

Reactivity Studies of N-Heterocyclic Carbene Complexes of Germanium(II)[†]

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The chemistry of three N-heterocyclic carbene (NHC) complexes of GeR₂, where R = Cl(1), O^tBu(2), Mes (3) (Mes = 2,4,6-trimethylphenyl), toward 2,3-dimethylbutadiene (DMB), 3,5-di-*tert*-butylorthoquinone, methyl iodide, pivalic acid, and benzophenone is reported. Upon heating, 2 and 3 cyclize with DMB to yield a germacyclopentene and free NHC. In contrast, 1 does not react with DMB. PB1PBE/ 6-311+G(d,p) model chemistry shows that the cycloaddition reactions of NHC-GeX₂ (X = F, Cl) with butadiene are not thermodynamically favorable. 3,5-Di-*tert*-butylorthoquinone reacts rapidly with 1–3 to form cyclic products; in the case of 1 and 2, the NHC remains coordinated to the germanium, resulting in a hypervalent species. Compounds 1–3 react with methyl iodide by displacement of I⁻; in each case [NHC-GeR₂Me]⁺ is produced. Only compound 3 reacts in a controlled fashion with pivalic acid; both 1:1 and 1:2 adducts were characterized. Benzophenone failed to react with 1 or 2 but did undergo cycloaddition with 3. In comparison with uncomplexed GeR₂ species, the NHC-GeR₂ complexes are less reactive. The prospect of using NHC-GeR₂ as a synthon for GeR₂ appears to be reaction specific.

Introduction

Simple germylenes (GeR₂) are amphoteric because of their unoccupied p orbital and lone pair of electrons. The addition

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of electron density to the empty p orbital, either by a donor ligand or by π donation, reduces the Lewis acidity while simultaneously increasing the nucleophilicity of the electron lone pair. As such, electronically stabilized germylenes often react primarily through their electron lone pair rather than as Lewis acids.¹

The chemistry of intermolecularly stabilized germylenes, with the exception of the substitution chemistry of GeCl₂ · (dioxane), is poorly studied.² We have utilized strong Lewis bases,³ with a focus on N-heterocyclic carbenes,^{4–6} for the intermolecular stabilization of GeR₂.⁷ Since N-heterocyclic carbenes are among the strongest known neutral donors,⁸ they are expected to significantly alter the reactivity of GeR₂ upon complexation: NHC-GeR₂ species are anticipated to be more nucleophilic and less electrophilic in comparison with noncoordinated germylenes.⁹

Although NHC-GeR₂ complexes have already proven to be valuable precursors for the synthesis of unprecedented

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(8) For a recent comparison of different neutral donors and their Lewis basicity see: Gusev, D. G. *Organometallics* **2009**, *28*, 763.

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⁽⁹⁾ Recently the oxidation of a N-heterocyclic carbene–N-heterocyclic germylene complex with N_2O was reported to form a basestabilized germanone. The corresponding N-heterocyclic germylene, without carbene coordination, is unreactive towards N_2O . See: Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466.



cationic germanium(II) complexes supported by cryptands,¹⁰ crown ethers,¹¹ or carbenes,⁶ a more systematic study of their reactivity is needed. In this report, the reactivity of three NHC-Ge^{II} species is examined (Chart 1). Compounds 1-3 were chosen because they are representative of NHC complexes of three different germylenes with a range of reactivities. **1** is a complex of dichlorogermylene; dihalogermylenes are intrinsically stable and among the least reactive GeR₂ compounds. Compound **2** is a complex of a dialkoxygermylene, which is intermediate in its reactivity. Compound **3** is a complex of a highly reactive and transient diarylgermylene.

Germylenes are valuable building blocks for the synthesis of germanium-containing compounds. Unfortunately, their potential utility is often limited by their nonspecific reactivity. The NHC-GeR₂ complexes may act as synthons of GeR₂ while being easier to isolate and handle. Therefore, the reactivity of 1-3 will be compared to the reactivity of uncoordinated germylenes and the potential use of 1-3 as synthetic equivalents of GeR₂ will be evaluated.

Results and Discussion

Reaction with 2,3-Dimethylbutadiene. 2,3-Dimethylbutadiene (DMB) is commonly used as a trapping reagent for transient¹² and stable¹³ germylenes since, in general, germylenes undergo cycloaddition with DMB to form a germacyclopentene in high yield.^{1,14}

As was previously reported, complex **3** acts as a synthetic equivalent of GeMes₂: when **3** was heated with DMB, germacyclopentene **4** was isolated (Scheme 1).⁴ We proposed that, upon heating, uncoordinated GeMes₂ was released from **3**, which then rapidly cyclized with DMB to give **4** and the NHC **5**. To ascertain the generality of the reaction of DMB with NHC-Ge^{II} species, the reactivity of **1** and **2** with DMB was examined.

A solution of 1 and DMB did not undergo any observable reaction, as determined by ¹H NMR spectroscopy, even after prolonged heating in the presence of excess DMB (Scheme 2). In contrast, GeCl₂ · (dioxane) readily reacts with DMB to form **6** under similar conditions.¹⁵ If it is assumed that for GeCl₂ to

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react with DMB it must be dissociated from any neutral donors, then the difference in reactivity between $\text{GeCl}_2 \cdot (\text{dioxane})$ and 1 toward DMB can be attributed to the much stronger coordination of the NHC to GeCl_2 compared to 1,4-dioxane. Under these conditions, the dissociation of GeCl_2 from the carbene in 1 is apparently not favored kinetically. The reaction may also not be thermodynamically favorable: GeCl_2 may prefer to coordinate with the NHC rather than form a germacyclopentene.

Interestingly, when **6** was added to a solution of the free NHC **5**, complex **7** was isolated from the reaction mixture (Scheme 3). The structure of complex **7** consists of a molecule of **6** coordinated by the carbene (Figure 1). Given that the germanium center in **6** has two electron-withdrawing chloride substituents, it is not surprising that the germanium is able to form a hypercoordinated species.¹⁶ When a solution of **7** in THF was heated in a sealed tube for 3 days, DMB and **1** were formed, as determined by ¹H NMR spectroscopy. Thus, the formation of **6** by the reaction between **1** and DMB appears to be thermodynamically unfavorable.

Heating a solution of complex **2** and excess DMB at 80 °C for 18 h resulted in the formation of **8** and carbene **5** (Scheme 4).¹⁷ Unlike the case for **6**, a coordination complex between **5** and **8** was not observed and heating **8** in the presence of **5** did not result in retrocyclization.

On the basis of the results illustrated in Schemes 1–4, the favorability of the reaction of a NHC-GeR₂ complex with DMB appears to be strongly substituent-dependent: both the Mes- and O^tBu-substituted compounds form the corresponding germacyclopentene, while the germanium dichloride complex favored coordination to NHC **5**. Using PBE1PBE/6-311+G(d,p) as the model chemistry, the energetics of a model system were examined computationally to gain further insight into the reaction of butadiene with a series of NHC-GeR₂ complexes.^{18,19}

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⁽¹⁷⁾ Compound 8 can also \overline{be} synthesized by the reaction of 2 equiv of KO^tBu with 6.

