

Regiodiscriminating Reactivity of Isolable NHC-Coordinated Disilylgermylene and Its Cyclic Isomer

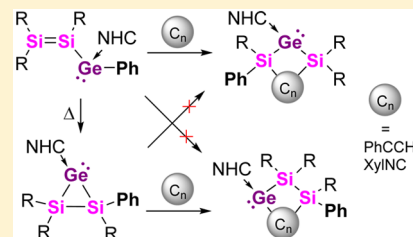
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S Supporting Information

ABSTRACT: An isolable NHC-coordinated disilylgermylene $R_2Si=SiR-GePh \cdot NHC^{iPr_2Me_2}$ (**5b**; $R = 2,4,6$ -triisopropylphenyl, $NHC^{iPr_2Me_2} = 1,3$ -diisopropyl-4,5-dimethylimidazol-2-ylidene) is obtained from the reaction of the α -chloro silyl functionalized heavier vinylidene analogue $R_2(Cl)Si-RSi=Ge \cdot NHC^{iPr_2Me_2}$ with phenyllithium. The disilylgermylene **5b** isomerizes at 40 °C to the NHC-adduct of the corresponding heavier cyclopropylidene analogue **6b**. Both **5b** and **6b** display near perfect regiodiscrimination in their reactions with phenylacetylene and xylil isocyanide, affording in the case of each reagent two different regioisomers of NHC-coordinated cyclic germylenes. DFT calculations reveal that the $Si=Si$ bond accounts for the high reactivity of **5b** even at low temperature while in the case of cyclic **6b** the low-valent germanium center requires a considerable thermal activation.



1. INTRODUCTION

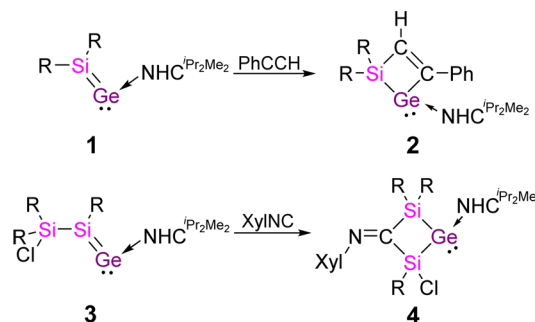
Unsaturated compounds of the heavier Group 14 elements are a cornerstone of modern main group chemistry.¹ Despite the significant steric and electronic stabilization required for their isolation, heavier alkene^{1a–d} and carbene analogues^{1e–j} usually remain highly reactive and offer a vast potential for further manipulation. In particular, derivatives with peripheral functional groups have been employed for the transfer of the uncompromised unsaturated moiety to organic and inorganic substrates.²

Recently, the concept of stabilization by external σ donors such as N-heterocyclic carbenes (NHCs) has provided further momentum to the field.³ In Group 14, NHC-stabilized silylenes and germylenes are now routinely accessible and have rapidly been established as preparative tools in low-valent Group 14 chemistry.⁴ For example, NHC-coordinated $GeCl_2$ is employed in the syntheses of base-stabilized $Ge(0)_2$.⁵ The NHC adducts of $GeCl_2$ and $SiBr_2$ are used for the preparation of a series of base-stabilized heavier vinylidene analogues.⁶ In selected cases, the coordination of NHC occurs in equilibrium^{4g} or is at least reversible, as shown by the subsequent removal of NHC by treatment with Lewis acids.⁷

Despite the emerging applications of heavier carbene analogues, for instance in catalytic processes,⁸ the number of access routes is still limited and typically either involves the reduction of precursors in the regular + IV oxidation state or nucleophilic substitution reactions with concomitant formation of salt or other byproducts in most cases.^{1e–j} A rare example for the formation of a Si(II)-species without byproducts is the quantitative thermal rearrangement of a silirene to a base-stabilized cyclic silylene.⁹ Due to their double functionality, the recently established NHC-stabilized heavier vinylidenes offer the opportunity for the generation of heavier carbene analogues

simply by the atom economic addition of an external reagent to the π -bond under retention of the low-valent center.⁶ The reaction of the base-stabilized silagermylenidene **1** with phenylacetylene yields cyclic germylene **2** as its NHC adduct,^{6a} and the treatment of α -chlorosilyl substituted silagermylenidene **3** with xylil isocyanide affords an NHC-coordinated germylene **4** (Scheme 1, $R = Tip = 2,4,6$ - $iPr_3C_6H_2$, $NHC^{iPr_2Me_2} = 1,3$ -diisopropyl-4,5-dimethylimidazol-2-ylidene, $Xyl = 2,6$ - $Me_2C_6H_3$).^{7c}

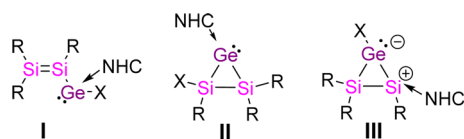
Scheme 1. NHC-Coordinated Silagermylenidenes **1** and **3** and Cyclic Germylenes **2** and **4**



In preceding studies, we have suggested the intermediacy of unstable disilylgermylenes of type I that evolve into occasionally stable cyclic rearrangement products **II** and **III** (Scheme 2).^{6b,10–12} In view of the comparatively shallow potential energy surface typically encountered with heavier

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Scheme 2. NHC-Coordinated Disilyl Germylene I and Cyclic Isomers II and III


main group elements,¹³ we anticipated that the proper choice of substituents might allow for the isolation of a stable open-chained representative of type I and thus for a systematic comparison of its reactivity to that of the corresponding strained cyclic isomer.

As we show here, a persistent NHC-coordinated disilyl germylene of type I can indeed be obtained from the reaction of silagermylenide **3** with PhLi. The isomeric cyclopropylidene–NHC adduct of type II is formed quantitatively upon mild heating. Surprisingly, the treatment of pure samples of the two isomers with phenylacetylene and xyllyl isocyanide leads to the selective formation of regiomer pairs of five- and four-membered cyclic germylene–NHC adducts, respectively. The observed regioselectivity is counterintuitive inasmuch as that the connectivity of the Si₂Ge scaffold does not correspond to the employed starting material, but rather to that of the other isomer in all cases. This is rationalized with the help of DFT calculations.

2. RESULTS AND DISCUSSION

2.1. Reaction of 3 with PhLi. As we previously reported, the reaction of MeLi with silagermylenide **3** affords the methyl substituted disilyl germylene **5a** as the initial product at low temperature, which, due to its thermal instability, could not be characterized in the solid state.¹² We anticipated that a sterically more demanding substituent could provide sufficient inertness to a disilyl germylene to allow for its isolation and full characterization.

