

Synthesis and Structure of N-Heterocyclic Carbene Complexes of Germanium(II)

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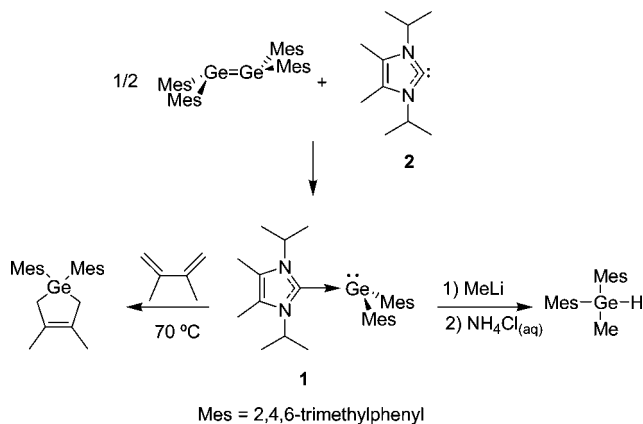
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The synthesis and structural characterization of a series of N-heterocyclic carbene (NHC) complexes of GeR_1R_2 are reported, where $\text{R}_1 = \text{R}_2 = \text{Mes}$ ($\text{Mes} = 2,4,6\text{-trimethylphenyl}$) (**1**), $\text{R}_1 = \text{R}_2 = \text{F}$ (**5**), $\text{R}_1 = \text{R}_2 = \text{Br}$ (**6**), $\text{R}_1 = \text{Cl}$, $\text{R}_2 = \text{OTf}$ ($\text{OTf} = \text{O}_3\text{SCF}_3$) (**7**), $\text{R}_1 = \text{R}_2 = \text{O}^t\text{Bu}$ (**10**), and $\text{R}_1 = \text{R}_2 = \text{NCS}$ (**11**). The bond length between the carbenic carbon and the germanium is observed to vary in accordance with the π -donating ability of the substituent on Ge. Efforts to synthesize stable complexes with small alkyl or aryl substituents were not successful; evidence for oligomerization of the GeR_2 fragment is presented. The reaction between **1** and **3** ($\text{R}_1 = \text{R}_2 = \text{Cl}$) resulted in the formation of an NHC-coordinated germylgermylene (**13**). The ^1H NMR spectra of **3–7**, **10**, and **11** display broad signals at room temperature. To rationalize the ^1H NMR spectra, mechanisms for conformational interchange, as well as intermolecular exchanges, are discussed.

Introduction

$\text{GeCl}_2 \cdot \text{dioxane}$, first synthesized in the mid 1960s by Nefedov and co-workers,¹ is a rare example of an intermolecularly stabilized germylene. Since the solid can be briefly handled under aerobic conditions and the ligand is readily displaced, this complex has proven to be extremely useful for the synthesis of a variety of germanium(II) and germanium(IV) compounds.^{2,3} Stabilization of the dichlorogermylene is achieved by the intermolecular donation of electron density from the Lewis base,

Scheme 1



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1,4-dioxane, into the empty p-orbital on germanium. Evidently, a relatively weak donor is sufficient to produce a stable complex because of the inherent stability of the dichlorogermylene.² Despite the obvious usefulness of $\text{GeCl}_2 \cdot \text{dioxane}$, it is somewhat surprising that the chemistry of stable intermolecular complexes of transient Ge(II) compounds is relatively unexplored.

Recently we reported the synthesis of **1** from the reaction of tetramesityldigermene⁴ with carbene **2**⁵ (Scheme 1); **1** was the first example of a transient diorganogermylene stabilized intermolecularly by an N-heterocyclic carbene (NHC).^{6–8} The use of a strong σ -donor was key for stabilization as, in general, intermolecular complexes of simple diarylgermylenes exist only as transient intermediates.⁹ Although occupation of the p-orbital

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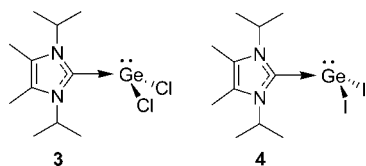
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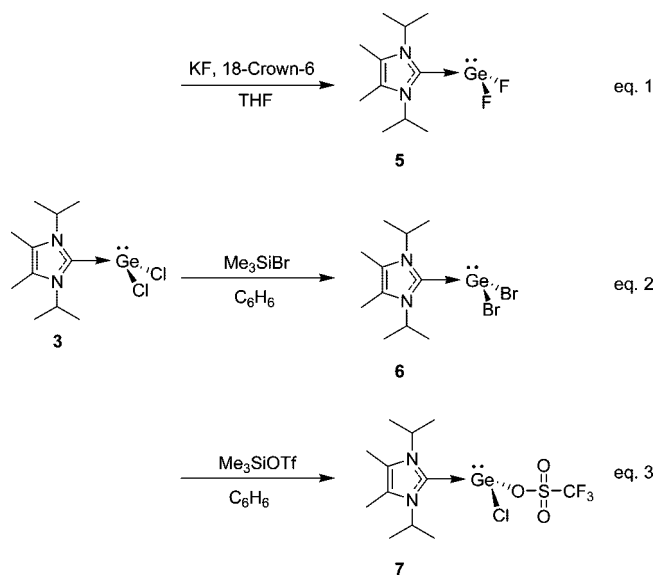
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Chart 1



Scheme 2



on Ge by the carbene lone pair is clearly necessary for the stabilization of **1**, steric shielding provided by the mesityl groups most likely also plays a role. Compound **1** is stable indefinitely under an inert atmosphere at room temperature. However, by reaction with a strong nucleophile, such as MeLi, at room temperature or by heating **1** in the presence of a good germylene trap, such as dimethylbutadiene, the ability of compound **1** to act as a masked germylene was demonstrated (Scheme 1).

We have also synthesized the NHC-complexed dichloro- and diiodogermynes **3** and **4** (Chart 1) with the expectation that these compounds could be utilized as precursors for the synthesis of other base-stabilized germanium(II) compounds and related species. Indeed, we were able to synthesize a germanium-centered dication by reaction of the diiodo derivative **4** with 2 equiv of an N-heterocyclic carbene.¹⁰

In this paper, we now describe the synthesis and structural characterization of a number of NHC-stabilized Ge(II) compounds derived from the dichloro derivative **3**. Our goal is to produce versatile reagents for the facile delivery of synthetically useful germynes. In a subsequent paper, we will report on the reactivity of the complexes described herein and their ability to act as germylene equivalents.