⁽¹⁸⁾ Calculations using standard density functionals such as B3LYP, BP86, B98, and PW91 have been endorsed as an excellent method for predicting bond lengths and bond dissociation energies of NHC complexes of metals. See: Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687.

⁽¹⁹⁾ A previous computational study examined substituent effects on the bonding in NHC-GeR₂ complexes. Both MP2/6-311+G(d,p) and PBE1PBE/6-311+G(d,p) model chemistries were used and found to give very similar results. Therefore, only PBE1PBE/6-311+G(d,p) was used in the present study; see: Ruddy, A. J.; Rupar, P. A.; Bladek, K. J.; Allan, C. J.; Avery, J. C.; Baines, K. M. *Organometallics* **2010**, *29*, 1362.

Scheme 3





Figure 1. Thermal ellipsoid plot (50% probability surface) of 7. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-C1 = 1.965(2); Ge1-C14 = 1.942(2); Ge1-C17 = 1.943(3); Ge1-C12 = 2.4007(7); Ge1-C13 = 2.5093(7); C12-Ge1-C13 = 169.09(3); C14-Ge1-C17 = 96.87(11); C1-Ge-C12 = 87.16(7); C1-Ge-C13 = 82.06(7).



To reduce computational costs, simplified analogues of the carbene complexes were studied (complexes 9-15), and butadiene was used in place of DMB (Chart 2). The energetics of the reactions of the NHC complexes of GeR₂ with butadiene was examined by comparing the three systems shown in Chart 3. The total energy of system A, the NHC-GeR₂ complex plus butadiene, was used as the reference point. System B, modeled after 7 (Scheme 3, Figure 1), consists of a complex of the NHC with the germacyclopentene. System C is the germacyclopentene with free carbene.

The results are tabulated in Table 1 and reveal a number of interesting trends. With five of the seven substitution patterns (R = OH, H, NH₂, Me, Ph), system C is the most stable. However, when the substituent on germanium is either fluorine or chlorine, system A is energetically preferred. System B is stable only when electronegative substituents (R = F, Cl, OH) are on germanium.¹⁶ With less electron-withdrawing substituents on germanium (R = H, NH₂, Me, Ph), system B is not stable and, upon geometry optimization, separates into uncoordinated carbene and germacyclopentene (system C).

The computational results are consistent with the experimental results. The formation of a dichlorogermacyclopentene was not observed in the reaction between 1 and DMB; the reaction of dichlorogermacyclopentene (6) with NHC 5



 Table 1. Relative Energies for the Reaction of NHC-GeR2

 Complexes with Butadiene

	rel $\Delta G^{\circ}_{298 \mathrm{K}}$ (kJ/mol)			
substituent R on Ge	system A	system B	system C	
Н	0	not stable	-30.8	
OH	0	12.3	-13.0	
NH_2	0	not stable	-44.3	
Me	0	not stable	-88.9	
F	0	5.6	30.8	
Cl	0	8.6	25.0	
Ph	0	not stable	-64.3	

produced the hypercoordinate 7. On the basis of the computational results, complex 7 is expected to be thermodynamically unstable toward the release of butadiene. Indeed, 7 dissociates upon heating by releasing DMB (Scheme 3) and forming 1.

The computations indicate that system B may be experimentally accessible when R = OH; however, in the $R = O^{t}Bu$ system, the corresponding pentacoordinated complex was not observed (Scheme 4). Presumably, the increased steric bulk of the O^tBu substituent compared to that of the OH group disfavors the formation of a pentacoordinate germanium species.

Both the experimental and computational results show that a dihalogenated germylene prefers to be coordinated to a NHC rather than form an adduct with butadiene, whereas the dialkoxy- and diorganogermylenes prefer the formation of a germacyclopentene.

Reactions with an Orthoquinone. As with DMB, 3,5-di*tert*-butylorthoquinone reacts rapidly in high yield with germylenes and, therefore, can be used as a trapping reagent



for reactive divalent germanium compounds (Scheme 5).²⁰ Due to the formation of two germanium—oxygen bonds and the aromatization of the quinone (Scheme 5), the reaction of 3,5-di-*tert*-butylorthoquinone with complexes 1-3 is expected to be more thermodynamically favorable compared to the analogous reactions with DMB.

Addition of the red 3,5-di-*tert*-butylorthoquinone to a colorless solution of 1 resulted in rapid discoloration of the quinone (Scheme 6). A white solid was isolated and was identified as 17 by X-ray crystallography. Figure 2 shows the solid-state structure of the cycloadduct: notably, the NHC remains coordinated to the germanium.¹⁶

The reaction of **2** and 3,5-di-*tert*-butylorthoquinone behaved in exactly the same manner as with **1** (Scheme 6). A white solid was isolated, and analysis by ¹H NMR spectroscopy confirmed the formation of a 1:1 adduct of the quinone with the NHC-coordinated germylene (**18**). Attempts to grow crystals of **18** suitable for single-crystal X-ray diffraction were not successful.

The addition of 3,5-di-*tert*-butylorthoquinone to a yellow solution of **3** resulted in the formation of a deep blue reaction mixture. The ¹H NMR spectrum of the solution was complex but clearly showed the presence of **19** (Scheme 6), which was subsequently isolated and characterized.²¹ Signals that could be clearly attributed to an NHC moiety, either coordinated or



Figure 2. Thermal ellipsoid plot (50% probability surface) of 17. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1-Ge = 1.995(2); Ge-Cl1 = 2.2738(10); Ge-Cl2 = 2.1541(9); Ge-O14 = 1.8136(16); Ge-O15 = 1.8906(17); O14-Ge-O15 = 86.86(7); O14-Ge-C1 = 132.33(8); O15-Ge-C1 = 87.42(8); O14-Ge-Cl2 = 113.95(6); O15-Ge-Cl2 = 94.33(6); C1-Ge-Cl2 = 113.66(7); O14-Ge-Cl1 = 85.58(6); O15-Ge-Cl1 = 168.48(5); C1-Ge-Cl1 = 91.25(7).

uncoordinated, were not visible in the ¹H NMR spectrum of the crude reaction mixture. Under the reaction conditions, the NHC appears to be reacting with the quinone; however, attempts to determine the fate of the NHC failed. The direct reaction of the NHC with 3,5-di-*tert*-butylorthoquinone also resulted in a visually similar deep blue solution. The ¹H NMR spectrum of the solution exhibited a multitude of signals, indicating a complex mixture of products. Efforts to identify any of the products derived from the reaction between the carbene and 3,5-di-*tert*-butylorthoquinone were not successful. Possibly, the quinone is abstracting an electron from the NHC, leading to the formation of a radical anion/cation pair which then undergoes further chemistry. The formation of a NHC radical cation upon exposure of **5** to oxidants has been reported previously.²²

In summary, 3,5-di-*tert*-butylorthoquinone reacts readily with 1-3 to give a cycloadduct in a manner similar to that observed with the corresponding free germylenes. The rapid rate at which the orthoquinone reacts with the NHC complexes suggests that 3,5-di-*tert*-butylorthoquinone is able to react directly with germanium while it is still complexed to the NHC. This is in contrast to DMB, which reacted slowly with **2** and **3**, even after extended periods of heating.