Indeed, treatment of **3** with 1 equiv of PhLi at –78 °C leads to quantitative conversion to a new product with ²⁹Si NMR signals at $\delta = 95.06$ and 73.88 ppm, consistent with the constitution as the disilyl germylene–NHC adduct **5b** (Scheme 3). The ¹H NMR shows a broad signal at $\delta = 5.69$

Scheme 3. Reaction of 3 with MeLi and PhLi Resulting in NHC-Coordinated Disilyl Germylenes 5a¹² and 5b and the Rearrangement of 5b to 6b


ppm, which is in the typical region for the methine protons of the CHMe₂ group of an NHC^{iPr₂Me₂} coordinated to a Ge(II)-center.^{4a,6b} In addition, the ¹³C NMR resonance at $\delta = 172.91$ ppm provides further support for NHC coordination to the Ge(II)-center. The red color of **5b** is due to the longest wavelength absorption in the UV/vis at $\lambda_{\text{max}} = 452$ nm ($\epsilon = 10900$ L mol⁻¹ cm⁻¹), which is identical to that of **3** ($\lambda_{\text{max}} = 452$ nm)^{6b} and blue-shifted when compared to the NHC^{iPr₂Me₂}-

stabilized disilyl silylene R₂Si=SiR-(R)Si: ($\lambda_{\text{max}} = 568$ nm; R = Tip = 2,4,6-*i*Pr₃C₆H₂).^{4g}

Red crystals suitable for X-ray diffraction were obtained from a concentrated solution of **5b** in mesitylene (1,3,5-trimethylbenzene) at –26 °C (Figure 1). The molecular structure of **5b**

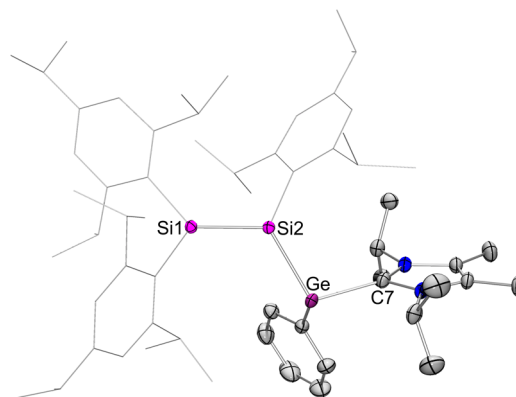


Figure 1. Molecular structure of **5b**·C₉H₁₂ in the solid state (thermal ellipsoids at 30%, H atoms and cocrystallized mesitylene omitted for clarity). Selected bond lengths [Å]: Ge–C7 2.056(2), Ge–Si2 2.4206(6), Si1–Si2 2.1706(8).

is in line with the NMR spectroscopic data and confirms the presence of a Si=Si moiety and the coordination of the NHC^{iPr₂Me₂} to the Ge(II)-center. The Si=Si moiety in **5b** is moderately twisted ($\tau = 11.4^\circ$) and only slightly *trans*-bent (θ , SiTip₂ = 3.1°; θ , SiTipGe = 1.8°).^{4g} As expected, the Ge–Si2 distance corresponds to a typical Ge–Si single bond (2.4206(6) Å). The Ge–C7 bond is, with 2.056(2) Å, comparable to the corresponding distance of **3** (2.061 Å),^{6b} but shorter than that of GeCl₂·NHC^{iPr₂Me₂} (2.106 Å).^{4a} The Si=Si bond is, with 2.1706(8) Å, in the typical range of disilenes¹⁴ and very similar to that of the above-mentioned disilyl silylene/NHC^{iPr₂Me₂} adduct (2.179 Å).^{4g}

At room temperature in solution, **5b** slowly, but selectively, rearranges to a new species with ²⁹Si NMR resonances at $\delta = -62.74$ and -68.81 ppm, which are very similar to that of previously reported heavier cyclopropylidene analogues of type II¹⁰ and therefore indicative of the formation of **6b** (see selected selected data for **5b**–**13** in Table 1). Accordingly, the characteristic ¹³C NMR resonance at $\delta = 172.75$ ppm is retained, suggesting that NHC^{iPr₂Me₂} is still coordinated to the Ge(II)-center.

Complete conversion to **6b** requires heating of **5b** in toluene to 40 °C for 14 h. Moreover, in the case of **6b**, no trace of an isomeric cyclization product of type III was observed. Yellow crystals of **6b** suitable for X-ray diffraction (Figure 2) were obtained from a concentrated toluene solution at room temperature after 1 day. The molecular structure in the solid state confirms the connectivity of the three-membered ring of **6b** predicted on the basis of multinuclear NMR spectroscopy. The Si1–Si2 bond length is, at 2.3775(7) Å, much shorter than that of the mesityl-substituted Si₂Ge-cyclopropylidene of type II (Scheme 2, X = Mes: 2.4448 Å¹⁰), which could be explained by the sterically more demanding mesityl group. The Ge–Si bond lengths of Ge–Si1 2.4232(5) and Ge–Si2 2.4452(5) Å in **6b**, however, are not significantly differing (Scheme 2, X = Mes: Ge–Si2 2.4319; Ge–Si1 2.4320 Å¹⁰).

The distance between the germanium(II) center and the carbenic carbon of 2.0589(17) Å is slightly elongated,

Table 1. Selected Structural Parameters as well as NMR and UV/Vis Data of 5b–13

	5b	6b	7	8	12	13
$\delta^{29}\text{Si1}$, ppm	95.06	-68.81	-15.39	-1.10	-3.92	-45.21
$\delta^{29}\text{Si2}$, ppm	73.88	-62.74	-1.51	-19.16	-1.74	-7.06
$\delta^{13}\text{C}$ (NCN), ppm	172.91	172.75	169.45	172.01	169.33	169.56
Ge-carbenic C, Å	2.056(2)	2.0589(17)	2.0496(16)	2.094(2)	2.020(3)	2.0446(19)
Ge–Si1, Å		2.4232(5)	2.4236(4)	2.5174(7)	2.3862(8)	
Ge–Si2, Å	2.4206(6)	2.4452(5)	2.4189(4)		2.4018(7)	2.4350(6)
λ_{max} , nm (ϵ , L mol ⁻¹ cm ⁻¹)	452 (10900)	438 (6400)	348 (8800)	425 (5500)	290–320 (br sh)	522 (3200)

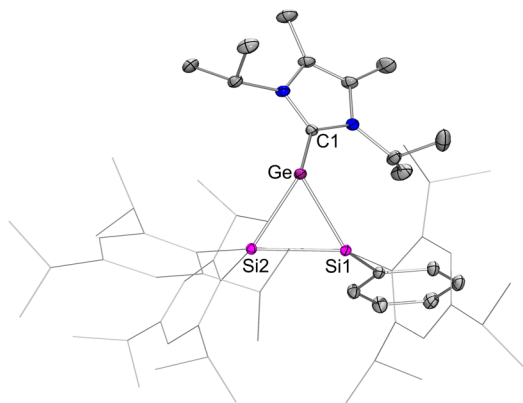


Figure 2. Molecular structure of **6b**·3C₇H₈ in the solid state (thermal ellipsoids at 30%, H atoms and cocrystallized toluene omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ge–C1 2.0589(17), Ge–Si1 2.4232(5), Ge–Si2 2.4452(5), Si1–Si2 2.3775(7); C1–Ge–Si1 116.96(5), C1–Ge–Si2 121.69(5), Si1–Ge–Si2 58.46(17).