Results and Discussion

The dichloro (**3**) and diiodo (**4**) N-heterocyclic carbene-germylene derivatives have been previously synthesized and characterized.¹⁰ To complete the halogen series, the difluoro and dibromo analogues were also synthesized. Reaction of **3** with excess potassium fluoride and a catalytic amount of 18-crown-6 resulted in the formation of the difluoro-substituted derivative **5**, while the addition of excess Me₃SiBr to **3** resulted in the formation of the dibromo analogue **6** (Scheme 2, eqs 1 and 2). The chemical shifts of the signals in the ¹H NMR spectra of the halogen derivatives **3**–**6** are very similar and, thus, are not very diagnostic. However, the four compounds, **3**–**6**, can be easily differentiated on the basis of the wavenumber for the Ge–X stretching vibration observed by FT-Raman spectroscopy (F = 530 cm^{−1}, Cl = 316 cm^{−1}, Br = 232 cm^{−1}, I = 205 cm^{−1}).¹¹

The structures of **5** and **6** were verified by single-crystal X-ray diffraction. The compounds are isomorphous to one another and to **3** and **4**.¹⁰ Only the structure of **6** is presented (Figure 1). One other NHC dihalogermylene complex has been structurally characterized, a diiodo derivative with a bulkier NHC (mesityl groups on nitrogen and unsubstituted at the alkenyl carbons); this complex was found to have similar metrics.¹² In general, the halide derivatives are monomeric in the solid state, showing no significant intermolecular interactions. However, the ger-

manium atoms of opposing molecules in the unit cell of **6** are within the sum of their van der Waals radii (4.30 Å)¹³ at 3.67 Å. This value greatly exceeds the bond length of a Ge–Ge single bond (typical range 2.41–2.46 Å)¹⁴ and is, most likely, a consequence of crystal packing rather than any meaningful bonding interaction.

Since a triflate–germanium bond (triflate = OTf = O₃SCF₃) is expected to ionize quite readily, and thus, be synthetically useful, we attempted to make the ditriflate derivative. Addition of Me₃SiOTf to **3**, followed by removal of the solvent, yielded a white powder (Scheme 2, eq 3). The ¹H NMR spectrum of the white powder was, predictably, similar to that of **3**, while the ¹⁹F NMR spectrum of the solid showed a signal whose chemical shift was consistent with a triflate moiety. Surprisingly, a signal attributable to a Ge–Cl bond stretch at 315 cm^{−1} was apparent in the FT-Raman spectrum of the powder. Crystals of the product were obtained; single-crystal X-ray diffraction confirmed the formation of **7**, an NHC-germylene complex with both a chloride and a triflate substituent present on the

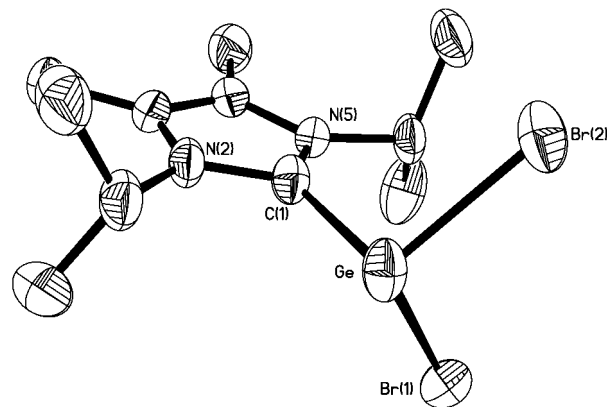


Figure 1. Thermal ellipsoid plot (50% probability surface) of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for compound **6**: C(1)–Ge = 2.089(5), Ge–Br(1) = 2.4514(9), Ge–Br(2) = 2.4572(8), Br(1)–Ge–Br(2) = 99.67(3), Br(1)–Ge–C(1) = 94.78(14), Br(2)–Ge–C(1) = 95.73(14). Selected bond lengths (Å) and angles (deg) for compound **5**: C(1)–Ge = 2.117(7), Ge–F(1) = 1.829(5), Ge–F(2) = 1.829(5), F(1)–Ge–F(2) = 95.1(3), F(1)–Ge–C(1) = 91.2(3), F(2)–Ge–C(1) = 94.6(3).

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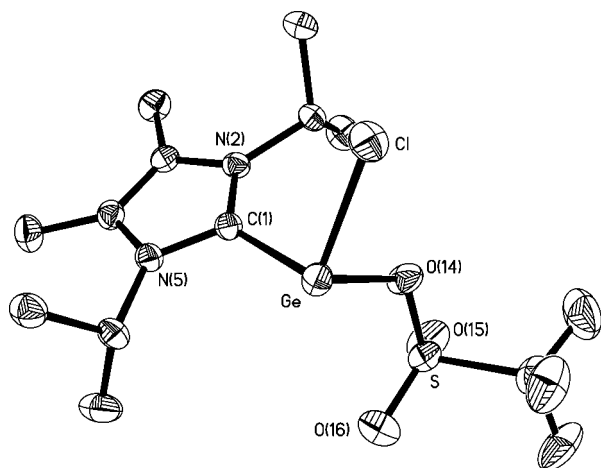


Figure 2. Thermal ellipsoid plot (50% probability surface) of **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Ge = 2.068(2), Ge–Cl = 2.2680(6), Ge–O(14) = 2.0342(16), S–O(14) = 1.4914(16), S–O(15) = 1.4273(19), S–O(16) = 1.4914(16), C(1)–Ge–Cl = 95.51, C(1)–Ge–O(14) = 89.81(8), Cl–Ge–O(14) = 92.69(6).

germanium center (Figure 2). The triflate is covalently bound to the germanium with a Ge–O bond length of 2.0342(16) Å (cf. 1.75–1.85 Å for a typical Ge–O bond).¹⁴ The carbenic carbon–germanium bond is reduced in length to 2.068(2) Å (from 2.106(3) Å in **3**), and the chlorine–germanium bond length has decreased to 2.2680(6) Å (from an average of 2.294 Å in **3**). These observations are consistent with a δ^+ charge on germanium due to the electron-withdrawing triflate group. As observed in the solid state structure of **6**, the germanium atoms in opposing molecules of **7** are within the sum of their van der Waals radii at 3.75 Å but, once again, far outside the distance expected of a Ge–Ge bond (typical range 2.41–2.46 Å).¹⁴

Efforts to replace both chlorides on **3** using a large excess of Me₃SiOTf were not successful; only **7** was isolated. Attempts to use AgOTf to facilitate chloride/triflate metathesis also failed; complex mixtures were formed and no single compound could be identified.

Unlike most Ge(II) compounds, many N-heterocyclic germylenes are indefinitely stable due to partial occupation of the empty p-orbital on germanium by the nitrogen lone pair of electrons.^{2g,3e,f} This partial occupation makes N-heterocyclic germylenes less Lewis acidic, and as a result, it was expected that the strength of a coordination complex with **2** would be weakened. Indeed, the addition of the dilithium salt **8** to a solution of **3** resulted in the formation of two compounds: free carbene **2** and N-heterocyclic germylene **9**¹⁵ (Scheme 3, eq 4). Complete dissociation of the carbene was confirmed by NMR spectroscopy: the ¹H NMR chemical shifts of the signals in the reaction mixture are identical to an independently prepared solution of **3** and **9** and to the chemical shifts of the signals in the ¹H NMR spectra of the isolated compounds. In addition, the ¹³C NMR spectrum of the reaction mixture showed a signal at 207 ppm, attributed to the carbenic carbon, which is identical to the ¹³C chemical shift of the carbenic carbon in a pure sample of **2**.⁵ The reaction between an annulated NHC with an annulated N-heterocyclic germylene has been examined; a weak bonding

interaction between the two fragments was observed both in solution and in the solid state.¹⁶ The substituents on the nitrogen atoms of the N-heterocyclic germylene are N-neopentyl rather than N-*tert*-butyl, as in **9**. The difference in the extent of complexation with an NHC between the two germylenes is likely due to a combination of the ring annulation, which increases Lewis acidity of the germanium,¹⁷ and the increased flexibility of the neopentyl group, which reduces steric bulk in comparison to the *tert*-butyl group.

