)_2)$, 29.1 $(CH(CH_3)_2)$, 49.4 (MeIPrCHGe), 122.8 (ArC), 124.8 (ArC), 128.4 (ArC), 130.5 (ArC), 132.0 (ArC), 140.2 (ArC), 147.4 (ArC), 158.8 (ArC), 162.3 (NCN). Anal. Calcd for C₆₀H₈₂Cl₂Ge₂N₄: C 67.01, H 7.69, N 5.21. Found: C 64.10, H 7.66, N 5.06%; despite repeated attempts, an acceptable value for C could not be obtained; please see Figures S2 and S3 for the ${}^{1}H$ and ${}^{13}C{}^{1}H$ NMR spectra of 2 as an indication of purity.¹³ mp (°C): 215 (dec). UV–Vis (THF): $\lambda_{max} = 424$ nm ($\varepsilon = 4010 \text{ L mol}^{-1} \text{ cm}^{-1}$).

Synthesis of $[{(^{Me}IPrCH)Ge}_2(\mu-CI)][BAr_4]$ (3). To an orangeyellow solution of 2 in 4 mL of Et₂O (0.112 g, 0.104 mmol) was added Na[BArF4] (0.093 g, 0.10 mmol), which resulted in an immediate color change to red-orange. This mixture was stirred for 2 h and then filtered through a 2 cm plug of diatomaceous earth. Removal of all volatiles from the filtrate in vacuo yielded 3 as a spectroscopically pure orange solid (0.198 g, 95%). This compound was recrystallized from a concentrated fluorobenzene solution that was layered with an equal volume of hexanes and stored at -30 °C for 48 h, yielding orange-yellow crystals of 3 suitable for single-crystal Xray diffraction. ¹H NMR (CD₂Cl₂, 700 MHz): δ 0.08 (s, 2H, -CH-Ge₂), 1.04 (d, 24H, ${}^{3}J_{HH} = 6.9$ Hz, CH(CH₃)₂), 1.12 (d, 24H, ${}^{3}J_{HH} =$ 6.8 Hz, $CH(CH_3)_2$), 1.86 (s, 12H, Im CH_3), 2.54 (sept, 8H, ${}^{3}J_{HH} =$ 6.8, $CH(CH_3)_2$), 7.21 (d, 8H, ${}^{3}J_{HH}$ = 7.8 Hz, Dipp-*m*-H), 7.45 (t, 4H, ${}^{3}J_{\text{HH}} = 7.8 \text{ Hz}, \text{ Dipp-}p\text{-}\text{H}), 7.56 \text{ (s, 4H, } [BAr^{F}_{4}]^{-} p\text{-}\text{H}), 7.72 \text{ (m, 8H, }$ $[BAr^{F}_{4}]^{-}$ m-H). $^{13}C{1H}$ NMR (CD₂Cl₂, 176 MHz): δ 10.3 (ImCH₃), 24.4 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 29.3 (CH(CH₃)₂), 50.8 (-CH-Ge₂), 118.0 (t, ${}^{3}J_{FC}$ = 3.8 Hz, [BAr^F₄]⁻ p-C), 125.2 (q, ${}^{1}J_{FC} = 272.4 \text{ Hz}, [BAr_{4}^{F}] - CF_{3}), 125.3 (N(CH_{3})C=C), 125.7 (Dipp$ *m*-C), 129.4 (qq, ${}^{2}J_{FC} = 31.5$ Hz, ${}^{4}J_{FC} = 2.8$ Hz, $[BAr_{4}^{F}]^{-}$ *m*-C), 130.5 (Dipp-*ipso*-C), 131.4 (Dipp-*p*-C), 135.4 ([BAr^F₄]⁻ *o*-C), 146.5 (Dippo-C), 157.1 (N₂CCH), 162.3 (q, ${}^{1}J_{BC} = 49.8 \text{ Hz}, [BAr_{4}^{F}]^{-} ipso-C$). ${}^{19}F$ NMR (CD₂Cl₂, 469 MHz): δ -62.9 (s, [BAr^F₄]⁻ CF₃). ¹¹B{¹H} NMR (CD₂Cl₂, 160 MHz): δ -6.6 (s, [BAr^F₄]⁻). Anal. Calcd for C92H94BClF24Ge2N4: C 58.06, H 4.98, N 2.94. Found: C 57.47, H

5.17, N 2.91%. **mp** (°C): 136–140. UV–Vis (THF): $\lambda_{max} = 317$ nm ($\varepsilon = 5520$ L mol⁻¹ cm⁻¹).

Synthesis of $[{(^{Me}IPrCH)Ge}_2(\mu-H)]^+$ ([4]⁺). To a dark yellow solution of 2 (387 μ mol), prepared in situ from 1 and GeCl₂ dioxane in THF (10 mL), was added a 1.0 M solution of Li[HBEt₃] in THF (773 μ L, 773 μ mol), which resulted in an immediate color change to orange. The reaction mixture was allowed to stir for 1 h, filtered through a glass fiber filter, and then stored at -30 °C for 2 d, upon which large, light-yellow crystals formed. The crystals were isolated, washed with pentane (2 mL) and benzene (6 mL), and dried in vacuo giving of a pale yellow solid (34.4-164 mg, depending on the effectiveness of crystallization) containing the $[{(^{Me}IPrCH)Ge}_2(\mu -$ H)]⁺ cation (see Figure S8). Note that the cationic fragment $[4]^+$ is formed reproducibly; however, despite multiple attempts the nature of the anion varies with different runs of the reaction (HBEt₃⁻, BEt₄⁻, and other ill-defined anions). The resulting yellow solid is unstable in THF at room temperature with decomposition occurring within a few hours under inert atmosphere (formation of 1 is observed), whereas the solid as well as the THF solutions can be stored at -30 °C for 10 d without sign of degradation by $^1\!\mathrm{H}$ NMR analysis. $^1\!\mathrm{H}$ NMR (THF d_{8} , 400 MHz): δ -1.27 (dd, 2H, ${}^{2}J_{\rm HH}$ = 13.2 Hz, ${}^{3}J_{\rm HH}$ = 2.0 Hz, $-CH-Ge_2$), -1.13 (dd, 1H, ${}^2J_{HH}$ = 14.5 Hz, 11.9 Hz, Ge-H-Ge), 0.44-0.48 (m, 5H, Anion), 0.77-0.78 (m, 7H, anion), 1.09 (d, 24H, ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, \text{CH}(\text{CH}_{3})_{2}), 1.20 \text{ (d, 24H, } {}^{3}J_{\text{HH}} = 6.8 \text{ Hz}, \text{CH}(\text{CH}_{3})_{2}),$ 1.87 (s, 12H, ImCH₃), 2.32 (sept, 8H, ${}^{3}J_{HH} = 6.9$ Hz, $CH(CH_{3})_{2}$), 7.29 (d, 8H, ${}^{3}J_{HH}$ = 7.8 Hz, Dipp-*m*-H), 7.55 (t, 4H, ${}^{3}J_{HH}$ = 7.8 Hz, Dipp-p-H).