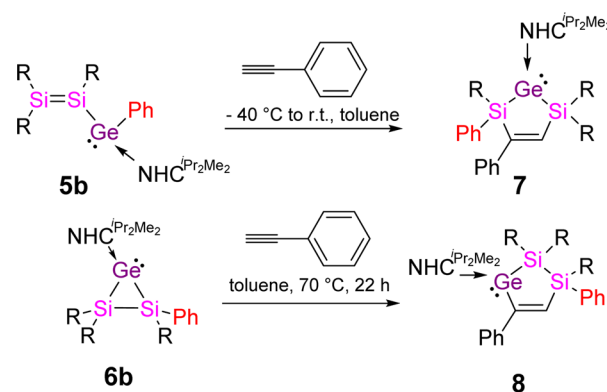
suggesting a somewhat weakened NHC-coordination. The yellow color of **6b** is due to the longest wavelength absorption in the UV/vis at $\lambda_{\text{max}} = 438$ nm ($\epsilon = 6400$ L mol⁻¹ cm⁻¹), which is slightly blue-shifted in comparison to the mesityl-substituted version ($\lambda_{\text{max}} = 454$ nm¹⁰).

2.2. Reaction of 5b and 6b with Phenylacetylene. The unprecedented opportunity that with **5b** and **6b** both the cyclic and open-chained germylene isomers were isolated allows for a systematic comparison of their reactivity. The potential of **5b** and **6b** for further manipulations is based on the simultaneous presence of the base-stabilized Ge(II)-center and a further degree of unsaturation, manifest as either a reactive Si=Si moiety (**5b**) or a strained three-membered ring (**6b**).

In order to explore whether **5b** could be a suitable precursor for extended (possibly conjugated) systems, the reaction with phenylacetylene was studied initially on grounds of the well-known reactivity of acetylenes toward heavier double bonds and carbene analogues.^{14,15} We thus treated disilynyl germylene **5b** with 1 equiv of PhCCH in toluene at -40 °C (Scheme 4). While slowly reaching room temperature, a color change from deep to pale red was observed. In the ²⁹Si NMR, two new signals at $\delta = -1.51$ and -15.39 ppm indicated the consumption of the Si=Si moiety. In contrast, the characteristic ¹³C resonance at $\delta = 169.45$ ppm suggested that NHC^{iPr₂Me₂} still coordinates to the germanium(II)-center.¹⁶

Yellow single crystals were obtained from a saturated toluene solution after 3 days at ambient temperature (see Table 2 for selected crystallographic details for **5b**–**13**). The X-ray structure analysis (Figure 3) confirmed the structure of a five-membered ring **7** with an NHC-coordinated Ge(II)-center and two tetracoordinate Si-atoms in accordance with the

Scheme 4. Reaction of **5b** and **6b** with PhCCH, Resulting in Regioisomeric NHC-Coordinated Heavier Cyclopentenylidene Derivatives **7** and **8**



spectroscopic data. Surprisingly, the connectivity of the SiSiGe-moiety in **7** with both silicon atoms directly adjacent to germanium has changed in comparison with **5b**. In addition, the phenyl group in **7** has migrated from germanium to the neighboring silicon center. The distance between Ge and the carbenic carbon atom (Ge–C9 2.0496(16) Å) is relatively short in comparison to Marschner's five-membered NHC^{Me₂}-coordinated cyclic germylenes (2.070 and 2.076 Å).¹⁶ In the absence of air and moisture, **7** is stable for months in the solid state and for several weeks in benzene solution.

The yellow color of **7** is due to the longest wavelength absorption in the UV/vis at $\lambda_{\text{max}} = 348$ nm ($\epsilon = 8800$ L mol⁻¹ cm⁻¹) and blue-shifted in comparison to **6b** ($\lambda_{\text{max}} = 438$ nm, $\epsilon = 6400$ L mol⁻¹ cm⁻¹) or similar compounds.¹⁷

According to naïve expectation, **7** could have arisen from the insertion of the C–C triple bond of phenylacetylene into the Si–Si single bond of three-membered ring **6b**. In order to check this possibility, **6b** was treated with 1 equiv of PhCCH at room temperature, but even after 24 h no discernible reaction took place, thus ruling out the intermediacy of **6b** in the generation of **7** from **5b**. After heating to 70 °C for 22 h, however, a single product is detected alongside about 50% of unreacted **6b**. Addition of one further equivalent of PhCCH completes conversion at 70 °C after another 22 h. The single product features ²⁹Si NMR signals at $\delta = -1.10$ and -19.16 ppm, in the typical range of tetracoordinate Si-atoms, but distinctly different from those of **7**. It is well-known that aryl acetylenes tend to polymerize under similar reaction conditions,^{17,18} which explains the excess of PhCCH required for complete conversion of **6b** to the new product. Alongside the diagnostic signal at $\delta = 172.01$ ppm for the carbenic carbon of Ge-coordinated NHC, the ¹³C NMR of the product reveals another downfield signal at $\delta = 187.94$ ppm (not observed in **7**). It is known that C=CPh-moieties attached to germanium

Table 2. Selected Crystallographic Details for 5b–13

	5b	6b	7	8	12	13
formula	C ₆₂ H ₉₄ GeN ₂ Si ₂ ·C ₉ H ₁₂	C ₆₂ H ₉₄ GeN ₂ Si ₂ ·3 C ₇ H ₈	C ₇₀ H ₁₀₀ GeN ₂ Si ₂	C ₇₀ H ₁₀₀ GeN ₂ Si ₂ ·1.25 C ₅ H ₁₂	C ₇₁ H ₁₀₃ GeN ₃ Si ₂ ·0.5 C ₇ H ₈	C ₇₁ H ₁₀₃ GeN ₃ Si ₂ ·2 C ₅ H ₁₂
T (K)	122(2)	173(2)	163(2)	143(2)	143(2)	152(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	Trigonal	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
space group	R $\bar{3}$	P $\bar{1}$	P $\bar{1}$	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a (Å)	37.7343(15)	15.9617(17)	11.4319(5)	12.6352(3)	12.7844(8)	13.2550(5)
b (Å)	37.7343(15)	16.6009(18)	14.6466(5)	23.8472(6)	22.7467(13)	25.4218(8)
c (Å)	25.323(3)	17.9948(19)	21.5014(9)	25.5287(7)	23.4180(11)	23.7680(8)
α (deg)	90	114.148(5)	100.5120(10)	90	90	90
β (deg)	90	112.883(5)	92.0450(10)	101.5350(10)	94.490(3)	101.111(2)
γ (deg)	120	96.575(5)	95.2650(10)	90	90	90
V (Å ³)	31226(4)	3790.4(7)	3519.7(2)	7536.8(3)	6789.1(7)	7858.9(5)
Z	18	2	2	4	4	4
d (g cm ⁻³)	1.069	1.114	1.123	1.047	1.148	1.075
μ (mm ⁻¹)	0.514	0.478	0.511	0.477	0.529	0.462
F(000)	10908	1378	1288	2586	2540	2776
θ _{max} (deg)	27.15	30.504	28.892	28.596	26.431	29.658
total reflns	134431	81062	64193	75564	50088	90578
independent reflns	15353	22760	18283	19229	13888	22144
R _{int}	0.0592	0.0332	0.0294	0.0316	0.0829	0.0325
restraints	9	0	244	42	0	305
parameters	723	786	1143	763	771	887
F ²	1.078	1.042	1.028	1.107	1.010	1.042
R ₁ (I > 2σ)	0.0526	0.0493	0.0385	0.0571	0.0523	0.0523
CCDC No.	1496393	1496388	1496389	1496390	1496391	1496392