In general, Ge(OR)₂ compounds rapidly oligomerize, which makes isolation and characterization of such germylenes difficult.² Even the sterically encumbered Ge(ODipp)₂ (Dipp = 2,6-diisopropylphenyl) derivative forms a dimer in the solid state.¹⁸ However, a few discrete dialkoxy¹⁹ and diaryloxy^{18,20–24} germylenes have been structurally characterized. An NHC could potentially stabilize the reactive dialkoxygermylenes through occupation of the p-orbital on the germanium and allow isolation of monomeric molecular complexes.²⁵ Nucleophilic substitution of the chlorides in **3** using 2 equiv of potassium *tert*-butoxide proceeded cleanly (Scheme 3, eq 5). The ¹H NMR spectrum of the white powder isolated from the reaction was consistent with the di(*tert*-butoxy)-substituted carbene-germylene complex **10**. The structure of the product was confirmed by X-ray crystallography (Figure 3). Two monomeric molecules of **10** were present in the asymmetric unit. Both molecules have identical connectivity and orientation, but differ significantly in the carbenic carbon–Ge bond length (2.120(9) Å vs 2.224(14) Å).

Ge(NCS)₂ has been studied previously; the germylene is stable in dilute solution but polymerizes rapidly upon isolation.²⁶ Again, coordination of the NHC should allow isolation of a monomeric base-stabilized Ge(NCS)₂. Two equivalents of KSCN underwent a reaction with **3** to form complex **11** as determined by FT-Raman and X-ray crystallography (Scheme 3, eq 6). Four chemically identical but crystallographically unique molecules of **11** are found in the asymmetric unit. Each molecule shows the same connectivity with two N-bonded thiocyanates attached to the germanium center (Figure 4). The central C(1)–Ge bond lengths vary (2.105(9), 2.072(9), 2.075(10), and 2.062(9) Å) with an average value of 2.078 Å. There are also short intermolecular contacts between the sulfur atoms and neighboring germanium atoms. The closest S–Ge approach is 3.61 Å, which is much longer than the length of a typical S–Ge single bond (the average S–Ge single bond length is 2.21–2.29 Å).¹⁴ In contrast to Ge(NCS)₂,²⁶ **11** is stable under an inert

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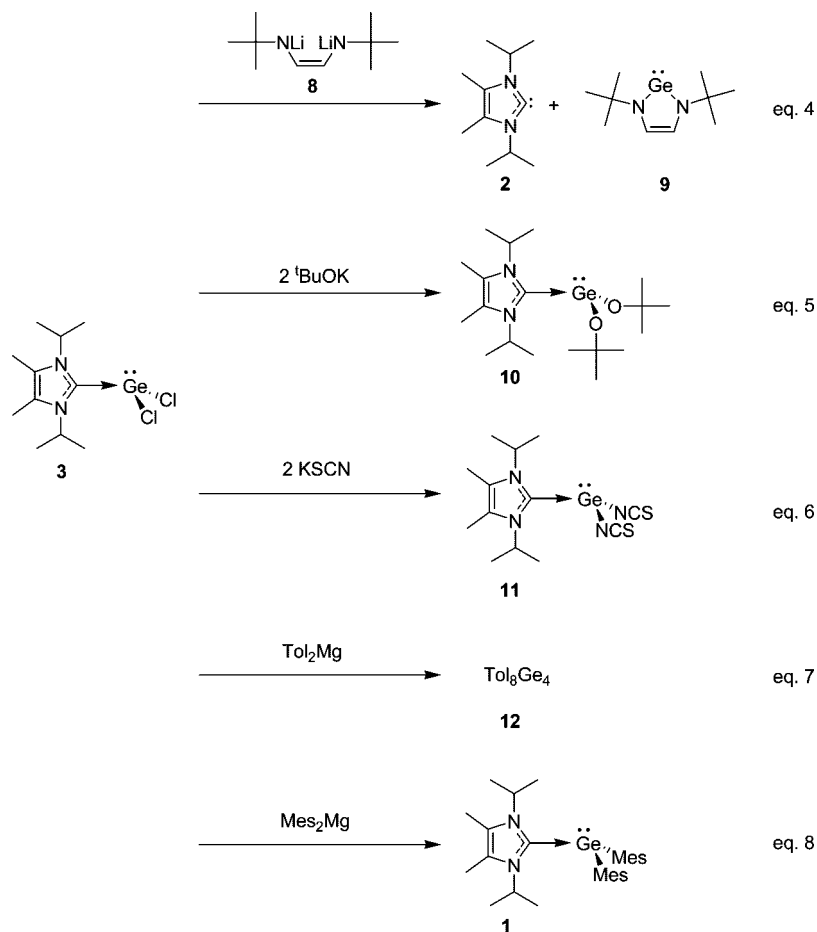
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Scheme 3



atmosphere both in the solid state or in solution. Both $\text{Ge}(\text{NCS})_2$ and **11** show Ge–N connectivity rather than Ge–S connectivity, which indicates that Ge(II) has a preference for the harder nitrogen atom over the softer sulfur atom. Only one other structurally characterized thiocyanato germanium compound, a tetraazacyclotetradecine Ge(IV) complex, is known; this compound also shows a preference for Ge–N bonding.²⁷

Simple dialkylgermylenes are extremely reactive intermediates and cannot be isolated under standard conditions.² Experimental evidence suggests that transient dialkylgermylenes form reversible donor–acceptor complexes with Lewis bases in

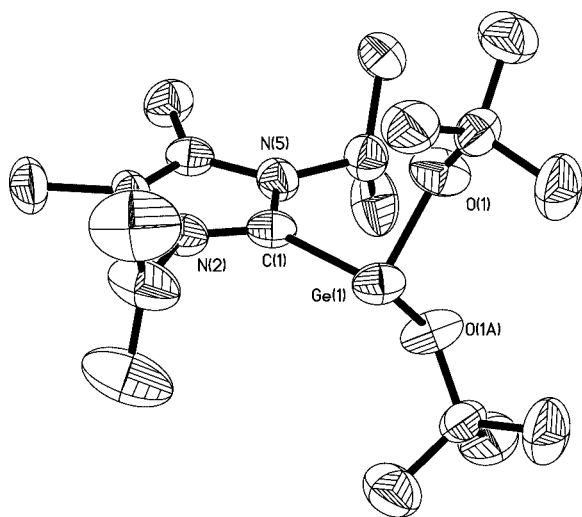


Figure 3. Thermal ellipsoid plot (50% probability surface) of **10**. Only one of the two molecules in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Ge = 2.120(9), O(1)–Ge(1) = 1.874(5), O(1)–Ge(1)–O(1a) = 95.4(4), O(1)–Ge(1)–C(1) = 89.5(2).