From multiple recrystallization attempts it was only once possible to obtain single crystals suitable for X-ray diffraction measurements with a well-defined [BEt₄]⁻ anion. This sample was obtained by dissolving the crude mixture of $[4][BH_xEt_y]$ (164 mg, see above) in 1 mL of CH₂Cl₂, layering with 5 mL of benzene, and storing the mixture at room temperature for one week, during which light yellow needle-shaped crystals of [4][BEt₄] formed. The crystals were isolated, washed with benzene (1 mL) and pentane $(2 \times 1 \text{ mL})$, and dried in vacuo to give [4][BEt₄] as light yellow crystals (80.1 mg, 18% yield based on starting amount of 2 used in the synthesis). In sharp contrast to the crude mixture, the isolated crystals with the welldefined $[BEt_4]^-$ anion are stable at room temperature, both in THF solution and in the solid state (under inert atmosphere). Data for [4][BEt₄]:¹H NMR (THF- d_8 , 400 MHz): δ -1.26 (dd, 2H, ³ J_{HH} = 13.2 Hz, ${}^{4}J_{HH} = 1.7$ Hz, $-CH-Ge_2$), -1.13 (dd, 1H, ${}^{3}J_{HH} = 14.8$ Hz, 11.5 Hz, Ge-H-Ge), -0.20 to -0.05 (m, 8H, BCH₂CH₃), 0.56-0.77 (m, 12H, BCH₂CH₃), 1.08 (d, 24H, ${}^{3}J_{HH} = 6.8$ Hz, CH(CH₃)₂), 1.20 (d, 24H, ${}^{3}J_{HH} = 6.8$ Hz, CH(CH₃)₂), 1.86 (s, 12H, ImCH₃), 2.31 (sept, ${}^{3}J_{HH} = 6.8, 8H, CH(CH_{3})_{2}$), 7.29 (d, 8H, ${}^{3}J_{HH} = 7.8$ Hz, Dipp*m*-H), 7.52 (t, 4H, ${}^{3}J_{HH} = 7.8$ Hz, Dipp-*p*-H). ${}^{13}C{}^{1}H$ NMR (THF d_{8} , **101 MHz**): δ 9.9 (ImCH₃), 12.5 (q, ²J_{CB} = 1.2 Hz, BCH₂CH₃), 18.1 (q, ¹J_{BC} = 40.8 Hz, BCH₂CH₃), 24.7 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 29.8 (CH(CH₃)₂), 31.1 (-CH-Ge₂), 124.6 (N(CH₃) C=C), 126.0 (Dipp-m-C), 130.3 (Dipp-ipso-C), 132.3 (Dipp-p-C), 147.8 (Dipp-o-C), 157.4 (N₂CCH). ¹¹B NMR (THF-d₈, 128 MHz): δ -16.4 (s, [BEt₄]⁻). High-resolution mass spectrometry (HRMS) (LIFDI, CH_2Cl_2): $m/z = 1005.4635 [(4 - BEt_4^{-})^+]$ Anal. Calcd for C₆₈H₁₀₃BGe₂N₄: C 72.11, H 9.17, N 4.95. Found: C 72.20, H 9.15, N 4.97%.

Synthesis of $[\{(^{Me}IPrCH)Ge\}_2(\mu-D)]^+$ $([4^D]^+)$. A dark yellow solution of 2 (387 μ mol) in THF (10 mL) was prepared in situ from 1 and GeCl₂·diox. A 0.53 M solution of Li[DBEt₃] in THF/hexanes (1.46 mL, 773 μ mol) was then added, which resulted in an immediate color change to orange. The reaction mixture was allowed to stir for 1 h, filtered through a glass fiber filter, and then stored at -30 °C for 2 d, upon which large, light yellow crystals formed. The crystals were isolated, washed with pentane (2 mL) and benzene (6 mL), and dried in vacuo giving 45.2 mg of a pale yellow solid containing the $[\{(^{Me}IPrCH)Ge\}_2(\mu-D)]^+$ cation (see Figure S12). Note that the cation can be formed reproducibly, which is analogous to $[\{(^{Me}IPrCH)Ge\}_2(\mu-H)]^+$; however, despite multiple attempts, the nature of the anion varies with different runs of the reaction. The crude yellow solid is unstable in THF solutions at room temperature