Reactions with Methyl Iodide. The reaction of germylenes with methyl iodide has been reported and usually results in the insertion of the germylene into the carbon–iodine bond and the formation of tetravalent germanium.^{13,23} If the germylene is stabilized by an intramolecular donor, nucleophilic attack of the germylene on MeI can result in the formation of a cationic germanium complex.²⁴ Since intermolecularly stabilized Ge(II) species have been less well studied, reports of their reactivity

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⁽²¹⁾ Compound **19** has been reported previously.^{20a}

⁽²²⁾ Radical cations derived from **5** were formed by one-electron oxidation of the NHC by tetracyanoethylene and ferrocenium. See: Ramnial, T.; McKenzie, I.; Gorodetsky, B.; Tsang, E. M. W.; Clyburne, J. A. C. *Chem. Commun.* **2004**, 1054.

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toward MeI or related electrophiles are limited. Previously it was demonstrated that the lone pair of electrons on Ge in 3 is chemically active by coordination of 3 to BH_3 .⁴ The reactions of methyl iodide with 1-3 are now presented.

Addition of an excess of MeI to a solution of 1 in C_6H_6 resulted in the appearance of several new signals in the ¹H NMR spectrum of the residue obtained after removal of the solvent, consistent with the formation of methylated adducts of 1. ESI-MS (positive mode) of the reaction mixture showed signals attributable to the expected adduct, as well as signals attributable to species in which one or both of the chlorides were replaced with iodides (Scheme 7). Also evident in both the mass spectrograph and the ¹H NMR spectrum were signals attributable to the methylated NHC cation, 5-Me⁺.²⁵ The origin of 5-Me⁺ is not entirely clear but could arise from the elimination of GeI₂ from 20⁺.

Although separation of the reaction products was not successful, **20**[I] could also be formed by the reaction of **21**⁶ with excess MeI (Scheme 8). Again, the formation of **5-Me**[I] was observed. Pale green crystals of **20**[I] were mechanically separated by inspection under an optical microscope. The structure of **20**[I] was confirmed by single-crystal X-ray diffraction (Figure 3); as expected, a methyl group occupies the empty coordination site that was evident in the structure of **21**. The germanium complex is cationic; the cation is separated from the iodide counterion, with the closest Ge–I approach being 4.305(1) Å. The Ge–C1 and Ge–I bond lengths are contracted in comparison to those in **21**,⁶ which can be understood given the conversion of the electron lone pair on germanium to a bonding electron pair and the cationic charge.

Complexes 2 and 3 both react rapidly with methyl iodide (Scheme 9). In each case, a white powder formed upon addition of a stoichiometric amount of methyl iodide to a solution of either 2 or 3. The precipitates were identified as 22[I] and 23[I], respectively, by ¹H NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (Figures 4 and 5).



Figure 3. Thermal ellipsoid plot (50% probability surface) of 20^+ . The iodide counteranion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge-C1 = 1.994(9); Ge-C20 = 1.930(8); Ge-I1 = 2.5405(10), Ge-I3 = 2.5299(13); C20-Ge-C1 = 112.9(4); C20-Ge-I2 = 108.1(3); C1-Ge-I2 = 118.2(3); C20-Ge-I1 = 111.3(3); C1-Ge-I1 = 101.3(2); I2-Ge-I1 = 104.57(4).



Qualitatively, compounds 1-3 react at noticeably different rates with methyl iodide. In solution, a precipitate (23[I]) was observed instantly upon addition of MeI to a solution of 3. The reaction of MeI and 2 was also quick, with precipitate formation occurring within a couple of minutes. Finally, 1 reacted very slowly with methyl iodide. The reaction took days to go to completion, even in the presence of excess MeI; furthermore, the chemistry of 1 and MeI was complicated by halogen exchanges (Scheme 7). Examination of the calculated energies of the HOMOs of model compounds (Table 2) shows a good correlation between the energy of the HOMO and the reactivity of the related experimental systems toward MeI.

Complex **23**[I] reacts rapidly with CDCl₃, resulting in dissociation of the carbene moiety and the quantitative formation of **24**,²⁷ which was subsequently characterized (Scheme 10).²⁸ Overall, the methylation of **3** followed by chlorination to give **24** is the synthetic equivalent of the insertion of GeMes₂ into MeCl,

^{(25) 5-}Me⁺ has been reported before and was synthesized by the direct reaction of 5 with MeI. See: Kuhn, N.; Göhner, M.; Steimann, M. Z. Naturforsch., B 2002, 57, 631.

⁽²⁶⁾ Using 12 (R = CH₃) as a model for the mesityl-substituted **3** is a fairly poor approximation. It would be expected that the HOMO in **3** would receive additional stabilization as a result of the sp² hybridization of the ipso mesityl carbon substituents.

⁽²⁷⁾ **24** was previously reported and was synthesized by the addition of MeLi to Mes₂GeCl₂. See: Duverneuil, G.; Mazerolles, P.; Perrier, E. *Appl. Organomet. Chem.* **1995**, *9*, 37.

⁽²⁸⁾ **5** is believed to form a salt of Cl₂, as was observed previously in the reaction of **5** with hexachloroethane. See: Kuhn, N.; Abu-Rayyan, A.; Göhner, M.; Steimann, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1721.



Figure 4. Thermal ellipsoid plot (50% probability surface) of **22**⁺. The iodide counteranion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge-C1 = 1.998(5); Ge-O1 = 1.764(3); Ge-O2 = 1.762(4); Ge-C22 = 1.924(5); O2-Ge-O1 = 109.18(18); O2-Ge-C22 = 106.8(2); O1-Ge-C22 = 119.7(2); O2-Ge-C1 = 106.71(19); O1-Ge-C1 = 105.46(19); C22-Ge-C1 = 108.3(2).



Figure 5. Thermal ellipsoid plot (50% probability surface) of **23**⁺. The iodide counteranion and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-C1 = 2.014(5); Ge1-C32 = 1.962(5); Ge1-C23 = 1.971(5); Ge1-C14 = 1.977(5); C32-Ge1-C23 = 109.4(2); C32-Ge1-C14 = 107.0(2); C23-Ge1-C14=116.4(2); C32-Ge1-C1=105.3(2); C23-Ge1-C1=110.0(2).

an otherwise difficult transformation to perform with a transient germylene. The reaction of **3** with ethyl iodide was also examined. Ethyl iodide reacts with **3**, forming the expected ethylated species 25[I]. Cation 25^+ also underwent a similar chlorination reaction to give 26 (Scheme 11).