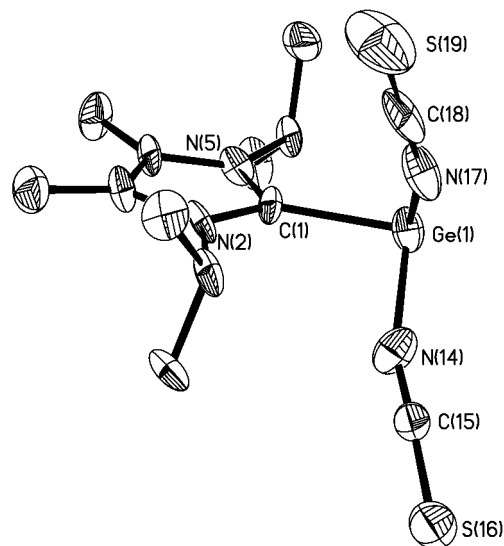


Figure 4. Thermal ellipsoid plot (50% probability surface) of **11**. Only one of the four molecules from the asymmetric unit is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Ge = 2.105(9), Ge(1)–N(14) = 1.983(8), Ge(1)–N(17) = 1.998(9), N(14)–C(15) = 1.146(11), N(17)–C(18) = 1.207(13), N(14)–Ge(1)–N(17) = 89.7(4), N(14)–Ge(1)–C(1) = 93.1(4), N(17)–Ge(1)–C(1) = 90.0(4).

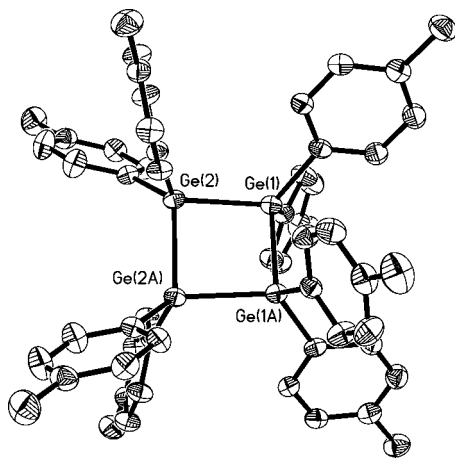


Figure 5. Thermal ellipsoid plot (50% probability surface) of **12**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–Ge(1A) = 2.4587(7), Ge(1)–Ge(2) = 2.4632(5), Ge(2)–Ge(2A) = 2.4555(7), Ge(1A)–Ge(1)–Ge(2) = 88.987(11), Ge(2A)–Ge(2)–Ge(1) = 89.061(11).

solution.² NHCs are among the strongest known neutral Lewis bases and, therefore, should form strong coordination complexes with dialkylgermylenes. Indeed, the isolation of **1** demonstrated that an unstable diarylgermylene can be isolated using NHC complexation. We attempted to form NHC complexes of GeR_2 (where R = small alkyl) by the reaction of **3** with alkyl Grignard or lithium reagents. Invariably, and independent of reaction conditions, only complex mixtures were formed.²⁸ Broad signals in the ^1H NMR spectra of the crude reaction mixture suggested that some polymeric material may be formed.

In addition to dialkyl complexes, the synthesis of other diaryl systems was also attempted. The reaction of ToI_2Mg with **3** gave **12** as the only isolated tolyl-containing product (Scheme 3, eq 7). The cyclotetragermane likely results from the oligomerization of four $\text{Ge}(\text{ToI})_2$ fragments. Broad signals attributable to tolyl groups in the ^1H NMR spectra of the crude reaction mixture suggest that larger oligomers are also formed. The identity of **12** was confirmed by ^1H NMR spectroscopy and X-ray crystallography (Figure 5).²⁹ The Grignard reagent Mes_2Mg ,³⁰ reacted with **3** to produce complex **1** and, thus, provides an alternate route to **1** that does not require the use of tetramesityldigermene⁴ as a starting material (Scheme 3, eq 8). The reaction proceeds slowly, taking three days at room temperature to complete.

The results from the attempted substitution reactions with organometallic reagents demonstrate that nucleophilic displacement of the chlorides from **3** is possible, but the NHC-diorganogermylene products are apparently unstable under the reaction conditions. In addition to coordination of a strong Lewis base, steric protection of the germanium center must be necessary for the isolation of complexed diorganogermynes. By virtue of its isolation and characterization, compound **1** meets these requirements.

A carbene-germanium(II) complex with both a mesityl and a chloro substituent would be useful in the synthesis of NHC-coordinated heteroleptic germylenes. Intermolecular ligand redistributions between germanium(II) compounds are known to occur between aryl and chloro substituents,³¹ and therefore, compounds **1** and **3** were dissolved in THF to determine if exchange would occur (Scheme 4). The ^1H NMR spectrum of the mixture was complex. Signals attributable to unreacted **1** were observed in addition to signals consistent with several compounds containing mesityl and carbene fragments. The formation of a thin metallic film, presumably elemental germanium, on the wall of the reaction vessel was also observed. A white powder precipitated upon addition of pentane to a C_6H_6 solution of the crude products. The ^1H NMR spectrum of the precipitate showed signals consistent with two nonequivalent mesityl groups in a 1:1 ratio and a carbene moiety. Crystals were grown and the structure was determined by X-ray crystallography to be germylgermylene **13** (Figure 6). The compound contains two germanium atoms: a three-coordinate Ge with a vacant coordination site that is presumably occupied by a lone pair of electrons, and a coordinately saturated Ge. Compound **13** is a rare example of a donor-stabilized germylgermylene; such compounds are important intermediates in a number of reactions involving germanium. Few have been directly observed and structurally characterized.^{32,33}

In the reaction producing **13**, compounds **1** and **3** are combined in an equal molar ratio; however, the ^1H NMR spectrum of the crude reaction mixture showed signals attributable to unreacted **1**. The low isolated yield of **13** (25%) and the complex product mixture indicates that other products are formed under the reaction conditions. The formation of a metallic film implies that redox chemistry is occurring. Unfortunately, efforts to identify other reaction products were unsuccessful. The reduction of main group compounds by NHCs has been reported. The reduction appears to be driven by the formal elimination of X_2 (X = halogen) from the main group element.³⁴

The formation of **13** was unexpected and arises, presumably, by the insertion of a molecule of **1** into the Ge–Cl bond of a molecule of **3**, with concomitant loss of a carbene. Germylenes are known to readily insert into many different types of bonds.² The formation of **12** and **13** provides some insight into why our attempts to synthesize carbene-germylene complexes with smaller aryl or alkyl groups on germanium failed. Presumably, the insertion reactions are more facile with smaller R groups on Ge, and thus, oligomerization occurs during the attempted syntheses of carbene-stabilized GeR_2 complexes.