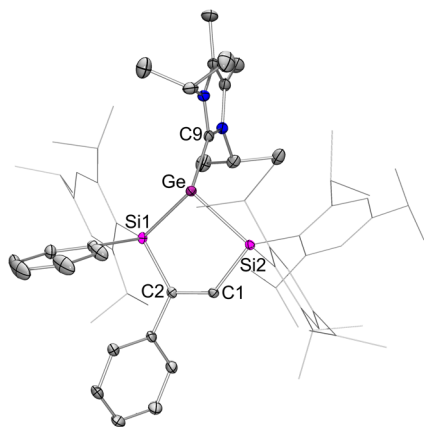


Figure 3. Molecular structure of 7 in the solid state (thermal ellipsoids at 30%, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ge–C9 2.0496(16), Ge–Si2 2.4189(4), Ge–Si1 2.4236(4), Si2–C1 1.8923(15), Si1–C2 1.9312(16), C1–C2 1.354(2); C9–Ge–Si2 110.73(5), C9–Ge–Si1 114.43(4), Si2–Ge–Si1 92.34(14).

give rise to ¹³C resonances between δ = 173 and 192 ppm in the ¹³C NMR.^{16,17,19}

Red single crystals were obtained at r.t. from a saturated pentane solution after 18 h. The analysis by X-ray diffraction determines the constitution of the new product as the NHC-adduct of five-membered cyclic germylene 8, which, in contrast to the regioisomeric 7, features the C=C double bond as directly attached to the Ge(II)-center (Figure 4). The bond length between germanium and the carbenic carbon atom is, with 2.094(2) Å, significantly longer than that of 7 (2.0496(16) Å). The red color of 8 is due to the longest wavelength

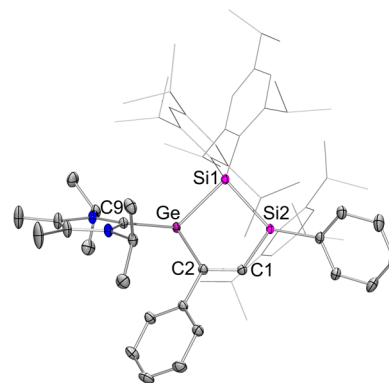


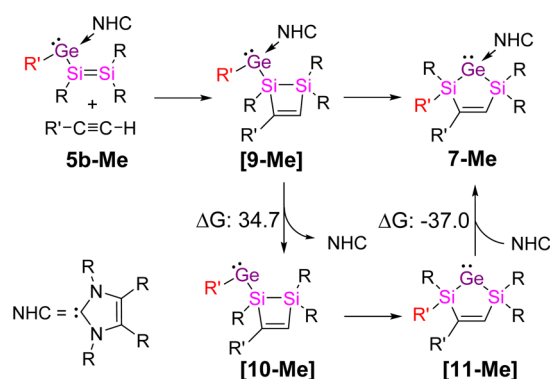
Figure 4. Molecular structure of 8 in the solid state (thermal ellipsoids at 30%, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ge–C9 2.094(2), Ge–Si1 2.5174(7), Si1–Si2 2.4040(9), Si2–C1 1.861(3), Ge–C2 2.004(2), C1–C2 1.359(3).

absorption in the UV/vis at λ_{max} = 425 nm (ε = 5500 L mol⁻¹cm⁻¹), which is strongly red-shifted in comparison to 7 (λ_{max} = 348 nm, ε = 8800 L mol⁻¹cm⁻¹).

The formation of 8 would be readily explained by invoking the intermediacy of open-chained isomer 5b: The disilylenyl germylene could plausibly react in a [2 + 3] cycloaddition reaction, which, however, can virtually be excluded based on the diametrically opposing regioselectivity during the reaction of isolated 5b (yielding 7 exclusively). In order to clarify the mechanism of the generation of 7 and 8, DFT calculations were carried out on simplified model systems (Me instead of Tip, Ph, and ⁱPr; see the Supporting Information for details) at the B3LYP/6-31G(d,p) level of theory. In view of the detailed studies by Baines and co-workers on the reaction of alkynes

with disilenes,^{1d} we anticipated that the formal cycloaddition of phenylacetylene to the Si=Si moiety of disilyl germylene **5b** would be favorable. Indeed, a stepwise, presumably ionic, pathway to the [2 + 2] cycloadduct featuring an exocyclic germylene functionality [9-Me] was identified for the model reaction of MeCCH with **5b-Me**. The highest barrier of $\Delta G^\ddagger = 13.0 \text{ kcal mol}^{-1}$ is well in line with a reaction occurring at room temperature (Figure S42). An alternative pathway via a CH addition of MeCCH to the Si=Si moiety can be excluded on the basis of the high activation barriers of up to $34.8 \text{ kcal mol}^{-1}$ (Figure S45). After formation of the intermediate [9-Me], two competitive pathways can be considered to obtain product 7-Me: The reaction may proceed either with or without dissociation of the NHC (Scheme 5). The highest barrier for

Scheme 5. Plausible Mechanism for the Formation of 7-Me (R = R' = Me)



the pathway without NHC-dissociation amounts to $31.5 \text{ kcal mol}^{-1}$ (Figure S43), a value that is likely even higher in the experimental case due to the bulkier substituents and thus incompatible with a reaction readily proceeding at room temperature. In light of the often facile NHC-dissociation in unsaturated heavier main group systems,^{4g,7,12} the dissociative pathway to 7-Me is a viable alternative (Figure S44). Although the liberation of NHC from [9-Me] to afford [10-Me] is, with $\Delta G = 34.7 \text{ kcal mol}^{-1}$, quite endergonic, it can reasonably be expected that the steric bulk in the experimental case will lower this value drastically and thus exert the opposite effect compared to the pathway without NHC-dissociation. Indeed, the calculations with inclusion of the bulky substituents (R = Tip; R' = Ph in Scheme 5) decrease the energy difference between [9] and [10] to $\Delta E = 16.0 \text{ kcal mol}^{-1}$ (optimization only). After the likely rate-determining dissociation of NHC, the ring expansion of [10-Me] to [11-Me] proceeds smoothly with a much smaller barrier of $\Delta G^\ddagger = 13.5 \text{ kcal mol}^{-1}$ for the required migration of one methyl group from the germanium center to the adjacent silicon atom as the rate-determining step. The reassociation of NHC with [11-Me] to give 7-Me is strongly exergonic, with $\Delta G = -37.0 \text{ kcal mol}^{-1}$, so that the overall pathway is also decidedly exergonic ($\Delta G = -22.8 \text{ kcal mol}^{-1}$, Figure S44).