Reaction with Pivalic Acid. Germylenes react with a carboxylic acid by insertion into the oxygen-hydrogen bond, resulting in the generation of a germyl ester.²⁹ To determine if NHC-coordinated germylenes will behave in the same manner, the reactivity of 1-3 toward a carboxylic acid was investigated.

Addition of pivalic acid to solutions of 1 and 2 formed complex mixtures, as ascertained by ¹H NMR spectroscopy. Attempts to identify any of the products were not successful. In contrast, **3** reacted cleanly with pivalic acid to form two different germanium-containing compounds, **27** and **28** (Scheme 12), in

Table 2. Calculated PBE1PBE/6-311+G(d,p) Energies of the HOMO of Model Compounds 10, 14, and 15 and the Qualitative Reaction Rate of Related Experimental Systems

compound	qualitative	substitution	HOMO energy (eV)
	reaction rate	of model	of the model compound
	with MeI	compound	(lone pair on Ge)
$\mathbf{I} (\mathbf{R} = \mathbf{CI})$	slow	14 (R = Cl)10 (R = OH)15 (R = Ph)	-6.21
$2 (\mathbf{R} = \mathbf{O}^{t}\mathbf{Bu})$	fast		-5.23
$3 (\mathbf{R} = \mathbf{Mes})^{26}$	fastest		-4.80

Scheme 10



Scheme 11



addition to the conjugate acid of the carbene $(5-H^+)$. Compound 27 is the same compound expected from the reaction of pivalic acid with free dimesitylgermylene; compound 28 was not anticipated as a product, and the mechanism for its formation was not immediately clear.³⁰

The ratio of **27** to **28** varied with the stoichiometry used in the reaction. Compound **27** was formed exclusively when **3** was added dropwise to a solution containing an excess of pivalic acid. Conversely, when 1 equiv of pivalic acid was slowly added to a solution of **3**, **28** was the only germaniumcontaining compound detected by ¹H NMR spectroscopy.

On the basis of these observations, it appears as if compound 28 is formed by the reaction of 27 with 3. Indeed, when 27 and 3 were combined in solution, both 28 and 5 were detected as products by ¹H NMR spectroscopy (Scheme 13).

Previous work has demonstrated that the mechanism for the addition of transient organogermylenes to carboxylic acids proceeds initially by complexation of the carbonyl oxygen to the germanium followed by proton transfer.²⁹ However, this mechanism is probably not operative in the formation of **27**, since the formally empty *p* orbital on the NHC-GeR₂ complex is occupied by the carbene and, therefore, the Lewis acidity is greatly diminished. Complex **3** is a Lewis base,⁴ and thus, the formation of **27** through initial proton transfer, followed by displacement of the carbene by pivalate, is proposed.

Reaction with Benzophenone. The stable germylene Ge[CH- $(SiMe_3)_2]_2$ reacts rapidly with phenones at room temperature to yield conjugated trienes.³¹ Therefore, the reactivity of 1-3 with benzophenone was examined to see if the NHC-stabilized germylenes react in the same manner as Ge[CH(SiMe_3)_2]_2.

⁽²⁹⁾ Huck, L. A.; Leigh, W. J. Organometallics 2007, 26, 1339.

⁽³⁰⁾ Adduct **28** has been previously reported and was formed by the direct reaction of tetramesityldigermene with pivalic acid: Hurni, K. L.; Rupar, P. A.; Payne, N. C.; Baines, K. M. *Organometallics* **2007**, *26*, 5569.

^{(31) (}a) Sweeder, R. D.; Edwards, F. A.; Miller, K. A.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **2002**, *21*, 457. (b) Sweeder, R. D.; Cygan, Z. T.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **2003**, *22*, 4613.

Scheme 12



Both 1 and 2 did not show any reactivity toward benzophenone even at elevated temperatures; however, complex 3 was found to react slowly with benzophenone over 24 h at 100 °C to form 29, which was isolated as a colorless powder after purification by chromatography (Scheme 14). Integration of the ¹H NMR spectrum of 29 clearly showed the formation of a 1:1 adduct of the Mes₂Ge moiety with benzophenone. Mass spectrometric data were also consistent with the formation of a 1:1 adduct.

The structure of **29** was determined by 1D and 2D NMR techniques. In the ¹H and ¹³C NMR spectrum of **29**, signals attributable to two different mesityl and two different phenyl moieties were detected. The ¹H $^{-13}$ C gHSQC spectrum of **29** was consistent with a 1,2-substitution pattern on one of the aromatic rings originating from benzophenone. The other phenone phenyl ring remained monosubstituted. The presence of the doubly benzylic proton was confirmed by gCOSY and ¹H $^{-13}$ C gHMBC spectroscopy.

On the basis of experimental evidence, the reaction of $Ge[CH(SiMe_3)_2]_2$ with phenones was proposed to occur via a concerted [4 + 2] cycloaddition.³¹ A similar mechanism is likely operative in the formation of **29**. As was previously proposed, **3** dissociates to Mes₂Ge and **5** (Scheme 15) at elevated temperature (70–80 °C). Dimesitylgermylene can then react with benzophenone, presumably via [4 + 2] cycloaddition. Subsequent rearomatization of the ring by a transfer of a hydrogen atom results in the formation of **29**. Attempts to observe the postulated triene intermediate by ¹H NMR spectroscopy were unsuccessful; the hydrogen shift is most likely catalyzed by the NHC **5**, a strong base.³² The reactions of the related R₂Si with benzophenone have also



been studied; the formation of both conjugated trienes ($R = C_5 Me_5$)³³ and rearomatized products ($R = NR'_2$, Me)^{34–36} have been reported.

Reactions That Did Not Proceed or Resulted in Intractable Mixtures. In addition to the chemistry described above, the reactions of 1-3 with a number of additional reagents were explored. The results are summarized in Table 3. Essentially, 1 and 2 were found to be unreactive toward many reagents under the reaction conditions examined. The NHC complex 3 was found to react with a wider array of reagents; however, the product mixtures were often complex. Typically, the ¹H NMR spectra of the crude reaction mixtures displayed either broad peaks indicative of the formation of polymeric material (benzaldehyde, P₄) or a large number of peaks suggesting a multitude of products. Attempts to separate the

⁽³²⁾ As a reference, the pK_a of the conjugate acid of the NHC used in this study has been calculated as approximately 36 in acetonitrile. See: Magill, A. M.; Cavell, K. J.; Yates, B. F. J. Am. Chem. Soc. **2004**, 126, 8717.

⁽³³⁾ Jutzi, P.; Eikenberg, D.; Bunte, E.-A.; Möhrke, A.; Neumann, B.; Stammler, H.-G. *Organometallics* **1998**, *15*, 1930.

⁽³⁴⁾ Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. Organometallics 1997, 16, 4861.