Secondary insertion reactions do not appear to be taking place during the synthesis of compounds **4**–**7**, **10**, and **11**, all of which

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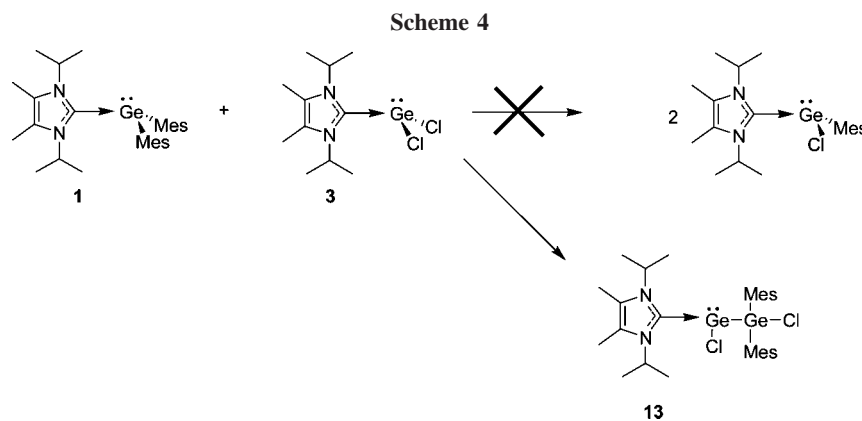
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(28) Substitution reactions with all of the dihalo derivatives **3**–**6** were attempted and gave similar results.

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(30) For the preparation of the mesityl Grignard reagent, the Schlenk equilibrium was driven toward Mes_2Mg by the precipitation of $\text{MgBr}_2 \cdot \text{dioxane}$. The addition of this Grignard reagent to **3** resulted in a higher yield for the formation of **1** in comparison to the addition of MesMgBr . See: Cannon, K. C.; Krow, G. R. In *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker: New York, 1996.

**Table 1.** Comparison of the Structural Parameters of NHC-GeR₂ Complexes

compound	substitution	bond length (Å)	R–Ge–R angle (deg)	NHC–Ge–R angle (deg) ^a	ref
9	diazabutadiene	n/a	n/a	n/a	15, this work
10	(O ^t Bu) ₂	2.120(9), 2.224(14) av 2.172	95.4(4), 89.4(3) av 92.4	89.5, 94.3 av 91.9	this work
5	F ₂	2.117(7)	95.1(3)	92.9	this work
3	Cl ₂	2.106(3)	97.82(3)	94.7	10
6	Br ₂	2.089(5)	99.67(3)	95.1	this work
4	I ₂	2.086(3)	99.865(17)	97.5	10
11	(NCS) ₂	2.105(9), 2.062(9), 2.075(10), 2.072(9) av 2.079	89.7(4), 91.6(3), 90.6(3), 90.6(3) av 90.6	91.6, 92.7, 91.4, 91.3 av 91.8	this work
1	Mes ₂	2.078(3)	112.61(9)	102.6	6
7	Cl, OTf	2.068(2)	92.69(5)	92.7	this work

^a Each entry is the average of two NHC–Ge–R angles on a given germanium atom.

have electron-withdrawing substituents bonded to germanium. Electron-withdrawing groups, which stabilize the germanium electron lone pair, appear to inhibit further reaction chemistry.

Structural Comparisons. The NHC-germylene complexes described in this work have similar solid state structures with metrics consistent with Ge(II) donor/acceptor complexes. The R–Ge–R bond angles are approximately 90°; the planes of the carbenic rings are orthogonal to the R–Ge–R planes and bisect the other substituents on the germanium atoms (Table 1). The metrics of compound **1** differ slightly from the metrics of the other complexes: the angles around germanium are more obtuse, which is likely due to the steric bulk of the mesityl substituents.

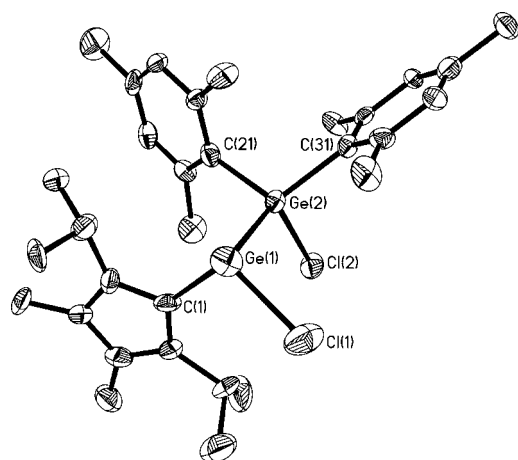


Figure 6. Thermal ellipsoid plot (50% probability surface) of **13**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–Ge(2) = 2.5355(19), C(1)–Ge(1) = 2.147(12), Ge(2)–C(21) = 2.017(5), Ge(2)–C(31) = 2.013(5), Ge(1)–Cl(1) = 2.147(12), Ge(2)–Cl(2) = 2.230(3), C(1)–Ge(1)–Cl(1) = 101.8(3), Cl(1)–Ge(1)–Ge(2) = 88.6(4), Cl(2)–Ge(2)–Ge(1) = 108.30(10), Cl(2)–Ge(2)–C(21) = 110.8(2), Cl(2)–Ge(2)–C(31) = 98.6(2), C(21)–Ge(2)–C(31) = 107.4(3).

Oláh et al. have recently examined the nature of Lewis acid–base interactions of silicon(II) or germanium(II) compounds with the neutral donors NH₃, PH₃, and AsH₃.³⁵ In general, π -donating substituents on the heavy group 14 element reduce the interaction energy between the substituted germylene and a donor presumably by transferring electron density into the empty p-orbital. For germanium, interaction energies decrease in the following order: (forms energetically most favorable complex) GeH₂, > GeHCH₃ > GeCl₂ $\approx$ GeF₂ > Ge(OH)₂ > Ge(NH₂)₂ (forms least energetically favorable complex).³⁵

A trend in the variation of the carbenic C–Ge bond length with respect to the π -donating ability of atoms located on germanium was observed in compounds **1**, **3–7**, **11**, and **12**. This is best illustrated by comparing the metrics of **1** (Mes-substituted) with **5** (F-substituted). On the basis of steric arguments and the electronegativity of the substituents, **5** may be expected to have the shortest C(1)–Ge bond length since fluorine has a very small atomic radius and is more electron-withdrawing than mesityl. Instead, **5** was observed to have one of the longest carbenic C(1)–Ge bond lengths, while **1** has one of the shortest (Table 1). This observation is consistent with Oláh et al.'s findings:³⁵ the lone pairs of electrons on fluorine donate electron density into the σ^* -orbital of the carbenic carbon–germanium bond, and consequently, the bond length between C(1) and Ge is elongated compared to the other compounds. In contrast, the π -electrons of the mesityl substituents are relatively poor electron donors and the carbenic carbon–germanium bond is one of the shortest in the series.

Further evidence for the weakening of the carbene C(1)–Ge bond by competing π -donation is apparent in the formation of **9**, where the strong electron-donating ability of the two nitrogen substituents on germanium provides enough electron density to the p-orbital to completely dislodge the carbene.