and decomposes within a few hours under an inert atmosphere, whereas the solid as well as the THF solutions can be stored at -30° C for 10 d without sign of degradation by ¹H NMR analysis. **Data for** $[4^{D}]^+$:¹H **NMR** (**THF**- d_8 , **498 MHz**): δ -1.28 (t, 2H, ${}^{3}J_{\text{HD}} = 1.9$ Hz, -CH-Ge₂), 0.52-0.61 (m, 12H, anion), 0.78-0.81 (m, 20H, anion), 1.09 (d, 24H, ${}^{3}J_{\text{HH}} = 6.8$ Hz, CH(CH₃)₂), 1.20 (d, 24H, ${}^{3}J_{\text{HH}} = 6.8$ Hz, CH(CH₃)₂), 1.20 (d, 24H, ${}^{3}J_{\text{HH}} = 6.8$ Hz, CH(CH₃)₂), 7.29 (d, 8H, ${}^{3}J_{\text{HH}} = 7.8$ Hz, Dipp-*m*-H), 7.53 (t, 4H, ${}^{3}J_{\text{HH}} = 7.8$ Hz, Dipp-*p*-H). ²H{¹H} **NMR** (**THF**, **61 MHz**): δ -1.08 (s), -2.71 (s, anion). ¹³C{¹H} **NMR** (**THF**- d_8 , **176 MHz**): δ 9.6 (ImCH₃), 24.5 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 29.6 (CH-(CH₃)₂), 122.4 (N(CH₃)C=C), 125.8 (Dipp-*m*-C), 130.1 (Dipp-*ipso*-C), 132.1 (Dipp-*p*-C), 147.6 (Dipp-*o*-C), 157.2 (N₂CCH). ¹¹B **NMR** (**THF**- d_8 , **128 MHz**): *No peaks were observed, possibly due to the asymmetric boron environment.*

Synthesis of (^{Me}IPrCH)Ge(CPh₃) (5). To a dark yellow suspension of 2 (0.118 g, 0.110 mmol) in 5 mL of Et₂O was added [Li(THF)₄][CPh₃] (0.118 g, 0.219 mmol) in 8 mL of Et₂O. Upon addition, the solution changed slightly to orange-red, and the reaction mixture was stirred for 1 h. At this point, the mixture was filtered, and the filtrate was dried in vacuo to afford the product as a dark orange solid (0.142 g, 87%). Crystals of 5 suitable for single-crystal X-ray diffraction were obtained by dissolving the product in 1 mL of Et₂O, layering with 3 mL of hexanes, and storing at -30 °C for 2 d, yielding orange crystals. ¹H NMR (C_6D_6 , 700 MHz): δ 1.08 (d, 12H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 1.23 (d, 12H, ${}^{3}J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 1.45 (s, 6H, ImCH₃), 2.81 (sept, 4H, CH(CH₃)₂), 5.70 (s, 1H, ^{Me}IPrCHGe), 6.85 (t, 3H, ${}^{3}J_{HH} = 7.7$ Hz, Trityl-*p*-H), 7.02 (t, 6H, ${}^{3}J_{\text{HH}} = 7.7$ Hz, Trityl-*m*-H), 7.08 (d, 4H, ${}^{3}J_{\text{HH}} = 7.7$ Hz, Dipp-*m*-H), 7.23 (t, 2H, ${}^{3}J_{HH} = 7.7$ Hz, Dipp-*p*-H), 7.34 (d, 6H, ${}^{3}J_{HH} = 7.7$ Hz, Trityl-*o*-H). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 176 MHz): δ 9.4 (NCCH₃), 24.0 $(CH(CH_3)_2)$, 24.5 $(CH(CH_3)_2)$, 29.0 $(CH(CH_3)_2)$, 71.9 (MeIPrCHGe), 120.6 (ArC), 123.9 (ArC), 124.5 (ArC), 125.4 (ArC), 128.6 (ArC), 130.6 (ArC), 131.2 (ArC), 146.6 (ArC), 149.6 (ArC), 159.8 (NCN). Anal. Calcd for C₄₉H₅₆GeN₂: C 78.93, H 7.57, N 3.76. Found: C 77.83, H 7.63, N 3.63%; despite repeated attempts, an acceptable value for C could not be obtained, presumably due to the high moisture sensitivity of this product; please see Figures S16 and S17 for the ¹H and ¹³C $\{^{1}H\}$ NMR spectra of 5 as an indication of purity.¹³ **mp** (°C): 157–159 UV–Vis (THF): $\lambda_{max} = 514$ nm ($\varepsilon = 5940$ L mol⁻¹ cm⁻¹), 339 nm ($\varepsilon = 36\ 600$ L mol⁻¹ cm⁻¹).

X-ray Crystallography. Crystals of appropriate quality for X-ray diffraction studies were removed from a vial (glovebox) and immediately covered with a thin layer of hydrocarbon oil (Paratone-N) or perfluorinated ether (Fomblin Y). A suitable crystal was then selected, attached to a glass fiber or a microsampler, and quickly placed in a low-temperature stream of nitrogen.³⁸ Data for 2, 3, and 5 were collected using a Bruker APEX II CCD detector/D8 diffractometer using Cu K α radiation, with the crystal cooled to -100 °C. Crystal structures were solved using intrinsic phasing (SHELXT)³⁹ and refined using SHELXL-2014.⁴⁰ The assignment of hydrogen atom positions were based on the sp²- or sp³-hybridization geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of their parent atoms. X-ray intensity data for [4]BEt₄ were measured on a Bruker D8 Venture system equipped with a Helios optic monochromator and a Mo TXS rotating anode ($\lambda = 0.71073$ Å) at -173.15 °C. A total of 2074 frames was collected. The total exposure time was 11.52 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 179 372 reflections to a maximum θ angle of 25.030° (0.84 Å resolution), of which 23 352 were independent (average redundancy 7.681, $R_{int} = 10.53\%$, $R_{sig} =$ 6.00%), and 17 764 (76.07%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.637(6) Å, b = 24.400(11) Å, c = 24.565(11) Å, α = 118.704(11)°, β = 91.502(15)°, γ = 93.284(15)°, and volume = 6620.(5) Å³ are based upon the refinement of the XYZ-centroids of 8904 reflections above $20\sigma(I)$, with $4.410^{\circ} < 2\theta < 50.56^{\circ}$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.899. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8260 and 0.8760. The final anisotropic full-matrix least-squares refinement on F^2 with 1430 variables converged at R1 = 5.57% for the observed data and at wR2 = 15.77% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 1.174 e⁻/Å³, and the largest hole was -0.780 e⁻/Å³ with a root-mean-square (RMS) deviation of 0.075 e⁻/Å³. On the basis of the final model, the calculated density was 1.136 g/cm³ and F(000), 2432 e⁻.