In order to gauge the influence of the phenyl group in the experimentally employed acetylene derivative, we have also investigated the mechanisms for the formation of [9-Ph] and 7-Ph (R = Me; R' = Ph). Except for the appearance of two new intermediates (see Supporting Information: 31-Ph in Figure S48 and 32-Ph in Figure S49), only minor differences compared to the methyl model were observed in the pathways

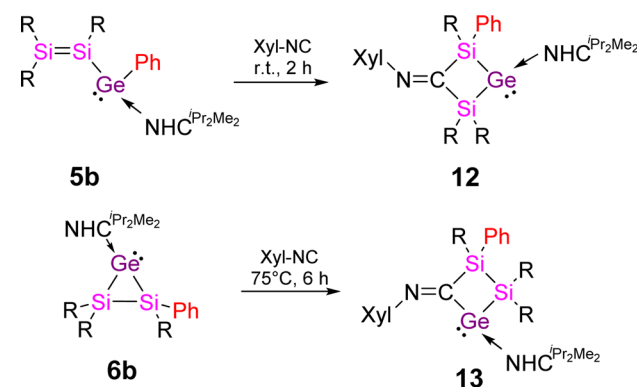
and energetics of the reactions with phenylacetylene (Figure S48–Figure S50).

The formation mechanism of **8** was also investigated with a simplified model system at the B3LYP/6-31G(d,p) level of theory. As discussed previously, regiomers **8** could plausibly form by [2 + 3] cycloaddition of **5b** to phenylacetylene. This pathway, however, exhibits very high energy barriers with up to $65.0 \text{ kcal mol}^{-1}$ (Figure S46), thus confirming the exclusion of this option based on the experiment. Conversely, the insertion of methylacetylene to the Si–Ge single bond of **6b-Me** results in **8-Me** in a straightforward manner, and the required energy barrier of $\Delta G^\ddagger = 29.7 \text{ kcal mol}^{-1}$ is entirely compatible with the reaction conditions of the experimental case, i.e. heating to 70°C for 48 h. Overall, the reaction is strongly exergonic by $\Delta G = -39.1 \text{ kcal mol}^{-1}$ (Figure S47).

2.3. Reaction of 5b and 6b with Xylyl Isocyanide. In view of the unexpected reactivity of **5b** and **6b** toward phenylacetylene, we sought to clarify whether the observed regioselective additions to the C–C triple bond can be generalized with other reagents. On the one hand, isonitriles spontaneously insert into strained heavier Group 14 cycles,^{7c,20} on the other hand, they readily react with Si–Si double bonds.²¹

As in the case of the reactions with PhCCH, treatment of **5b** with 1 equiv of xylyl isocyanide led to selective conversion to a new product **12** in 2 h at room temperature, while heating to 75°C for 6 h was necessary to complete the reaction of **6b** with the same reagent to afford **13** (Scheme 6). Similar to the synthesis of **8**, a 1.5-fold excess of xylyl isocyanide was necessary for full conversion due to the tendency of isocyanides to polymerize at higher temperatures.²²

Scheme 6. Reaction of 5b and 6b with Xyl-NC Resulting in NHC-Coordinated Heavier Cyclic Germylenes 12 and 13



For both **12** and **13**, two ^{29}Si NMR signals in the typical region of the tetracoordinate silicon atom were observed (**12**: $\delta = -1.74, -3.92 \text{ ppm}$; **13**: $\delta = -7.06, -45.21 \text{ ppm}$), as was one ^{13}C resonance, confirming the coordination of the NHC to the germanium center (**12**: $\delta = 169.33 \text{ ppm}$; **13**: $\delta = 169.56 \text{ ppm}$).

X-ray diffraction studies on single crystals of **12** (Figure 5) and **13** (Figure 6) confirm the four-membered ring connectivities, which exactly reiterate the counterintuitive regioselectivity observed in the case of the reactions of **5b** and **6b** with phenylacetylene. The exocyclic imino functionality of **12** is situated between the two silicon atoms, Si1 and Si2, whereas in **13** it is directly adjacent to the Ge(II)-center. The evident conjugation with the NHC-coordinated low-valent germanium center has no effect on the C–N bond length of the

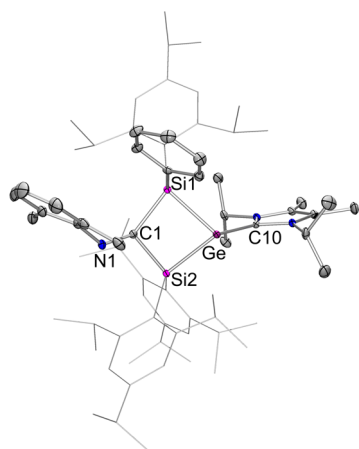


Figure 5. Molecular structure of **12** in the solid state (thermal ellipsoids at 30%, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ge–C10 2.020(3), Ge–Si1 2.3862(8), Ge–Si2 2.4018(7), Si1–C1 2.020(3), Si2–C1 1.965(3), C1–N1 1.286(3).

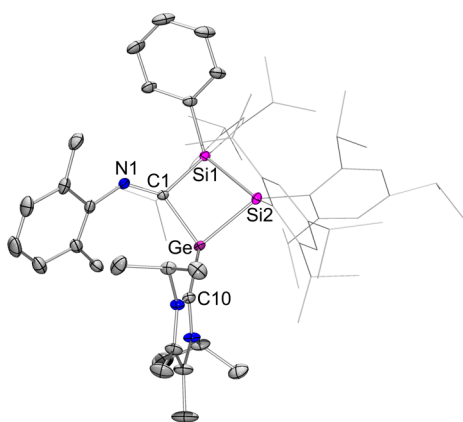
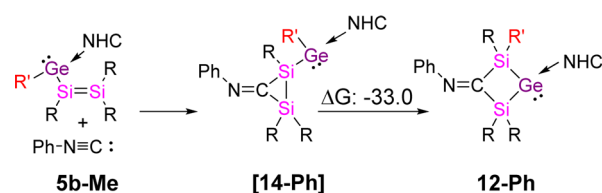


Figure 6. Molecular structure of **13** in the solid state (thermal ellipsoids at 30%, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ge–C10 2.0446(19), Ge–C1 2.0019(18), Ge–Si2 2.4350(6), Si1–Si2 2.4089(7), Si1–C1 1.9438(19), C1–N1 1.289(2).

exocyclic imine functionality (C1–N1 **12**: 1.286(3); **13**: 1.289(2) Å). Conversely, the bond distance of the carbenic carbon atom to germanium, Ge–C10, is slightly longer in the case of **13** (**12**: 2.020(3); **13**: 2.045(2) Å). In the related derivative **4**, the corresponding C–Ge distance was found to be much shorter (**4**: 1.986 Å) than in either **12** or **13**, suggesting a much stronger dative interaction of the NHC with the vacant orbital at the Ge(II)-center. In line with more pronounced conjugative effects, the longest wavelength UV/vis absorption of red **13** is bathochromically shifted to $\lambda_{\max} = 522$ nm ($\epsilon = 3200$ L mol⁻¹cm⁻¹) in comparison to **12** ($\lambda_{\max} = 290$ – 320 nm, broad shoulder).