The short carbene C(1)–Ge bond in **7** can be attributed to the electron-withdrawing triflate group. Although the germanium

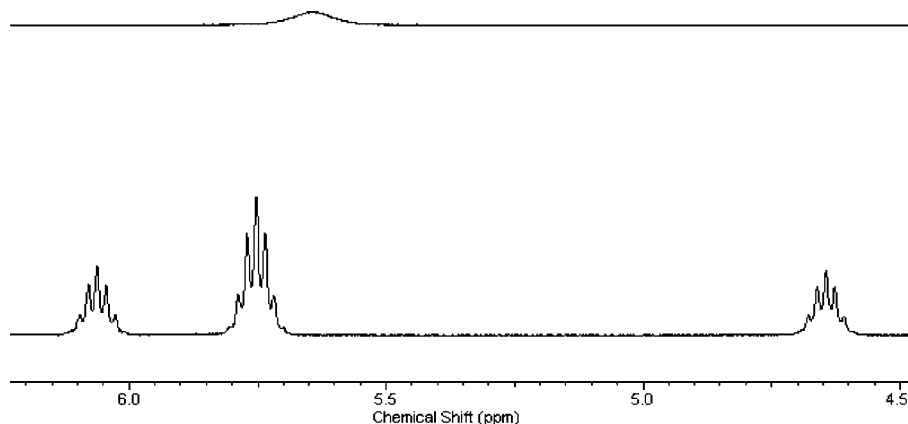
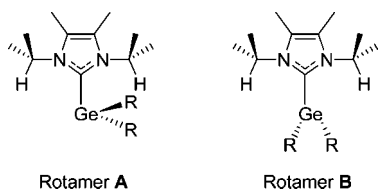


Figure 7. ^1H NMR spectra of compound **3** focusing on the isopropyl methyne region (4.5–6.2 ppm) at 26 °C (top) and at -90 °C (bottom) in $\text{THF-}d_8$.

Chart 2



atom has a potential π -donor (the chlorine), the effect of the triflate appears to dominate.

Variable-Temperature ^1H NMR Spectroscopy. The signals observed in the room-temperature ^1H NMR spectra of compounds **3–7**, **10**, and **11** are broad. As expected, the signal assigned to the vinylic methyls of the carbene is a singlet and the signal assigned to the methyls of the isopropyl moiety is a broadened doublet. However, the signal assigned to the methyne ^1H is not the expected septet; instead, it is very broad, often disappearing into the baseline of the spectrum.

Variable-temperature ^1H NMR spectroscopy was performed on compounds **3–7**, **10**, and **11**; the results obtained were similar, and thus, only the results for compound **3** will be discussed. At -90 °C, the broad signal assigned to the methyne ^1H resolved into three septets, which integrated in a 1:2:1 ratio (Figure 7). To explain this observation, the following model is proposed: at 26 °C, hindered rotation about the CH–N bond results in line broadening in the ^1H NMR spectrum. At -90 °C, this rotation halts, along with rotation about the C(1)–Ge bond, and two conformations predominate. In one conformation, depicted as rotamer **A** in Chart 2, the methyne ^1H 's are not equivalent because of the orientation of the GeCl_2 moiety. The second conformation, rotamer **B** in Chart 2, occurs with the GeCl_2 moiety in such an orientation that the methyne ^1H 's are equivalent. The upfield region of the ^1H NMR spectrum of **3** at -90 °C showed numerous, overlapping signals consistent with the reduced symmetry of the rotamers. All of the remaining halogenated complexes (**4**, **5**, and **6**) showed the same behavior as **3**. Compound **10** also displayed three different methyne ^1H signals at low temperature in the ^1H NMR spectrum, although complete resolution of the septets was not achieved. For compounds **7** and **11**, the broad signals did not completely resolve into different signals at low temperatures. Presumably, resolution of the signals would be achieved at temperatures lower than -90 °C. Finally, for compounds **1** and **13**, rotation about the CH–N bond appears to have stopped at room temperature (the methyne signal is sharp); however, rotation about the C(1)–Ge bond has not (only one methyne signal is observed).

Intermolecular exchange between the carbene and germylene moieties on the NMR time scale is an alternative explanation for the line broadening of the signals in the ^1H NMR spectra of **3–7**, **10**, and **11** at room temperature. Either dissociative or associative exchange is possible. No reaction was observed at room temperature when 2,3-dimethylbutadiene (DMB), a well-known germylene trap, was added to solutions of **3–7**, **10**, and **11** in C_6H_6 . Thus, the formation of free germylene in solution is unlikely at room temperature, and the dissociative mechanism was discarded. The possibility of associative exchange is more difficult to rule out. In the ^1H NMR spectra of **1** and **13**, with the bulkiest substituents at germanium, the signals are sharp, whereas the signals in the ^1H NMR spectra of compounds with small substituents at germanium (**3–7**, **10**, and **11**) are broad. Possibly, the compounds with small substituents undergo associative exchange of the ligands on the NMR time scale. However, compounds with bulky substituents are unable to approach each other and, thus, do not undergo exchange.

Conclusions

In summary, **3** is a versatile reagent that we have used to synthesize a series of stable N-heterocyclic carbene complexes of germanium(II) via substitution chemistry. The goal of stabilizing transient germylenes with an NHC was partially successful: complexes **1**, **10**, **11**, and **13** are all stable derivatives of otherwise transient germylenes. NHC **2** appears to be unsuitable for the stabilization of simple diorganogermylenes; perhaps a more basic³⁶ or sterically encumbered³⁷ carbene would allow the formation of stable Ge(II) complexes. An attempted ligand exchange between **1** and **3** to form a complexed heteroleptic germylene resulted in the unexpected formation of germylgermylene **13**.

The structural characterization of the carbene-germylene complexes **3–7**, **10**, and **11** showed that the length of the carbenic carbon–germanium bond is significantly influenced by the nature of the substituents on germanium. Substituents with an available lone pair of electrons lengthen the C(1)–Ge bond by competing with the carbene for occupancy of the p-orbital on germanium.