Computational Methodology. Geometry optimizations of the gas-phase structures were performed using DFT with the B3LYP⁴¹ functional and the cc-pVD Z^{42} basis set for compounds 2, 3, 4 (only the cations were considered, referred to as $[3]^+$ and $[4]^+$ hereafter, respectively), and 5. In addition, the non-hydrogen bridged cyclic digermylene $Ge(\mu - R)_2 Ge$ as well as the dicationic analogue $[Ge(\mu \mathbf{R}_{2}\mathbf{Ge}^{2+}$ were modeled at the same level of theory. The initial structures were taken from the experimental obtained X-ray structures of the respective compounds. For $[Ge(\mu-R)_2Ge]^{2+}$ and $Ge(\mu-R)_2Ge$ the structure of $[4]^+$ of was taken as a starting geometry for optimization with the bridging H atom removed manually. To investigate if the cyclic-Ge(μ -R)₂Ge or acyclic-RGeGeR form of the digermylene is energetically favored, the acyclic isomer of RGeGeR was optimized at the B3LYP/cc-pVDZ level of theory starting from the cis and trans-arrangement of the N-heterocyclic vinyl ligands about the Ge₂ core. Notably, both starting geometries (cis/trans) led to an optimized geometry being basically identical (trans arrangement) with a total energy difference of only $\Delta E = 0.0133$ kcal mol⁻¹. The initial structures of R_2Ge^{7f} and ${}^{B}R_2Ge=Ge^{9}$ were taken from the respective cif files deposited at the CCSD. Initial starting geometry of $R_2Ge=Ge$ was obtained by manually placing a Ge atom to the optimized R₂Ge structure. RGeCl was obtained by manually removing one RGeCl unit from the optimized structure of 2. $RGe(\mu-R)Ge$ was obtained by modeling a transition state of the smaller anionic NHO ligand ($[(HCNMe)_2C=CH]^-$) and taking the obtained structure for the more bulkier ^{Me}IPrCH-ligand. Subsequent frequency analysis of all investigated compounds confirmed the obtained structures to be local minima on their respective potential energy surfaces. All calculations were performed with the Gaussian16 software.⁴³ The geometries of all optimized structures are available as a separate xyz file.¹³ The wave function files were used for a topological analysis of the electron density according to the AIM space-partitioning scheme¹⁶ using AIM2000,⁴⁴ whereas DGRID⁴⁵ was used to generate and analyze the ELI-D related real-space bonding descriptors⁴⁶ applying a grid step size of 0.05 au. The NCI¹⁷ grids were computed with NCIplot.⁴⁷ Bond paths are displayed with and ELI-D and NCI figures are displayed with MolIso⁴ AIM2000,4 and VMD,⁴⁹ respectively. The molecular orbitals (MOs) were extracted from the Gaussian16 checkpoint files, and the final molecular geometries were used to compute the NBOs using the NBO6 program.⁵⁰ The MOs and NBOs are visualized with VMD.⁴

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01449.

Optimized molecular structures (XYZ)

Full crystallographic and computational details, along with copies of all NMR spectra for all newly reported compounds (PDF)

Accession Codes

CCDC 1816455–1816458 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: erivard@ualberta.ca.

ORCID 0

Emanuel Hupf: 0000-0003-0121-7554 Robert McDonald: 0000-0002-4065-6181 Michael J. Ferguson: 0000-0002-5221-4401 Fritz E. Kühn: 0000-0002-4156-780X Eric Rivard: 0000-0002-0360-0090

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Author Contributions

[§]These authors contributed equally. Experimental design was performed by E.R., P.A.L., and F.K., with synthetic investigations by P.A.L., F.K., E.H., and M.M.D.R. Crystallography data collection and refinement for compounds **2**, **3**, and **5** was performed by R.M. and M.J.F., with collection and data refinement for **4** by F.K. All computational investigations were performed by E.H. The manuscript was written with the help of all coauthors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

E.R. thanks the NSERC of Canada for Discovery, Discovery Accelerator, and CREATE funding, the Canada Foundation for Innovation, the donors of the American Chemical Society Petroleum Research Fund, and the Univ. of Alberta, Faculty of Science (Research Award) for funding. E.H. thanks the German Research Foundation (Deutsche Forschungsgemeinschaft DFG) for a research fellowship (HU 2512/1-1). F.K. acknowledges the "Fonds der Chemischen Industrie" for his fellowship and the IRTG 2022 "ATUMS" (DFG) for financial support. The computational studies in this work were made possible by the facilities of the Shared Hierarchical Academic Computing Network (SHARCNET: www.sharcnet.ca), West-Grid (www.westgrid.ca), and Compute/Calcul Canada (www. computecanada.ca). E.R. is also grateful to the Alexander von Humboldt Foundation for a visiting professorship. We also gratefully acknowledge M. Miskolzie at the Univ. of Alberta for the measurement of the ${}^{2}H{}^{1}H{}$ NMR spectrum.

DEDICATION

This article is dedicated to the memory of Prof. Håkon Hope.

REFERENCES

(1) (a) Rivard, E.; Power, P. P. Multiple Bonding in Heavier Element Compounds Stabilized by Bulky Terphenyl Ligands. *Inorg. Chem.* **2007**, *46*, 10047–10064. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Stable Heavier Carbene Analogues. *Chem. Rev.* **2009**, *109*, 3479–3511. (c) Fischer, R. C.; Power, P. P. π -Bonding and the Lone Pair Effect in Multiple Bonds Involving Heavier Main Group Elements: Developments in the New Millennium. *Chem. Rev.* **2010**, *110*, 3877–3923. (d) Asay, M.; Jones, C.; Driess, M. N-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands. *Chem. Rev.* **2011**, *111*, 354–396. (e) Power, P. P. Stable Two-Coordinate, Open-Shell (d¹–d⁹) Transition Metal Complexes. *Chem. Rev.* **2012**, *112*, 3482–3507. (f) He, G.; Shynkaruk, O.; Lui, M. W.; Rivard, E. Small Inorganic Rings in the

21st Century: From Fleeting Intermediates to Novel Isolable Entities. Chem. Rev. 2014, 114, 7815–7880. (g) Matsuo, T.; Tamao, K. Fused-Ring Bulky "Rind" Groups Producing New Possibilities in Elemento-Organic Chemistry. Bull. Chem. Soc. Jpn. 2015, 88, 1201–1220. (h) Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; Inoue, S. NHCs in Main Group Chemistry. Chem. Rev. 2018, 118, 9678–9842. (i) Saito, M. Transition-Metal Complexes Featuring Dianionic Heavy Group 14 Element Aromatic Ligands. Acc. Chem. Res. 2018, 51, 160–169. (j) Goettel, J. T.; Braunschweig, H. Recent advances in boron-centered ligands and their transition metal complexes. Coord. Chem. Rev. 2019, 380, 184–200.