⁽³⁵⁾ Ando, W.; Ikeno, M.; Sekiguchi, A. J. Am. Chem. Soc. 1977, 99, 6447.

⁽³⁶⁾ Xiong, Y.; Yao, S.; Driess, M. Chem. Eur. J. 2009, 15, 5545.

Table 3. Summary of the Outcome of Reactions between NHC-GeR₂ and Various Reagents^a

reagent	1	2	3
TEMPO ³⁸	N/R	N/R	dec ^{b,c}
benzaldehyde ^{36,39}	N/R	N/R	$dec^{b,c}$
bis(trimethylsilyl)acetylene	N/R	N/R	N/R
phenylacetylene ⁴⁰	N/R	N/R	$dec^{b,c}$
triethylsilane ¹	N/R	N/R	N/R
P_4^{41}	N/R	N/R	$dec^{b,c}$
C–H activation with phenyl iodide ⁴²	N/R	N/R	N/R

 a N/R = no reaction. Reactions were performed at 70 °C unless otherwise noted. b Attempted at room temperature in THF. c Attempted at -30 °C.

products through selective crystallization, selective precipitation, or chromatography were not successful.

One of the contributing factors that may be leading to the complicated reaction mixtures is that NHC **5** can be released from germanium. Since NHCs are versatile organic catalysts for a wide range of reactions, the presence of free NHC **5** may lead to undesirable side reactions.³⁷

Conclusions

In summary, the chemistry of 1-3 toward a variety of reagents was explored. In some cases, the NHC-GeR₂ complexes formed reaction products similar to those of uncoordinated germylenes, while in other situations, their behavior was quite different from that of uncoordinated germylenes.

Compounds 2 (R = O^tBu) and 3 (R = Mes) reacted with DMB to give germacyclopentenes 4 and 8 in a manner identical with that of uncoordinated germylenes. The dichloro derivative 1 did not react with DMB. PBE1PBE/6-311+G(d,p) calculations suggest that dichlorogermylene thermodynamically prefers to be coordinated by the NHC rather than the diene.

3,5-Di-*tert*-butylorthoquinone was found to react quickly with 1-3 to produce a cycloadduct. The rapid reaction of the quinone with 1-3 suggests that the reaction occurs while the NHC remains coordinated to the germanium; in the case of 1 and 2, the NHC ligand remained coordinated to germanium even after cycloaddition. With the mesityl-substituted system 3, the NHC was released from the germanium upon reaction with the orthoquinone. The uncoordinated NHC reacted rapidly with available 3,5-di-*tert*-butylorthoquinone, producing a complex reaction mixture.

Like intramolecularly stabilized germylenes, complexes 1-3 acted as nucleophiles toward methyl iodide by quaternizing the germanium and forming cationic complexes. The qualitative rate of the reaction was inversely proportional to the energy of the HOMO of model germanium compounds. The alkylation reaction is limited to unhindered alkyl iodides as substrates. Alkyl chlorides and alkyl bromides were found to be unreactive

toward 1-3. Treatment of 23[I] or 25[I] with CDCl₃ chlorinated the germanium to give 24 and 26, respectively.

Pivalic acid formed a complex product mixture upon addition with 1 and 2. In the mesityl system 3, two products were formed and subsequently isolated and characterized. The expected germylene/pivalic acid adduct 27 was isolated, along with the unexpected 28, which can also be formed by the addition of 3 to 27. The formation of either 27 or 28 can be favored by manipulation of the reaction conditions.

Benzophenone was found to be unreactive with both 1 and 2 under the reaction conditions examined. Upon prolonged heating, 3 reacted with benzophenone to give 29, which likely arises from a [4 + 2] cycloaddition between dimesitylgermylene and benzophenone, followed by a hydrogen shift. The reactivity of 3 toward benzophenone is similar to what was reported for uncoordinated germylenes and silylenes.

The reactivity of several additional reagents toward 1-3 was examined. In general, 1 and 2 were found to be unreactive. The mesityl-substituted 3 did react in some cases, but the identities of the products were not determined because of the complexity of the reaction mixtures.

In general, the substituent effects on the reactivity of uncoordinated germylenes are similar to those observed for the NHC germylene complexes. As a result of the intrinsic stability of the corresponding dichlorogermylene and a HOMO stabilized by the electronegative chlorines on the germanium center, **1** was the least reactive of the complexes. Compound **3** was the most reactive, likely because of the inherent instability of the related uncoordinated germylene (Mes₂Ge) and the higher energy of its HOMO as a result of having less electronegative carbon substituents on the germanium center. The reactivity of the O^tBusubstituted **2** was intermediate between that of **1** and **3**.

After examination of the reactivity of 1-3, and a comparison of the reactivity of the complexed GeR₂ compounds to their uncomplexed analogues, the likelihood of using NHC-GeR₂ as synthons for GeR₂ appears to be situation-specific. The release of carbene **5** is a concern, given the strongly basic nature of the NHC which may lead to undesired side reactions.

Experimental Section

Reactions were performed under an inert atmosphere of nitrogen using standard techniques. Solvents were purified according to literature procedures⁴³ and stored over 4 Å molecular sieves under N2. All NMR spectra were acquired using C_6D_6 , THF- d_8 , or CD₃CN as the solvent. ¹H NMR spectra were referenced to residual C_6D_5H (7.15 ppm), residual CD_2HCN (1.94 ppm), or the upfield signal of THF- d_7 (3.58 ppm). Melting points were determined under a N2 atmosphere and are uncorrected. FT-Raman spectra were acquired on bulk samples sealed in a melting point tube under nitrogen. Compounds 1,⁶ $2^{5}_{,5}$ $3^{4}_{,4}$ and $21^{6}_{,6}$ were synthesized by following literature procedures. All other chemicals were purchased from commercial suppliers. Pivalic acid was dried prior to use by first dissolving it in THF and storing over 4 Å molecular sieves under N₂. 2,3-Dimethylbutadiene was dried under N₂ over 4 Å molecular sieves prior to use. Elemental analyses were performed at Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Attempted Reaction of 1 with DMB. In a screw-cap vial filled with THF (2 mL) was added 1 (0.05 g, 0.155 mmol) and DMB (0.113 mL, 1 mmol). The reaction mixture was stirred for 18 h at room temperature. Analysis of an aliquot by ¹H NMR spectroscopy showed that no reaction had occurred. The screw cap vial was sealed and heated to 100 °C for 3 days, after which analysis of an aliquot by ¹H NMR spectroscopy showed no reaction.