Compounds **3–7**, **10**, and **11** display broad signals in their room-temperature ^1H NMR spectra. Two explanations were

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Table 2. Crystallographic Data

	5	6	7	10
empirical formula	C ₁₁ H ₂₀ N ₂ GeF ₂	C ₁₁ H ₂₀ N ₂ GeBr ₂	C ₁₂ H ₂₀ N ₂ GeClF ₃ O ₃ S	C ₁₉ H ₃₈ GeN ₂ O ₂
fw	290.88	412.70	574.46	399.10
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	<i>Cc</i>	<i>Pccn</i>	<i>P</i> $\bar{1}$	<i>Pm</i>
<i>a</i> (Å)	12.124(2)	14.3290(4)	8.9383(3)	8.7579(6)
<i>b</i> (Å)	9.830(2)	17.6782(3)	9.2138(3)	14.0465(11)
<i>c</i> (Å)	11.487(2)	12.3781(5)	11.3287(5)	9.2646(6)
α (deg)	90	90	95.712(2)	90
β (deg)	103.38(3)	90	105.712(2)	102.212(4)
γ (deg)	90	90	96.726(6)	90
volume (Å ³)	1331.8(5)	3135.51(16)	883.50(6)	1113.92(14)
<i>Z</i>	4	8	2	2
no. of data/restraints/params	1877/2/152	3644/0/151	4047/0/214	4752/2/261
goodness-of-fit	1.068	1.049	1.070	1.046
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0578	0.0569	0.0396	0.0709
<i>wR</i> ² (all data)	0.1501	0.1668	0.0914	0.1997
largest diff peak and hole (e Å ⁻³)	0.754, -0.905	1.420, -1.237	0.594, -1.058	2.725, -0.707
	11	12	13	
empirical formula	C ₁₃ H ₂₀ GeN ₄ S ₂	C ₅₆ H ₅₆ Ge ₄	C ₂₉ H ₄₂ Cl ₂ Ge ₂ N ₂	
fw	369.04	1019.37	634.73	
cryst syst	triclinic	monoclinic	monoclinic	
space group	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P2</i> ₁ / <i>c</i>	
<i>a</i> (Å)	10.3332(4)	21.5323(8)	20.4418(6)	
<i>b</i> (Å)	19.2660(7)	10.8763(3)	9.6341(2)	
<i>c</i> (Å)	19.3942(9)	20.9354(5)	15.6432(4)	
α (deg)	105.353(2)	90	90	
β (deg)	104.885(2)	97.4440(16)	93.422(2)	
γ (deg)	104.763(2)	90	90	
volume (Å ³)	3375.2(2)	4861(3)	3075.25(14)	
<i>Z</i>	8	4	4	
no. of data/restraints/params	15 215/0/746	5577/0/275	5363/0/305	
goodness-of-fit	1.121	1.058	1.040	
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0742	0.0424	0.1090	
<i>wR</i> ² (all data)	0.2476	0.1218	0.2846	
largest diff peak and hole (e Å ⁻³)	3.00, -1.842	0.853, -1.046	3.534, -2.359	

provided for these observations: hindered rotation or an associative exchange of ligands. However, further experiments are required to determine the basis for the line broadening in the room-temperature ¹H NMR spectra of **3–7**, **10**, and **11**.

We are currently investigating the reactivity of these complexes and their ability to act as germylene equivalents and will report on this in due course.

Experimental Section

Reactions were performed under an inert atmosphere of nitrogen using standard techniques. Solvents were purified according to literature procedures³⁸ and stored over 4 Å molecular sieves under N₂. All NMR spectra were acquired using C₆D₆ or THF-*d*₈ as the solvent. ¹H NMR spectra were referenced to residual C₆D₅H (7.15 ppm) or the upfield THF-*d*₇ transition (3.58 ppm). ¹³C spectra were referenced to the ¹³C central transition (128.0 ppm) of C₆D₆. ¹⁹F spectra were referenced externally to C₆H₅F (-113.1 ppm relative to CFCl₃). The signals in the ¹³C NMR spectra of the complexes were broad at both room temperature and -90 °C, and thus, the data are not listed. Melting points were determined under an N₂ atmosphere and are uncorrected. FT-Raman spectra were acquired on bulk samples sealed in a melting point tube under nitrogen. Compounds **3**,¹⁰ **4**,¹⁰ and **8**¹⁵ were synthesized according to literature procedures. Mes₂Mg and Tol₂Mg were prepared using modified literature procedures.³⁰ Elemental analyses were performed at Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Synthesis of 5. To a colorless solution of **3** (0.77 mmol, 0.25 g) in THF (4 mL) were added KF (2.0 mmol, 0.12 g) and 18-crown-16 (0.03 mmol, 0.01 g). The reaction mixture was stirred for 2

days at room temperature. After this time, a white precipitate (presumed to be KCl) was removed by centrifugation and was discarded. The solvent was removed under high vacuum to yield a white powder, which was triturated with Et₂O (2 mL × 2). The white powder was dried under high vacuum to give **5** (0.15 g, 67%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated C₆H₆ solution. Mp: 103–108 °C (dec). ¹H NMR (C₆D₆): δ 1.15 (d, ³J_{HH} = 7 Hz, 12 H), 1.42 (s, 6 H), 5.46 (broad, 2 H). ¹⁹F NMR: δ -112. FT-Raman: 209 (s), 530 (m), 888 (m), 1084 (w), 1142 (w), 1286 (w), 1324 (w), 1352 (w), 1399 (m), 1458 (m), 1637 (m), 2941 (s), 2985 (s).

Synthesis of 6. To a colorless solution of **3** (1.0 mmol, 0.32 g) in C₆H₆ (5 mL) was added Me₃SiBr (0.52 mL, 4.0 mmol, 0.12 g). The reaction mixture was stirred for 24 h, and then hexanes (10 mL) were added. A white precipitate was collected, triturated with hexanes (2 mL × 2), and dried under high vacuum to give **6** (0.29 g, 71%). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated C₆H₆ solution. Mp: 150 °C (dec). ¹H NMR (C₆D₆): δ 1.09 (d, ³J_{HH} = 7 Hz, 12 H), 1.37 (s, 6 H), 5.52 (broad, 2 H). FT-Raman (cm⁻¹): 106 (m), 133 (w), 213 (m), 232 (s), 886 (w), 1284 (m), 1414 (m), 1443 (m), 1624 (m), 2940 (s), 2982 (m). Anal. Calcd for C₁₁H₂₀N₂GeBr₂: C, 32.01; N, 6.79; H, 4.88. Found: C, 32.08; N, 6.42; H, 5.24.

Synthesis of 7. To a colorless solution of **3** (1.0 mmol, 0.32 g) in C₆H₆ (6 mL) was added Me₃SiOTf (2 mmol, 0.36 mL). The reaction mixture was allowed to stir for 2 h, after which time the solvent was removed under high vacuum to yield a white powder. The powder was triturated with hexanes (3 mL × 2) and was dried under high vacuum. The white powder was identified as **7** (0.36 g, 62%). Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow diffusion of pentane into a saturated C₆H₆

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solution. Mp: 101–103 °C (dec). ^1H NMR (C_6D_6): δ 1.08 (d, $^3J_{\text{HH}} = 7$ Hz, 12 H), 1.30 (s, 6 H), 5.18 (broad, 2H). ^{19}F NMR (C_6D_6): δ -78. FT-Raman (cm^{-1}): 100 (m), 315 (s), 585 (w), 764 (m), 888 (m), 973 (m), 1235 (w), 1287 (m), 1447 (m), 1623 (m), 2949 (s), 2994 (m). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{GeClF}_3\text{O}_3\text{S}$: C, 32.95; N, 6.40; H, 4.61. Found: C, 33.05; N, 6.42; H, 4.91.