(2) (a) Power, P. P. Main-group elements as transition metals. Nature 2010, 463, 171-177. (b) Spikes, G. H.; Fettinger, J. C.; Power, P. P. Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound. J. Am. Chem. Soc. 2005, 127, 12232-12233. (c) Mandal, S. K.; Roesky, H. W. Group 14 Hydrides with Low Valent Elements for Activation of Small Molecules. Acc. Chem. Res. 2012, 45, 298-307. (d) Chu, T.; Nikonov, G. I. Oxidative Addition and Reductive Elimination at Main-Group Element Centers. Chem. Rev. 2018, 118, 3608-3680. (e) Su, Y.; Li, Y.; Ganguly, R.; Kinjo, R. Engineering the Frontier Orbitals of a Diazadiborinine for Facile Activation of H₂, NH₃, and an Isonitrile. Angew. Chem., Int. Ed. 2018, 57, 7846-7849. (f) Weetman, C.; Inoue, S. The Road Travelled: After Main-Group Elements as Transition Metals. ChemCatChem 2018, 10, 4213-4228. (g) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. Synthesis, structure and reaction chemistry of a nucleophilic aluminyl anion. Nature 2018, 557, 92-95. (3) (a) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. Low Coordinate Germanium(II) and Tin(II) Hydride Complexes: Efficient Catalysts for the Hydroboration of Carbonyl Compounds. J. Am. Chem. Soc. 2014, 136, 3028-3031. (b) Nikonov, G. I. New Tricks for an Old Dog: Aluminum Compounds as Catalysts in Reduction Chemistry. ACS Catal. 2017, 7, 7257-7266. (c) Rao, B.; Kinjo, R. Boron-Based Catalysts for C-C Bond-Formation Reactions. Chem. - Asian J. 2018, 13, 1279-1292. (d) Hadlington, T. J.; Driess, M.; Jones, C. Low-valent group 14 element hydride chemistry: towards catalysis. Chem. Soc. Rev. 2018, 47, 4176-4197.

(4) (a) Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. Novel twocoordinate germanium(II) arylamides: Ge(NHAr)₂, ArN[Ge- $(NHAr)]_2(\mu$ -NAr) and $[Ge(\mu$ -NAr)]_2 (2), and the X-ray structures of 2 and $Sn(NHAr)_2$ (Ar = $C_6H_2Bu_3^t$ -2,4,6). J. Chem. Soc., Chem. Commun. 1990, 1587-1589. (b) Merrill, W. A.; Wright, R. J.; Stanciu, C. S.; Olmstead, M. M.; Fettinger, J. C.; Power, P. P. Synthesis and Structural Characterization of a Series of Dimeric Metal(II) Imido Complexes $\{M(\mu - NAr^{\#})\}_{2}$ $[M = Ge, Sn, Pb; Ar^{\#} = C_{6}H_{3}-2, 6-(C_{6}H_{2}-2)]$ 2,4,6-Me₃ $)_2$ and the Related Monomeric Primary Amido Derivatives $M{N(H)Ar^{\#}}_{2}$ (M = Ge, Sn, Pb): Spectroscopic Manifestations of Secondary Metal-Ligand Interactions. Inorg. Chem. 2010, 49, 7097-7105. (c) Merrill, W. A.; Rivard, E.; DeRopp, J. S.; Wang, X.; Ellis, B. D.; Fettinger, J. C.; Wrackmeyer, B.; Power, P. P. Synthesis and Characterization of the M(II) (M = Ge, Sn, or Pb) Phosphinidene Dimers $\{M(\mu-PAr')\}_2$ $(Ar' = C_6H_3-2_6-(C_6H_3-2_6-Pr_2)_2)$. Inorg. Chem. 2010, 49, 8481-8486. (d) Ghadwal, R. S.; Roesky, H. W.; Pröpper, K.; Dittrich, B.; Klein, S.; Frenking, G. A Dimer of Silaisonitrile with Two-Coordinate Silicon Atoms. Angew. Chem., Int. Ed. 2011, 50, 5374-5378. (e) Li, Z.; Chen, X.; Andrada, D. M.; Frenking, G.; Benkö, Z.; Li, Y.; Harmer, J. R.; Su, C.-Y.; Grützmacher, H. $(L)_2C_2P_2$: Dicarbondiphosphide Stabilized by N-Heterocyclic Carbenes or Cyclic Diamido Carbenes. Angew. Chem., Int. Ed. 2017, 56, 5744-5749. (f) Rottschäfer, D.; Neumann, B.; Stammler, H.-G.; Ghadwal, R. S. N-Heterocyclic Vinylidene-Stabilized Phosphorus Biradicaloid. Chem. - Eur. J. 2017, 23, 9044-9047. (g) Ochiai, T.; Szilvási, T.; Franz, D.; Irran, E.; Inoue, S. Isolation and Structure of Germylene-Germyliumylidenes Stabilized by N-Heterocyclic Imines. Angew. Chem., Int. Ed. 2016, 55, 11619-11624. (h) Graham, C. M. E.; Pritchard, T. E.; Boyle, P. D.; Valjus, J.; Tuononen, H. M.; Ragogna, P. J. Trapping Rare and Elusive Phosphinidene Chalcogenides. Angew. Chem., Int. Ed. 2017, 56, 6236-6240. (i) Schulz, A. Group 15 biradicals: synthesis and reactivity of cyclobutane-1,3-diyl and

cyclopentane-1,3-diyl analogues. *Dalton Trans.* **2018**, *47*, 12827–12837. (j) Rottschäfer, D.; Neumann, B.; Stammler, H.-G.; Kishi, R.; Nakano, M.; Ghadwal, R. S. A Phosphorus Analogue of *p*-Quinodimethane with a Planar P_4 Ring: A Metal-Free Diphosphorus Source. *Chem. - Eur. J.* **2019**, *25*, 3244–3247.