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Synthesis of 7. To a solution of 6 (0.1 g, 0.44 mmol) in C_6H_6 (3 mL) was added 5 (0.08 g, 0.44 mmol). The solution was stirred for 10 min. Hexanes (10 mL) was added to induce the formation of a white precipitate. The precipitate was identified as 7 (0.14 g, 78%). Crystals suitable for single-crystal X-ray diffraction were grown by the slow diffusion of pentane into a concentrated solution of 7 in C_6H_6 . Mp: 136–142 °C. ¹H NMR (C_6D_6): 1.28 (d, ³J_{HH} = 7 Hz, 12 H, ⁱPr-Me), 1.36 (s, 6 H, =C(N)Me), 1.87 (s, 6 H, =C(CH₂)Me)), 2.97 (s, 4 H, CH₂), 5.13 (sept, ³J_{HH} = 7 Hz, 2 H, ⁱPr-CH). FT-Raman (cm⁻¹): 137 (m), 161 (w), 250 (m), 460 (w), 526 (w), 581 (w), 695 (s), 780 (w), 891 (w), 1166 (w), 1305 (w), 1394 (m), 1447 (m), 1625 (m), 2915 (s), 2944 (s), 2984 (s). Anal. Calcd for $C_{17}H_{31}Cl_2$ -GeN₂: C, 50.17; N, 6.88; H, 7.68. Found: C, 49.79; N, 6.99; H, 7.86.

Thermolysis of 7. A solution of 7 (0.02 g, 0.11 mmol) dissolved in C_6H_6 (5 mL) was heated in a sealed screw-cap bottle for 3 days. Analysis of an aliquot by ¹H NMR spectroscopy showed the quantitative formation of 1 and DMB.

Reaction of 2 with DMB. To a solution of 2 (0.05 g, 0.13 mmol) in THF (2 mL) was added excess DMB (1 mL, 8.8 mmol). The reaction mixture was placed in a sealed tube and heated to 70 °C for 4 days. Analysis of an aliquot by ¹H NMR spectroscopy showed the quantitative formation of **8** and **5**.

Synthesis of 8. To a solution of 6 (0.1 g, 0.44 mmol) dissolved in THF (3 mL) was added KO^tBu (0.1 g, 0.88 mmol). The reaction mixture was stirred overnight. The solvent was removed under vacuum, yielding a colorless residue. The residue was taken up in Et₂O (10 mL). A white suspension, presumed to be KCl, was removed by centrifugation. The solvent was removed under vacuum to yield a colorless liquid that was identified as 8 (0.11 g, 85%). ¹H NMR (C₆D₆): δ 1.38 (s, 18 H, ¹Bu), 1.60 (s, 6 H, =CMe), 1.73 (s, 4 H, CH₂). EI/MS : *m/z* 302 [M⁺, 29%], 287 [M⁺ – Me, 18%], 205 [⁺Ge(O^tBu)₂ – Me, 100%], 147 [GeO^tBu, 85%], 82 [⁺DMB, 35%]. High-resolution EI/MS for C₁₄H₂₈⁷⁴GeO₂: *m/z* calcd 302.1303, found 302.1292.

Reaction of 1 with 3,5-Di-tert-butylorthoquinone. 3,5-Di-tertbutylorthoquinone (0.07 g, 0.31 mmol) dissolved in THF (5 mL) was added dropwise over 2 min to a solution of 1 (0.10 g, 0.31 mmol) in THF (2 mL). During the addition, the red color of the orthoquinone quickly faded. After the addition was complete, the solvent was evaporated under high vacuum to yield an off-white powder. The powder was washed with hexanes (2 mL) to give a brilliant white solid identified as 17 (0.16 g, 94%). Crystals suitable for single-crystal X-ray diffraction were acquired by the slow diffusion of Et₂O into a saturated solution of 17 in C₆H₆. Mp: 196–202 °C. ¹H NMR (C₆D₆): δ 1.06 (d, ³J_{HH} = 7 Hz, 12 H, ⁱPr-Me), 1.28 (s, 6 H, =CMe), 1.37 (s, 9 H, ^tBu), 1.71 (s, 9 H, ^tBu), 5.67 (sept, ³J_{HH} = 7 Hz, 2 H, ⁱPr-CH), 7.06 (s, 1 H, ArCH), 7.26 (s, 1 H, ArCH). FT-Raman (cm⁻¹): 109 (s), 177 (w), 243 (s), 270 (w), 319 (m), 381 (m), 547 (w), 642 (w), 812 (w), 888 (w), 915 (m), 1029 (w), 1103 (w), 1201 (w), 1292 (w), 1330 (w), 1424 (s), 1447 (s), 1581 (w), 1598 (w), 1625 (m), 2874 (s), 2942 (s), 2986 (s). Anal. Calcd for C₂₉H₄₂N₂GeCl₂: C, 55.08; N, 5.14; H, 7.58. Found: C, 55.29; N, 4.90; H, 7.85.

Reaction of 2 with 3,5-Di*tert*-butylorthoquinone. 3,5-Di*-tert*butylorthoquinone (0.04 g, 0.18 mmol) dissolved in hexanes (5 mL) was added dropwise over 2 min to a solution of **2** (0.07 g, 0.18 mmol) in hexanes (5 mL). During the addition, the color of the orthoquinone solution (green) quickly faded. After the addition was complete, the solvent was evaporated under high vacuum, leaving behind an off-white powder. The powder was determined to be **18** (0.10 g, 91%). Mp: 120–122 °C. ¹H NMR (C₆D₆): δ 1.13 (d, ³J_{HH} = 7 Hz, 12 H, ⁱPr-Me), 1.41 (s, 6 H, =CMe), 1.42 (s, 9 H, ^tBu), 1.66 (s, 18 H, O^tBu), 1.82 (s, 9 H, ^tBu), 5.56 (sept, ³J_{HH} = 7 Hz, 2 H, ⁱPr-CH), 6.98 (d, ⁴J_{HH} = 2 Hz, 1 H, ArCH), 7.10 (d, ⁴J_{HH} = 2 Hz, 1 H, Ar-CH). Raman (cm⁻¹): 138 (w), 229 (m), 271 (w), 451 (w), 599 (m), 780 (w), 831 (w), 887 (w), 918 (w), 1108 (w), 1202 (m), 1238 (m), 1331 (w), 1448 (s), 1597 (w), 1636 (w), 2700 (w), 2924 (s), 2967 (s).

Reaction of 3 with 3,5-Di-*tert*-**butylorthoquinone.** Compound **3** (0.16 g, 0.32 mmol) was dissolved in THF (10 mL), resulting in a yellow solution. 3,5-Di-*tert*-butylorthoquinone (0.07 g, 0.32 mmol), dissolved in THF (5 mL), was added dropwise to the THF

solution of **3**. During the addition, the color of the reaction mixture turned from yellow to dark blue. The reaction mixture was extracted with an NH₄Cl aqueous solution (10 mL). The aqueous layer was extracted with Et₂O (10 mL \times 3). The organic layers were combined, dried over MgSO₄, and filtered. Evaporation of the solvent yielded compound **19** (0.11 g, 65%) as a white residue which was identified by ¹H NMR spectroscopy and EI/MS.²¹

Reaction of 1 with Methyl Iodide. To a solution of 1 (0.10 g, 0.31 mmol) in C_6H_6 (4 mL) was added excess methyl iodide (0.19 mL, 3.1 mmol). The solution was stirred overnight, after which time it was pale green. Hexanes (10 mL) was added to the reaction mixture, causing a pale yellow solid to precipitate. The precipitate was collected, redissolved in THF (3 mL), and analyzed by ESI/MS (positive mode).