In order to clarify whether similar mechanistic pathways as in the phenylacetylene case are active in the reactions with xyllyl isocyanide, the formation of **12** was also addressed by DFT computations. We assumed the intermediacy of the germylene functionalized iminodisilirane [**14-Ph**], and indeed the largest energy barrier to its formation in a formal [1 + 2] cycloaddition is calculated to be $\Delta G^\ddagger = +6.3$ kcal mol⁻¹ (Scheme 7). After formation of intermediate [**14-Ph**], the reaction undergoes a cyclization step to form **12-Ph** in a stepwise fashion including the necessary migration of one methyl group from the

Scheme 7. Plausible Mechanism for the Formation of 12-Ph (R = R' = Me)



germanium to the silicon atom. The overall pathway is found to be strongly exergonic by the $\Delta G = -44.2$ kcal mol⁻¹ (Figure S52).

Despite its carbene-like character, xyllyl isocyanide reiterates the reactivity of the C–C triple bond of PhCCH toward **5b** and **6b** perfectly, as, in both cases, the same unexpected Si–Si–Ge connectivities are obtained as a function of the starting material employed. It is therefore reasonable to assume that similar mechanistic scenarios apply.

3. CONCLUSION

In conclusion, the NHC-coordinated disilyl germylene **5b** and its rearrangement product **6b**, a heavier cyclopropylidene analogue, were isolated and crystallographically analyzed. They show an unexpected regioselectivity in their reactions with either phenylacetylene or xyllyl isocyanide. While the open-chained disilyl germylene **5b** rapidly reacts even below room temperature, the three-membered ring isomer **6b** requires prolonged heating to about 70 °C in order to generate the regiomer products with near perfect selectivity. The counter-intuitive connectivities of five-membered cyclic germylenes **7** and **8** (phenylacetylene reactions) and four-membered cyclic germylenes **12** and **13** (xyllyl isocyanide) are rationalized on the basis of DFT calculations on model species for **7** and **8**. The behavior of **5b** is governed by an initial fast reaction at the Si=Si moiety but subsequently requires dissociation of the NHC as the rate-determining step to form **7**. Conversely, the formation of **8** plausibly proceeds in a concerted manner via the insertion of the C–C triple bond of phenylacetylene into the Si–Ge single bond of three-membered ring **6b**.

The selective access to isomeric heterocycles which incorporate germanium(II) centers with simple unsaturated organic reagents offers significant opportunities for the incorporation of these cycles as building blocks of extended systems. Moreover, in the light of the current interest in maingroup catalysis, this study adds to the understanding of viable (possibly competing) reaction pathways that may be active in alkyne activation.

4. EXPERIMENTAL SECTION

General Methods and Instrumentation. All experiments were carried out under argon and with dry and oxygen-free solvents. Silagermylidene **3^{6b}** was synthesized according to our published procedure. PhLi (1.9 M in *n*-dibutyl ether) and xyllyl isocyanide were purchased from Sigma-Aldrich and used as received. Phenylacetylene (Sigma-Aldrich) was distilled and stored over molecular sieve (4 Å). ¹H and ¹³C{¹H} NMR spectra were referenced to external SiMe₄ using the residual solvent signals. ²⁹Si{¹H} NMR spectra were referenced to external SiMe₄. Melting points were determined under argon in closed NMR tubes and are uncorrected. CHN analyses were performed on an Elementar Vario Micro Cube. UV/vis spectra

were measured at a PerkinElmer Lambda 35 spectrometer using quartz cells with a path length of 0.1 cm.

1,3-Diisopropyl-4,5-dimethyl-2-(phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)disilylgermylidene)-2,3-dihydro-1H-imidazole (5b). A solution of PhLi (1.9 M in *n*Bu₂O, 0.605 mL, 1.15 mmol) is added quickly to a solution of 1.10 g of **3** (1.15 mmol) in 5 mL of toluene at -78°C . After 30 min at -20°C the color of the solution has turned into deep-red and the ¹H NMR indicates full conversion. All volatiles are rapidly distilled off in vacuum at -10°C . The red solid is dried for 2 h at 2×10^{-2} mbar and afterward digested with 100 mL pentane. Insoluble parts are removed by filtration at -20°C , the volume of the solution is reduced to about one-third in vacuum and stored at -26°C . After 2 days at this temperature the mother liquor is decanted from the microcrystalline precipitate and 0.77 g (67%) of **5b** are obtained as orange powder. Red single crystals of **5b** suitable for X-ray diffraction were obtained from a concentrated mesitylene solution after 3 days at -26°C . mp. $128\text{--}131^{\circ}\text{C}$ (full conversion into **6b**). ¹H NMR (300.13 MHz, toluene-*d*₈, 300 K, TMS) $\delta = 7.97$ (br, 2H, PhH), 7.17–6.93 (m, 9H, overlap with toluene-*d*₈, TipH and PhH), 5.69 (br, 2H, CH(CH₃)₂ of NHC), 4.88–4.79 (m, 1H, CH(CH₃)₂ of Tip), 4.43 (br, 1H, CH(CH₃)₂ of Tip), 4.05–3.82 (m, 4H, CH(CH₃)₂ of Tip), 2.78–2.64 (m, 3H, CH(CH₃)₂ of Tip), 1.57–1.53 (m, 9H, CH(CH₃)₂ of Tip and CH₃ of NHC), 1.37–1.29 (m, 18H, CH(CH₃)₂ of Tip and CH(CH₃)₂ of NHC), 1.20–1.13 (m, 24H, CH(CH₃)₂ of Tip and of CH(CH₃)₂ of NHC), 0.90–0.84 (m, 6H, CH(CH₃)₂ of Tip and of CH₃ of NHC), 0.76–0.65 (m, 16H, CH(CH₃)₂ of Tip), 0.50 (d, 6H, CH(CH₃)₂ of Tip) ppm. ¹H NMR (300.13 MHz, toluene-*d*₈, 253 K, TMS) $\delta = 8.13$ (br, 2H, PhH), 7.24–6.87 (m, 9H, overlap with toluene-*d*₈, TipH and PhH), 5.76 (br, 2H, CH(CH₃)₂ of NHC), 4.99 (br, 1H, CH(CH₃)₂ of Tip), 4.53 (br, 1H, CH(CH₃)₂ of Tip), 4.06 (br, 2H, CH(CH₃)₂ of Tip), 3.83 (br, 2H, CH(CH₃)₂ of Tip), 2.76–2.65 (m, 3H, CH(CH₃)₂ of Tip), 1.64 (d, 3H, CH₃ of NHC), 1.47–1.38 (m, 22H, CH(CH₃)₂ of Tip and CH(CH₃)₂ of NHC), 1.23–1.15 (m, 22H, CH(CH₃)₂ of Tip and CH(CH₃)₂ of NHC), 0.91–0.87 (m, 6H, CH(CH₃)₂ of Tip and CH₃ of NHC), 0.62–0.48 (m, 22H, CH(CH₃)₂ of Tip) ppm. ¹³C NMR (75.56 MHz, toluene-*d*₈, 253 K, TMS) $\delta = 172.91$ (br, NCN), 156.26, 155.16, 154.34, 154.10, 149.31, 149.21, 148.85, 139.53, 138.64, 138.01, 136.87 (ArC_{quart}), 153.91 (NCCN), 137.73, 129.28, 128.34, 127.64, 125.33 (masked by toluene-*d*₈), 126.43, 122.87, 121.85, 121.75, 121.21 (ArCH), 54.14 (br, CH(CH₃)₂ of NHC), 38.56, 37.70, 37.21, 36.28, 35.04 (CH(CH₃)₂ of Tip), 27.74, 26.20, 24.97, 24.70, 24.55, 24.46, 24.30 (masked by toluene-*d*₈), 24.12, 23.88, 23.71, 21.29 (CH(CH₃)₂ of Tip and NHC), 20.35 (masked by toluene-*d*₈, CH(CH₃)₂ of Tip), 34.67, 23.00, 14.53 (*n*-pentane), 9.89 (CH₃ of NHC) ppm. ²⁹Si NMR (59.62 MHz, toluene-*d*₈, 253 K, TMS) $\delta = 95.06$ (SiTip₂), 73.88 (SiTip) ppm. UV/vis (hexane) $\lambda_{\text{max}} = 452$ nm ($\epsilon = 10900$ L mol⁻¹cm⁻¹), 373 nm ($\epsilon = 13900$ L mol⁻¹cm⁻¹), 308 nm ($\epsilon = 14200$ L mol⁻¹cm⁻¹). Anal. Calcd for C₆₂H₉₄GeN₂Si₂·0.25 C₇H₈ (1019.3): C, 75.12; H, 9.49; N, 2.75. Found: C, 74.66; H, 9.29; N, 2.65.