(5) Hydride ligands (H⁻) can often form bridging interactions in the main group; however, they alone are not able to support low-coordinate environments in the condensed phase. For recent articles involving main group hydrides (and bridging interactions), see: (a) Aldridge, S.; Downs, A. J. Hydrides of the Main-Group Metals: New Variations on an Old Theme. *Chem. Rev.* 2001, *101*, 3305–3366. (b) Rivard, E. Group 14 inorganic hydrocarbon analogues. *Chem. Soc. Rev.* 2016, *45*, 989–1003. (c) Schneider, J.; Sindlinger, C. P.; Eichele, K.; Schubert, H.; Wesemann, L. Low-Valent Lead Hydride and Its Extreme Low-Field ¹H NMR Chemical Shift. *J. Am. Chem. Soc.* 2017, *139*, 6542–6545. (d) Bonyhady, S. J.; Collis, D.; Holzmann, N.; Edwards, A. J.; Piltz, R. O.; Frenking, G.; Stasch, A.; Jones, C. Anion stabilised *hypercloso*-hexaalane Al₆H₆. *Nature Commun.* 2018, *9*, 3079.

(6) For selected examples of cooperative halide and hydride binding by multiple main group centers, see: (a) Katz, H. E. Hydride sponge: complexation of 1,8-naphthalenediylbis(dimethylborane) with hydride, fluoride, and hydroxide. J. Org. Chem. 1985, 50, 5027-5032.
(b) Williams, V. C.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Collins, S.; Marder, T. B. New Bifunctional Perfluoroaryl Boranes. Synthesis and Reactivity of the ortho-Phenylene-Bridged Diboranes 1,2-[B(C₆F₅)₂]₂C₆X₄ (X = H, F). J. Am. Chem. Soc. 1999, 121, 3244-3245. (c) Hudnall, T. W.; Chiu, C.-W.; Gabbaï, F. P. Fluoride Ion Recognition by Chelating and Cationic Boranes. Acc. Chem. Res. 2009, 42, 388-397. For a related example in silicon chemistry, see: (d) Panisch, R.; Bolte, M.; Müller, T. Hydrogen- and Fluorine-Bridged Disilyl Cations and Their Use in Catalytic C-F Activation. J. Am. Chem. Soc. 2006, 128, 9676-9682.

(7) (a) Roy, M. M. D.; Rivard, E. Pushing Chemical Boundaries with N-Heterocyclic Olefins (NHOs): From Catalysis to Main Group Element Chemistry. Acc. Chem. Res. 2017, 50, 2017-2025. For earlier studies on complexes involving anionic NHO ligands, see: (b) Kuhn, N.; Göhner, M.; Steimann, M. Synthese und Deprotonierung eines Phosphinomethylimidazoliumsalzes. Zur Delokalisierung der π -Elektronen in Aminovinylphosphanen. Z. Anorg. Allg. Chem. 2002, 628, 896-900. (c) Al-Rafia, S. M. I.; Ferguson, M. J.; Rivard, E. Interaction of Carbene and Olefin Donors with [Cl₂PN]₃: Exploration of a Reductive Pathway toward (PN)3. Inorg. Chem. 2011, 50, 10543-10545. (d) Ghadwal, R. S.; Reichmann, S. O.; Engelhardt, F.; Andrada, D. M.; Frenking, G. Facile access to silyl-functionalized Nheterocyclic olefins with HSiCl₃. Chem. Commun. 2013, 49, 9440-9442. (e) Paisley, N. R.; Lui, M. W.; McDonald, R.; Ferguson, M. J.; Rivard, E. Structurally versatile phosphine and amine donors constructed from N-heterocyclic olefin units. Dalton Trans. 2016, 45, 9860-9870. (f) Hering-Junghans, C.; Andreiuk, P.; Ferguson, M. J.; McDonald, R.; Rivard, E. Using N-Heterocyclic Vinyl Ligands to Access Stable Divinylgermylenes and a Germylium Cation. Angew. Chem., Int. Ed. 2017, 56, 6272-6275. (g) Rottschäfer, D.; Sharma, M. K.; Neumann, B.; Stammler, H.-G.; Andrada, D. A.; Ghadwal, R. S. Modular Access to Divinyldiphosphenes with a Strikingly Small HOMO-LUMO Energy Gap. Chem. - Eur. J. 2019, DOI: 10.1002/ chem.201901204. (h) Sharma, M. K.; Blomeyer, S.; Neumann, B.; Stammler, H.-G.; Ghadwal, R. S. Crystalline Divinyldiarsenes and Cleavage of the As = As Bond. Chem. - Eur. J. 2019, DOI: 10.1002/ chem.201901857. (i) Roy, M. M. D.; Ferguson, M. J.; McDonald, R.; Zhou, Y.; Rivard, E. A vinyl silylsilylene and its activation of strong homo- and heteroatomic bonds. Chem. Sci. 2019, DOI: 10.1039/ C9SC01192G.

(8) For a related anionic ligand based on [CAAC=CR]⁻ units (CAAC = cyclic(alkyl)amino carbene), see: Liu, L. L.; Cao, L. L.; Zhou, J.; Stephan, D. W. Facile Cleavage of the P=P Double Bond in Vinyl-Substituted Diphosphenes. *Angew. Chem., Int. Ed.* **2019**, *58*, 273–277.

(9) Rit, A.; Campos, J.; Niu, H.; Aldridge, S. A stable heavier group 14 analogue of vinylidene. *Nat. Chem.* **2016**, *8*, 1022–1026.