Addition of 8 to 3. A solution of **8** (1 mmol) dissolved in THF (3 mL) was added dropwise to a stirring solution of **3** (0.36 g, 1.1 mmol) dissolved in THF (10 mL), which was cooled in a dry ice/acetone bath. The reaction mixture was stirred for 18 h, during which time it was allowed to warm to room temperature. After this time, the reaction mixture was orange in color. The solvent was evaporated under high vacuum, leaving behind an orange residue. The residue was taken up in C_6D_6 . Insoluble salts (presumed to be LiCl) suspended in the C_6D_6 solution were removed by centrifugation. ^1H and ^{13}C NMR spectra of the solution were consistent with the formation of **2**⁵ and **9**.¹⁵

Synthesis of 10. $^t\text{BuOK}$ (1.8 mmol, 0.20 g) was added to a colorless solution of **3** (0.93 mmol, 0.30 g) dissolved in THF (3 mL). The reaction mixture was allowed to stir for 18 h at room temperature, after which time a white precipitate (presumed to be KCl) was collected by centrifugation and discarded. The solvent was removed under vacuum, yielding **10** (0.32 g, 89%). Crystals suitable for single-crystal X-ray diffraction were grown by placing a saturated Et_2O solution in a freezer at -20 °C for 1 week. Mp: 94–102 °C (dec). ^1H NMR (C_6H_6): δ 1.28 (d, $^3J_{\text{HH}} = 7$ Hz, 12 H), 1.53 (s, 6 H), 1.67 (s, 18 H), 6.07 (broad, 2H). FT-Raman (cm^{-1}): 84 (m), 120 (m), 295 (w), 464 (w), 531 (w), 608 (w), 765 (m), 887 (w), 1233 (w), 1295 (w), 1451 (s), 1628 (w), 2912 (s), 2937 (s), 2970 (s). Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{GeN}_2\text{O}_2$: C, 57.17; N, 7.02; H, 9.60. Found: C, 56.88; N, 6.84; H, 9.68.

Synthesis of 11. To a colorless solution of **3** (0.93 mmol, 0.3 g) in THF (5 mL) was added KSCN (1.86 mmol, 0.18 g). The reaction mixture was allowed to stir for 2 days at room temperature, after which time the solvent was removed under vacuum to yield a white residue. The residue was suspended in C_6H_6 (6 mL); a white solid (presumed to be KCl) was removed by centrifugation and then discarded. Hexanes was added to the C_6H_6 solution; the white precipitate was collected. The solid was dried under vacuum to give **11** (82%, 0.28 g). Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow diffusion of pentane into a saturated C_6H_6 solution. Mp: 122–124 °C (dec). ^1H NMR (C_6D_6): δ 0.94 (d, $^3J_{\text{HH}} = 7$ Hz, 12 H), 1.27 (s, 6 H), 4.94 (broad, 2H). FT-Raman (cm^{-1}): 152 (w), 191 (w), 226 (w), 290 (m), 457 (w), 486 (w), 584 (w), 863 (m), 887 (m), 1287 (m), 1359 (w), 1442 (m), 1623 (m), 2046 (s), 2059 (s), 2936 (s), 2973 (m). Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{N}_4\text{GeS}_2$: C, 42.30; N, 15.18; H, 5.46. Found: C, 42.33; N, 14.82; H, 6.49.

Synthesis of 1 via 3. Compound **3** (0.13 g, 0.4 mmol) was added to a stirring solution of Mes_2Mg (0.4 mmol) in THF/dioxane (4 mL of THF, 1 mL of dioxane). The solution became yellow in color and was allowed to stir for 3 days at room temperature. A white precipitate (presumed to be $\text{MgCl}_2 \cdot \text{dioxane}$) was removed by centrifugation. The ^1H NMR spectrum of the bright yellow solution was consistent with quantitative formation of **1**.⁶

Reaction of ToI_2Mg with 3. To a solution of **3** (0.16 g, 0.5 mmol) dissolved in THF (4 mL) was added ToI_2Mg (0.5 mmol) dissolved in THF/dioxane (4 mL of THF, 2 mL of dioxane). The color of the solution became yellow and was allowed to stir for 18 h at room temperature. After 18 h, the white precipitate (presumed to be $\text{MgCl}_2 \cdot \text{dioxane}$) was removed by centrifugation. The solvent was removed to yield a pale yellow residue. The residue was dissolved in C_6H_6 (3 mL). Vapor diffusion of Et_2O into the

C_6H_6 solution resulted in the formation of crystals of **12**. Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow diffusion of pentane into a saturated C_6H_6 solution. ^1H NMR (C_6D_6): δ 2.00 (s, 24 H), 6.92 (d, $^3J_{\text{HH}} = 7$ Hz, 16 H), (d, $^3J_{\text{HH}} = 7$ Hz, 16 H).

Synthesis of 13. To a deep yellow solution of **1** (0.32 mmol) dissolved in THF (10 mL) was added **3** (0.10 g, 0.32 mmol). The reaction mixture was stirred for 2 days, after which time it became orange in color. The solvent was removed under vacuum to yield an orange-yellow residue, which was then resuspended in C_6H_6 (2 mL). The orange solution was turbid; the fine particulates were removed by centrifugation and discarded. Pentane (4 mL) was added to the C_6H_6 solution, and a pale yellow solid precipitated. The pale yellow solid was collected, triturated with pentane (2×2 mL), and dried under high vacuum to give **13** (0.06 g, 25%). Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow diffusion of pentane into a saturated C_6H_6 solution. Mp: 180–183 °C (dec). ^1H NMR (C_6H_6): δ 0.79 (d, $^3J_{\text{HH}} = 7$ Hz, 6 H), 1.23 (d, $^3J_{\text{HH}} = 7$ Hz, 6 H), 1.47 (s, 6 H), 2.07 (s, 3 H), 2.09 (s, 3 H), 2.62 (s, 6 H), 2.84 (s, 6 H), 5.61 (sept, $^3J_{\text{HH}} = 7$ Hz, 2 H), 6.66 (s, 2 H), 6.71 (s, 2 H). FT-Raman (cm^{-1}): 102 (s), 276 (w), 324 (w), 354 (w), 534 (w), 561 (m), 584 (w), 760 (w), 887 (w), 992 (w), 1284 (s), 1344 (m), 1380 (m), 1442 (m), 1601 (m), 1628 (m), 2730 (w), 2916 (m), 2978 (w). Anal. Calcd for $\text{C}_{29}\text{H}_{42}\text{N}_2\text{GeCl}_2$: C, 54.87; N, 4.41; H, 6.67. Found: C, 54.58; N, 4.06; H, 6.75.

Single-Crystal X-ray Diffraction. Data were collected at low temperature (-123 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN.³⁹ Absorption corrections were applied using HKL2000 DENZO-SMN (SCALEPACK).

The SHELXTL/PC V6.14 suite of programs was used to solve the structures by direct methods.⁴⁰ Subsequent difference Fourier syntheses allowed the remaining atoms to be located. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

Both compounds **12** and **13** showed signs of nonmerohedral twinning in the E-statistics, and the F_{obs} values were consistently higher than the F_{calcs} . WinGX⁴¹ was used to “detwin” the data. ROTAX⁴² found the twin law. “Make HKLF5” was used to generate the detwinned file used in further refinement.

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Supporting Information Available: Crystallographic data in .cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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