1,3-Diisopropyl-4,5-dimethyl-2-(1-phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)-1,2,3-disilagermoran-3-ylidene)-2,3-dihydro-1H-imidazole (6b). A solution of 700 mg of **5b** (0.70 mmol) in 4 mL of toluene is heated to 40°C for 14 h. The solvent is evaporated in vacuum and the yellow residue digested in 40 mL of hexane and filtered. The solution is concentrated in vacuum to half the volume resulting in the precipitation of

yellow microcrystals. After 3 days at room temperature the supernatant solution is removed by cannula and the solid dried in vacuum yielding 0.57 g of **6** (82%) as yellow powder. Orange crystals suitable for X-ray diffraction are obtained by storing a concentrated toluene solution at room temperature for 2 days. mp. $179\text{--}181^{\circ}\text{C}$ (dec.). ¹H NMR (300.13 MHz, C₆D₆, 300 K, TMS) $\delta = 7.70$ (br, 2H, PhH), 7.30 (br, 2H, TipH), 7.24 (br, 1H, PhH), 7.14–7.00 (m, 4H, TipH and PhH overlay with cocrystallized toluene), 6.87 (br, 3H, TipH), 6.00–5.81 (m, 3H, CH(CH₃)₂ of Tip and CH(CH₃)₂ of NHC), 4.59 (sept, 1H, CH(CH₃)₂ of Tip), 4.33 (sept, 1H, CH(CH₃)₂ of Tip), 4.06–3.96 (m, 2H, CH(CH₃)₂ of Tip), 3.69 (sept, 1H, CH(CH₃)₂ of Tip), 2.99–2.73 (m, 3H, CH(CH₃)₂ of Tip), 2.12 (CH₃ of cocrystallized toluene), 1.83 (d, 3H, CH(CH₃)₂ of Tip), 1.68 (br, 3H, CH(CH₃)₂ of Tip), 1.58–1.52 (m, altogether 12H, 6H of CH(CH₃)₂ of Tip and 6H of CH₃ of NHC), 1.40–1.19 (m, altogether 36H, 24H of CH(CH₃)₂ of Tip and 12H of CH(CH₃)₂ of NHC), 1.09 (br, 3H, CH(CH₃)₂ of Tip), 0.87 (d, 3H, CH(CH₃)₂ of Tip), 0.75 (br, 3H, CH(CH₃)₂ of Tip), 0.63–0.58 (br, 12H, CH(CH₃)₂ of Tip) ppm. ¹³C NMR (75.56 MHz, C₆D₆, 300 K, TMS) $\delta = 172.75$ (NCN), 157.64, 155.97, 155.21, 154.62, 154.11, 149.24, 148.99, 148.02, 147.68 (br), 142.17, 141.26, (ArC_{quart}), 156.54 (br, 2C, NCCN), 137.88, 129.33, 128.56, 125.69 (toluene), 136.79, 128.24, 127.91 (masked by C₆D₆), 126.64, 122.59, 122.37, 121.98, 121.48, 121.14, 121.03 (ArCH and PhCH), 54.05, 53.52 (br, CH(CH₃)₂ of NHC), 37.74, 36.29, 36.19, 34.94, 34.81, 34.73, 34.64, 34.57, 34.15 (CH(CH₃)₂ of Tip), 30.07, 28.38, 27.73, 27.43, 27.04, 25.59, 25.12, 24.74, 24.53, 24.45, 24.41, 24.38, 24.31, 24.22, 23.84, 23.46, 22.52, 22.23, 21.44, 20.15 (CH(CH₃)₂ of Tip and NHC), 10.85, 10.42 (br, CH₃ of NHC) ppm. ²⁹Si NMR (59.62 MHz, C₆D₆, 300 K, TMS) $\delta = -62.74$ (SiTip₂), -68.81 (SiTip) ppm. UV/vis (hexane) $\lambda_{\text{max}} = 438$ nm ($\epsilon = 6400$ L mol⁻¹cm⁻¹), 370 nm ($\epsilon = 11100$ L mol⁻¹cm⁻¹), 311 nm ($\epsilon = 14200$ L mol⁻¹cm⁻¹), 272 nm ($\epsilon = 21700$ L mol⁻¹cm⁻¹). Anal. Calcd for C₆₂H₉₄GeN₂Si₂·0.3 C₇H₈ (1023.9): C, 75.19; H, 9.49; N, 2.74. Found: C, 74.27; H, 9.47; N, 2.90.