(10) For previous examples of $[(\mu-R)GeCl]_2$ dimers supported by bridging alkoxide, amide, or phosphide ligands, see: (a) Veith, M.; Hobein, P.; Rösler, R. Cyclische Diazastannylene, XXX. Symmetrisch und asymmetrisch substituierte German- und Stannandiyle mit Amid-, Alkoholate- und Thiolat-Liganded, Teil I. Z. Naturforsch., B: J. Chem. Sci. 1989, 44, 1067-1081. (b) Druckenbrodt, C.; du Mont, W.-W.; Ruthe, F.; Jones, P. G. Dimere Dialkylphosphanylgermylene: Ylidische Diphosphadigermetane. Z. Anorg. Allg. Chem. 1998, 624, 590-594. (c) Khrustalev, V. N.; Glukhov, I. V.; Borisova, I. V.; Zemlyansky, N. N. New stable germylenes, stannylenes, and related compounds. 8. Amidogermanium(II) and - tin(II) chlorides $R_2N-E^{14}-Cl$ ($E^{14} = Ge$, $R = Et; E^{14} = Sn, R = Me)$ revealing new structural motifs. Appl. Organomet. Chem. 2007, 21, 551-556. (d) Kunz, T.; Schrenk, C.; Schnepf, A. Reactions of GeCl₂ with the Thiolate LiSC(SiMe₃)₃: From thf Activation to Insertion of GeCl₂ Molecules into C-S Bonds. Chem. - Eur. J. 2019, 25, 7210-7217.

(11) (a) Al-Rafia, S. M. I.; Momeni, M. R.; McDonald, R.; Ferguson, M. J.; Brown, A.; Rivard, E. Controlled Growth of Dichlorogermanium Oligomers from Lewis Basic Hosts. *Angew. Chem., Int. Ed.* 2013, 52, 6390–6395. For related studies involving silicon, see:
(b) Uhlemann, F.; Schnepf, A. IPr₃Si₃Cl₅⁺: A Highly Reactive Cation with Silanide Character. *Chem. - Eur. J.* 2016, 22, 10748–10753.
(c) Olaru, M.; Hesse, M. F.; Rychagova, E.; Ketkov, S.; Mebs, S.; Beckmann, J. The Weakly Coordinating Tris(trichlorosilyl)silyl Anion. *Angew. Chem., Int. Ed.* 2017, 56, 16490–16494.

(12) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. Donor/acceptor stabilization of Ge(II) dihydride. *Chem. Commun.* **2009**, 7119–7121.

(13) For full crystallographic and computational details, along with copies of all newly reported compounds, see the Supporting Information.

(14) (a) Seiler, P. The crystal structure of [1.1.1]propellane at 138 K. *Helv. Chim. Acta* **1990**, 73, 1574–1585. (b) Nied, D.; Breher, F. New perspectives for "non-classical" molecules: heavy [1.1.1]propellanes of group 14. *Chem. Soc. Rev.* **2011**, 40, 3455–3466 and references therein.

(15) (a) Glendening, E. D.; Landis, C. R.; Weinhold, F. Natural bond orbital methods. WIRES. *Comput. Mol. Sci.* 2012, 2, 1-42.
(b) Weinhold, F. Natural bond orbital analysis: a critical overview of relationships to alternative bonding perspectives. *J. Comput. Chem.* 2012, 33, 2363-2379.

(16) Bader, R. F. W. Atoms in Molecules. A Quantum Theory; Oxford University Press: Oxford, U.K., 1990.

(17) Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W. Revealing Noncovalent Interactions. J. Am. Chem. Soc. **2010**, 132, 6498–6506.

(18) Purkait, T. K.; Swarnakar, A. K.; De Los Reyes, G. B.; Hegmann, F. A.; Rivard, E.; Veinot, J. G. C. One-pot synthesis of functionalized germanium nanocrystals from a single source precursor. *Nanoscale* **2015**, *7*, 2241–2244.

(19) Henneberger, T.; Klein, W.; Dums, J. V.; Fässler, T. F. $[(\mu_2 - H)(\eta^2 - Ge_4)ZnPh_2]^{3-}$, an edge-on protonated E_4 cluster establishing the first three-center two-electron Ge–H–Ge bond. *Chem. Commun.* **2018**, 54, 12381–12384.

(20) NHO-based ligands have also been used to support bridging B-H-B interactions, see: (a) Ghadwal, R. S.; Schürmann, C. J.; Andrada, D. M.; Frenking, G. Mono- and di-cationic hydrido boron compounds. *Dalton Trans.* **2015**, *44*, 14359–14367. (b) Ghadwal, R. S. Carbon-based two electron σ -donor ligands beyond classical N-heterocyclic carbenes. *Dalton Trans.* **2016**, *45*, 16081–16095. (c) Hering-Junghans, C.; Watson, I. C.; Ferguson, M. J.; McDonald, R.; Rivard, E. Organocatalytic hydroborylation promoted by N-heterocyclic olefins. *Dalton Trans.* **2017**, *46*, 7150–7153.

(21) Crestani, M. G.; Muñoz-Hernández, M.; Arévalo, A.; Acosta-Ramírez, A.; García, J. J. σ -Borane Coordinated to Nickel(0) and Some Related Nickel(II) Trihydride Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 18066–18073.

(22) Powers, K.; Hering-Junghans, C.; McDonald, R.; Ferguson, M. J.; Rivard, E. Improved synthesis of *N*-heterocyclic olefins and evaluation of their donor strengths. *Polyhedron* **2016**, *108*, 8–14.

(23) Because of the instability of $[4][BH_xEt_y]$ mixtures in solution and the possible hydride donating ability of the anions, the use of $[4]^+$ in catalysis was not explored; cf. Lummis, P. A.; Momeni, M. R.; Lui, M. W.; McDonald, R.; Ferguson, M. J.; Miskolzie, M.; Brown, A.; Rivard, E. Accessing Zinc Monohydride Cations through Coordinative Interactions. *Angew. Chem., Int. Ed.* **2014**, *53*, 9347–9351.