Reaction of 21 with Methyl Iodide. To a solution of **21** (0.08 g, 0.15 mmol) in C_6H_6 (6 mL) was added MeI (80 μ L, 1.2 mmol). The reaction mixture was stirred for 3 days. Hexanes (10 mL) was added to induce precipitation of a pale green solid which was collected. Crystals suitable for single-crystal X-ray diffraction were acquired by the slow diffusion of Et₂O into a saturated CH₃CN solution. Both yellow and pale green single crystals were grown. The yellow crystals were identified to be **5-Me**⁺ by comparison of the unit cell of the crystals to the reported literature values for **5-Me**⁺.²⁵ The pale green crystals were analyzed by single-crystal X-ray diffraction and found to be **20**[I].

Reaction of 2 with Methyl Iodide. To a solution of **2** (0.05 g, 0.13 mmol) in C₆H₆ (2 mL) was added methyl iodide (8 μ L, 0.13 mmol). After 5 min, a white precipitate formed. The solution was stirred for an additional 10 min. Hexanes (10 mL) was added to the reaction solution to complete the precipitation. The white precipitate was collected and identified as **22**[**I**] (0.06 g, 86%). Crystals suitable for single-crystal X-ray diffraction were acquired by the slow diffusion of Et₂O into a saturated CH₃CN solution of **22**[**I**]. Mp: 160–165 °C. ¹H NMR (CD₃CN): δ 1.30 (s, 3 H, Me), 1.35 (s, 18 H, ¹Bu), 1.56 (d, ³J_{HH} = 7 Hz, 12 H, ¹Pr-Me), 2.35 (s, 6 H, =CMe), 5.37 (s, ³J_{HH} = 7 Hz, 2 H, ¹Pr-CH). ESI-MS (positive mode): *m*/*z* 415 [**22**⁺, 100%]. Raman (cm⁻¹): 597 (m), 1293 (w), 1447 (m), 1459 (m), 1629 (m), 2910 (s), 2973 (s).

Reaction of 3 with Methyl Iodide. To a yellow solution of 3 (0.08 g, 0.16 mmol) in C₆H₆ (5 mL) was added MeI (10 μ L, 0.16 mmol). A white precipitate formed immediately. Hexanes (10 mL) was added to the reaction solution to complete the precipitation of 23[I] (0.05 g, 50%). The ¹H NMR spectrum of 23[I] taken in CD₃CN was complicated at room temperature with numerous broad signals and was difficult to interpret. As the temperature was decreased, the spectrum changed but was still complicated. High-temperature NMR experiments were also attempted but resulted in compound decomposition. Crystals suitable for singlecrystal X-ray diffraction were grown by diffusing pentane into a concentrated THF solution of 23[I]. Mp: 198-202 °C. ¹H NMR (CD₃CN, room temperature): 1.29 (s)-1.31 (bs, 15 H total, ¹Pr-Me and Me), 2.13 (bs, 12 H, Mes-o-Me), 2.28, 2.36 (both s, 6 H, Mes-p-Me and =CMe), 4.57 (bs, 2 H, ⁱPr-CH), 6.78 (s, 4 H, Mes-CH). Raman (cm⁻¹): 106 (w), 229 (w), 557 (m), 596 (m), 887 (w), 1047 (w), 1292 (m), 1384 (m), 1450 (m), 1604 (m), 1629 (w), 2736 (w), 2927 (s), 2982 (s). ESI-MS (positive mode): m/z 507 [23⁺, 100%]. Anal. Calcd for C₃₀H₄₅GeIN₂: C, 56.90; N, 4.42; H, 7.16. Found: C, 56.78; N, 4.29; H, 7.29.

Reaction of 23[I] with CDCl₃. 23[I] (2.00 g, 0.32 mmol) was dissolved in CDCl₃ (2 mL), resulting in a colorless solution. After 10 min the reaction mixture turned brown. The solvent was extracted with a saturated NH₄Cl solution (10 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The organic layers were combined, dried over MgSO₄, and filtered. Removal of the solvent yielded a brown residue. The residue was redissolved in hexanes and passed through a short silica plug. Removal of the hexanes yielded a colorless residue identified as 24 (0.08 g, 70%). The identity of 24 was confirmed by comparison of the ¹H NMR spectral data and EI/MS data to the literature values.²⁷

Table 4. Crystallographic Data for Compounds 7, 17, 20[I], 22[I], and 23[I]

param	7	17	20 [I]	22 [I]	23 [I]
empirical formula	C17H30Cl2GeN2	C ₂₅ H ₄₀ Cl ₂ GeN ₂ O ₂	C12H23GeI3N2	C ₂₀ H ₄₁ GeIN ₂ O ₂	C ₃₀ H ₄₅ GeIN ₂
formula wt	405.92	544.10	648.61	541.06	633.19
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_{1}/c$	$P\overline{1}$	$P2_{1}2_{1}2_{1}$	$P2_1/c$	$P2_1$
a (Å)	15.9298(5)	8.5449(17)	10.246(2)	11.821(2)	11.251(2)
$b(\mathbf{A})$	8.3530(2)	8.8873(18)	12.522(3)	13.765(3)	18.190(4)
c(Å)	16.5558(5)	18.880(4)	14.850(3)	15.378(3)	15.163(3)
α (deg)	90	78.89(3)	90	90.00	90
β (deg)	115.8120(14)	79.44(3)	90	92.14(3)	107.22(3)
γ (deg)	90	81.13(3)	90	90.00	90
$V(A^3)$	1983.15(10)	1372.5(5)	1905.2(7)	2500.6(9)	2964.1(11)
Z	4	2	4	4	4
no. of data/restraints/params	4554/0/204	6266/0/301	5559/0/171	5678/0/248	13 307/1/641
goodness of fit	1.066	1.043	0.994	1.155	1.057
R1 $(I > 2\sigma(I))$	0.0409	0.0380	0.0526	0.0526	0.0428
wR2 (all data)	0.1084	0.0958	0.1357	0.1582	0.1042
largest diff peak, hole (e $Å^{-3}$)	0.570, -0.738	0.544, -0.696	1.266, -1.759	3.340, -1.171	0.732, -0.979

Reaction of 3 with Ethyl Iodide. To a yellow solution of **3** (0.17 g, 0.32 mmol) in C₆H₆ (5 mL) was added EtI (26μ L, 0.32 mmol). The reaction mixture was stirred for 2 h, over which time the bright yellow solution of **3** faded to a pale straw color. Hexanes (5 mL) was added to induce the precipitation of **25**[I], which was collected as an off-white sticky residue. As with **22**[I], the ¹H NMR spectrum of **25**[I] was complicated at room temperature with numerous broad signals. ESI-MS (positive mode): m/z 521 [M⁺, 35%], 209 [**5-Et**⁺, 90%], 181 [**5-H**⁺, 100%].