(24) (a) Nagase, S.; Kobayashi, K.; Takagi, N. Triple bonds between heavier Group 14 elements. A theoretical approach. J. Organomet. Chem. 2000, 611, 264–271. (b) Lein, M.; Krapp, A.; Frenking, G. Why Do the Heavy-Atom Analogues of Acetylene E_2H_2 (E = Si–Pb) Exhibit Unusual Structures? J. Am. Chem. Soc. 2005, 127, 6290–6299.

(25) Roy, M. M. D.; Lummis, P. A.; Ferguson, M. J.; McDonald, R.; Rivard, E. Accessing Low-Valent Inorganic Cations by Using an Extremely Bulky N-Heterocyclic Carbene. *Chem. - Eur. J.* **2017**, *23*, 11249–11252.

(26) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. A Digermyne with a Ge–Ge Single Bond That Activates Dihydrogen in the Solid State. J. Am. Chem. Soc. **2011**, 133, 18622–18625.

(27) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelly, K. K.; Wagram, D. Selected values of the thermodynamic properties of the elements; American Society for Metals: Metals Park, OH, 1973. The enthalpy of sublimation was used to include the formation of elemental germanium, and therefore the energy diagram is plotted as relative enthalpies for consistency.

(28) Despite multiple efforts a transition state (TS) illustrating the ligand migration from the *cyclic*-Ge(μ -R)₂Ge or *acyclic*-RGeGeR isomers to RGe(μ -R)Ge and R₂Ge=Ge could only be detected using the less sterically encumbered [(HCNMe)₂C=CH]⁻ ligand. Note that the optimized gas-phase structures of *cyclic*-Ge(μ -R)₂Ge, *acyclic*-RGeGeR, RGe(μ -R)Ge, and R₂Ge=Ge all proved to be local minima on the potential energy surface.

(29) For comparison, the geometry of ${}^{B}R_{2}Ge=Ge$ was reoptimized using the B3LYP/cc-pVDZ level of theory for consistency.

(30) Liptrot, D. J.; Power, P. P. London dispersion forces in sterically crowded inorganic and organometallic molecules. *Nature Rev. Chem.* **2017**, *1*, 0004.

(31) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.

(32) Fernández, I.; Martínez-Viviente, E.; Breher, F.; Pregosin, P. S. ⁷Li, ³¹P, and ¹H Pulsed Gradient Spin-Echo (PGSE) Diffusion NMR Spectroscopy and Ion Pairing: On the Temperature Dependence of the Ion Pairing in Li(CPh₃), Fluorenyllithium, and Li[N(SiMe₃)₂] amongst Other Salts. *Chem. - Eur. J.* **2005**, *11*, 1495–1506.

(33) Savoia, D.; Trombini, C.; Umani-Ronchi, A. Potassium-graphite as a metalation reagent. Synthesis of aldehydes and ketones by alkylation of imines and dihydro-1,3-oxazine. *J. Org. Chem.* **1978**, 43, 2907–2910.

(34) Dieke, H. t.; Svoboda, M.; Greiser, T. Bis(diazadien)metall(O)-Komplexe, IV. Nickel(O)-bis(chelate) mit aromatischen N-Substituenten. *Z. Naturforsch., B: J. Chem. Sci.* **1981**, *36*, 823–832.

(35) Brown, H. C.; Krishnamurthy, S.; Hubbard, J. L. Addition compounds of alkali metal hydrides. 15. Steric effects in the reaction of representative trialkylboranes with lithium and sodium hydrides to form the corresponding trialkylborohydrides. *J. Am. Chem. Soc.* **1978**, *100*, 3343–3349.

(36) Gaillard, S.; Bantreil, X.; Slawin, A. M. Z.; Nolan, S. P. Synthesis and characterization of IPr^{Me}-containing silver(I), gold(I) and gold(III) complexes. *Dalton Trans.* **2009**, 6967–6971.

(37) IPrCH₂ has been prepared previously using a similar procedure, see: Ghadwal, R. S.; Schürmann, C. J.; Engelhardt, F.; Steinmetzger, C. Unprecedented Borylene Insertion into a C-N Bond. *Eur. J. Inorg. Chem.* **2014**, 2014, 4921–4926.

(38) Hope, H. X-Ray Crystallography: A Fast. First-Resort Analytical Tool. Prog. Inorg. Chem. **1994**, 41, 1–19.

(39) Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *A71*, 3–8.

(40) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, C71, 3–8.

(41) (a) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(42) (a) Dunning, T. H., Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. **1989**, 90, 1007–1023. (b) Woon, D. E.; Dunning, T. H., Jr. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. J. Chem. Phys. **1993**, 98, 1358–1371.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision A.03; Gaussian, Inc.: Wallingford, CT, 2016.

(44) Biegler-König, F.; Schönbohm, J.; Bayles, D. Software news and updates—AIM2000—A program to analyze and visualize atoms in molecules. *J. Comput. Chem.* **2001**, *22*, 545–559.

(45) Kohout, M. DGRID-4.6; Max Planck Institute, 2015.

(46) (a) Kohout, M. A measurement of electron localizability. *Int. J. Quantum Chem.* **2004**, *97*, 651–658. (b) Kohout, M.; Wagner, F. R.; Grin, Y. Electron localizability indicator for correlated wavefunctions. III: singlet and triplet pairs. *Theor. Chem. Acc.* **2008**, *119*, 413–420.

(47) Contreras-García, J.; Johnson, E.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D.; Yang, W. NCIPLOT: A Program for Plotting Noncovalent Interaction Regions. *J. Chem. Theory Comput.* **2011**, 7, 625–632.

(48) Hübschle, C. B.; Luger, P. MolIso-a program for colourmapped iso-surfaces. J. Appl. Crystallogr. 2006, 39, 901–904.

(49) Humphrey, W.; Dalke, A.; Schulten, K. VMD - Visual molecular dynamics. J. Mol. Graphics 1996, 14, 33–38.

(50) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. *NBO* 6.0.; Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.