Synthesis of 26. 25[I] (0.07 g, 0.1 mmol) was dissolved in CDCl₃ (2 mL), resulting in a colorless solution. After 10 min the reaction mixture turned brown. The solvent was extracted with a saturated NH₄Cl solution (10 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The organic layers were combined, dried over MgSO₄, and filtered. Removal of the solvent yielded a brown residue. The residue was redissolved in hexanes and passed through a short silica plug. Removal of the hexanes yielded a colorless residue identified as 26 (0.035 g, 94%). ¹H NMR (C₆D₆): δ 1.19 (t, ³*J*_{HH} = 8 Hz, 3 H, CH₂CH₃), 1.64 (q, ³*J*_{HH} = 7 Hz, 2 H, CH₂CH₃), 2.04 (s, 6 H, Mes-*p*-Me), 2.38 (s, 12 H, Mes-*o*-Me), 6.64 (s, 4 H, Mes-CH). EI/MS: *m*/*z* 376 [M⁺, 18%], 347 [M⁺ - Et, 100%], 311 [GeMes₂ - H]. High-resolution MS/EI for C₂₀H₂₇⁷⁰-Ge³⁵Cl: *m*/*z* calcd 372.1043, found 372.1028.

Reaction of 3 with Excess Pivalic Acid. To a solution of pivalic acid (0.14 g, 1.4 mmol) in THF (2 mL) was added dropwise a solution of 3 (0.08 g, 0.16 mmol) in THF (1 mL) over 5 min. The rate of addition was such that the yellow color of 3 was allowed to dissipate before the next drop was added. The solvent was removed under vacuum, yielding a colorless residue. A ¹H NMR spectrum of the residue revealed the presence of $27, 5-H^+$, and pivalic acid. The residue was suspended in Et₂O (10 mL) and then extracted with a concentrated NH₄Cl solution (10 mL). The organic layer was separated, dried over MgSO₄, and evaporated under vacuum, leaving a colorless waxy residue. The residue was placed under high vacuum for 1 week to remove most of the pivalic acid; however, it was not possible to completely remove all traces of pivalic acid from 27. ¹H NMR (C₆H₆): δ 1.19 (s, 9 H, ^tBu), 2.04 (s, 6 H, Mes-p-Me), 2.44 (s, 12 H, Mes-o-Me), 6.67 (s, 4 H, Mes-CH), 7.33 (s, 1 H, GeH). EI-MS: m/z 413 [M⁺, 20%], High-resolution MS/EI for C₂₃H₃₁⁷⁴GeO₂: m/z calcd 413.1539, found 413.1519.

Reaction of 3 with Limiting Pivalic Acid. Pivalic acid (8 mg, 0.08 mmol), dissolved in THF (0.45 mL), was added dropwise to a solution of **3** (0.08 g, 0.16 mmol) in THF (10 mL) over 5 min. During this time the yellow color of **3** faded to give a colorless solution. After the addition was complete, the solvent was evaporated under high vacuum, leaving behind a colorless residue. The residue was redissolved in Et₂O (10 mL). The Et₂O solution was extracted with NH₄Cl (10 mL \times 2) and then dried over MgSO₄. After filtration and removal of the solvent by evaporation under vacuum, **28** was isolated (0.04 g, 67%). The identity of **28** was confirmed by comparison with an authentic sample.³⁰

Reaction of 3 with Benzophenone. To a solution of 3 (0.08 g, 0.16 mmol) in THF (5 mL) was added benzophenone (0.03 g, 0.16 mmol) in a screw-cap-sealed vial. The reaction mixture was heated to 80 °C and stirred for 18 h. The reaction mixture was extracted with NH4Cl (10 mL \times 2), which in turn was extracted with Et₂O (10 mL \times 3). The organic layers were combined and then dried over MgSO4 and filtered. Removal of the solvent by evaporation under vacuum gave a colorless residue which was purified by silica gel chromatography using 90% $CH_2Cl_2/10\%$ hexanes as the eluent to give 29 (0.02 g, dsing 90.76 CH₂Cl₂/10.76 ncxales as the clutch to give 25 (0.02 g, 25%). ¹H NMR (CD₂Cl₂): δ 2.23 (s, 3H, C²³H₃), 2.28 (s, 3H, C²²H₃), 2.41 (s, 6H, C²⁰H₃), 2.43 (s, 6H, C²¹H₃), 6.20 (s, 1H, C¹⁹H), 6.81 (s, 2H, C¹²H), 6.86 (s, 2H, C¹³H), 7.05-7.07 (m, 1H, C¹⁰H), 7.15-7.24 (m, 5H, C¹⁷H + C¹⁴H + C¹⁶H), 7.27-7.31 (m, 2H, C¹¹H + C¹⁵H), 7.84-7.86 (m, 1H, C¹⁸H). ¹³C NMR (CD₂Cl₂): δ 21.27 (C23), 21.39 (C22), 23.18 (C21), 24.21 (C20), 83.87 (C19), 125.16 (C18), 127.62 (C17), 127.81 (C16), 128.04 (C15), 128.86 (C14), 129.37 (C13), 129.59 (C12), 129.78 (C11), 132.28 (C10), 135.47 (C9), 136.23 (C8), 137.82 (C7), 139.90 (C6), 140.18 (C5), 143.05 (C4), 143.09 (C3), 146.38 (C2), 152.81 (C1). High-resolution EI/MS for $C_{31}H_{32}^{74}$ GeO: m/z calcd 494.1665, found 494.1649.



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Computational Details. The geometries of the model compounds (systems B and C) were optimized with the GAUSSIAN 03^{44} program using the PBE1PBE density functional and the 6-311+G(d,p) basis set. Tight convergence criteria for the selfconsistent field (SCF = Tight) and ultrafine integration grids (Int = Grid = Ultrafine) were used during the calculations. All optimized geometries did not have any imaginary frequencies and, therefore, are minima on the potential energy surface. The optimized geometries are given in the Supporting Information.

Single-Crystal X-ray Diffraction Experimental Details. 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.⁴⁵ Absorption corrections were applied using HKL2000 DENZO-SMN (SCALEPACK). Crystallographic data for compounds 7, 17, **20**[I], **22**[I], and **23**[I] are given in Table 4.

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The SHELXTL/PC V6.14 suite of programs was used to solve the structures by direct methods.⁴⁶ Subsequent difference Fourier syntheses allowed the remaining atoms to be located. All of the nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The maximum/minimum electron difference peaks are large for 20[I] and 22[I]. The analyses unambiguously establish the structures of the two salts. The large maximum/minimum electron difference peaks are due to poor absorption correction, and in the latter case, also due to the large crystal size.

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Supporting Information Available: CIF files giving crystallographic data, figures giving NMR spectra, and text and tables giving computational details. This material is available free of charge via the Internet at http://pubs.acs.org.