2-(3,4-Diphenyl-1,1,3-tris(2,4,6-triisopropylphenyl)-1,3-dihydro-2H-1,3,2-disilagermol-2-ylidene)-1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1H-imidazole (7). At -20°C , 98.5 μL of phenylacetylene (92 mg, 0.902 mmol) are added by microsyringe to a solution of 855 mg of **5b** (0.896 mmol) in 4 mL of toluene. The reaction mixture is allowed to warm to room temperature and stirring is maintained for 2 h. The solvent is evaporated to dryness in vacuum and the solid residue is digested with 60 mL of hexane. After filtration, the hexane is concentrated to half the volume and 0.58 g of **7** (59%) are obtained as a yellow microcrystalline precipitate. Yellow single crystals of **7** suitable for X-ray diffraction were obtained from a saturated toluene solution after 3 days at room temperature. mp. $> 220^{\circ}\text{C}$ (dec.). ¹H NMR (300.13 MHz, C₆D₆, 300 K, TMS) $\delta = 7.85$ (s, 1H, PhC = CH), 7.63 (br, 1H, CH(CH₃)₂ of NHC), 7.36 (br, 1H, PhH), 7.19 (br, 4H, ArH), 7.16 (br, 2H, masked by C₆D₆, ArH), 7.07–6.83 (m, 8H from PhH, TipH and 1H from CH(CH₃)₂ of Tip), 6.79 (br, 1H, PhH), 5.03 (sept, 1H, CH(CH₃)₂ of NHC), 4.69 (sept, 1H, CH(CH₃)₂ of Tip), 3.87–3.61 (m, 4H, CH(CH₃)₂ of Tip), 2.92–2.67 (m, 3H, CH(CH₃)₂ of Tip), 1.80–1.74 (m, 9H, CH(CH₃)₂ of Tip), 1.61–1.38 (m, 16H, CH(CH₃)₂ of Tip, CH₃ and CH(CH₃)₂ of NHC), 1.31–1.19 (m, 26H, CH(CH₃)₂ of Tip), 0.90 (br, 3H, CH(CH₃)₂ of Tip), 0.68 (br, 3H, CH(CH₃)₂ of Tip), 0.60 (d, 3H, CH(CH₃)₂ of Tip), 0.51 (d, 3H, CH(CH₃)₂ of Tip), 0.46–

0.42 (m, 6H, CH(CH₃)₂ of Tip), 0.30 (br, 3H, CH(CH₃)₂ of Tip), 0.16 (d, 3H, CH(CH₃)₂ of Tip) ppm. ¹³C NMR (75.56 MHz, C₆D₆, 300 K, TMS) δ = 169.45 (NCN), 166.17 (HC = CPh), 162.50 (HC = CPh), 156.26, 156.02, 155.36, 154.92, 154.18, 152.76, 152.73, 148.75, 148.38, 148.31, 148.24, 142.36, 138.54, 137.71 (ArC_{quart}), 128.60, 128.52, 128.18, 128.05, 127.97, 127.73, 127.67, 125.32 (ArCH, 5C's masked by C₆D₆), 126.32 (br, 2C, NCCN), 122.97, 122.83 (br), 122.69, 122.47, 121.63, 120.91 (PhCH), 56.78, 53.22 (CH(CH₃)₂ of NHC), 35.42, 35.28, 34.65, 34.49, 34.11, 33.41, 33.03 (CH(CH₃)₂ of Tip), 28.57, 27.59, 25.64, 25.50, 25.27, 25.11, 24.56, 24.47, 24.36, 24.32, 24.18, 23.77, 22.03, 21.33, 20.16 (CH(CH₃)₂ of Tip and NHC), 10.41, 10.01 (CH₃ of NHC) ppm. ²⁹Si NMR (59.62 MHz, C₆D₆, 300 K, TMS) δ = -1.51 (SiTip₂), -15.39 (SiTipPh) ppm. UV/vis (hexane) λ_{max} = 348 nm (ε = 8800 L mol⁻¹cm⁻¹). Anal. Calcd for C₇₀H₁₀₀GeN₂Si₂ (1098.7): C, 76.55; H, 9.18, N, 2.55. Found: C, 75.70; H, 9.32; N, 2.31.

2-((1R)-1,4-diphenyl-2-(2,4,5-triisopropylphenyl)-1,2-bis-(2,4,6-triisopropylphenyl)-1,2-dihydro-3H-1,2,3-disilagermetan-3-ylidene)-1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1H-imidazole (8). At room temperature, 126 μL phenylacetylene (117 mg, 1.145 mmol) are added by microsyringe to 570 mg of **6b** (0.572 mmol) in 4 mL toluene. The solution is heated to 70 °C for 22 h. All volatiles are distilled off in vacuum and a pale red solid remains. The product is dissolved in 35 mL of warm hexane and filtered. Concentration of the solvent to approximately one-third of the volume results in precipitation of a red solid. The supernatant solution is decanted by cannula and the residue dissolved in 2.5 mL of warm pentane. After 18 h at room temperature cubic red crystals suitable for X-ray diffraction are obtained. The combined yield of three crops of crystals of **8** is 0.49 g (77%). mp. 202–204 °C (dec.). ¹H NMR (300.13 MHz, C₆D₆, 300 K, TMS) δ = 8.13 (br, 2H, PhH), 7.87 (s, 1H, PhC = CH), 7.49 (br, 2H, H-PhC = CH), 7.26 (br, 1H, PhH), 7.24–7.19 (m, 2H, TipH and PhH), 7.15–6.92 (m, 8H, TipH, PhH and 1H of CH(CH₃)₂ of NHC), 6.86 (br, 1H, PhH), 6.78 (br, 1H, PhH), 5.29 (sept, 1H, CH(CH₃)₂ of Tip), 5.10 (sept, 1H, CH(CH₃)₂ of Tip), 4.33–4.13 (m, 2H, CH(CH₃)₂ of Tip and CH(CH₃)₂ of NHC), 3.72 (sept, 1H, CH(CH₃)₂ of Tip), 3.44 (sept, 1H, CH(CH₃)₂ of Tip), 3.00 (sept, 1H, CH(CH₃)₂ of Tip), 2.88–2.62 (m, 3H, CH(CH₃)₂ of Tip), 1.81 (d, 3H, CH(CH₃)₂ of NHC), 1.62–1.52 (m, 15H, CH(CH₃)₂ of Tip and CH₃ of NHC), 1.39–1.14 (m, 32H, CH(CH₃)₂ of Tip, CH₃ of NHC and cocrystallized pentane), 0.88 (cocrystallized pentane), 0.69 (d, 3H, CH(CH₃)₂ of Tip), 0.41–0.38 (m, 6H, CH(CH₃)₂ of Tip), 0.30–0.24 (m, 9H, CH(CH₃)₂ of Tip), 0.05 (d, 3H, CH(CH₃)₂ of NHC), 0.01 (d, 3H, CH(CH₃)₂ of NHC) ppm. ¹³C NMR (75.56 MHz, C₆D₆, 300 K, TMS) δ = 187.94 (HC = CPh), 172.01 (NCN), 158.22, 156.50, 155.25, 154.84, 153.77, 152.47, 152.12, 149.05, 148.49, 147.50, 145.94, 139.97, 133.80 (ArC_{quart}), 145.21 (HC = CPh), 145.50, 137.40, 128.34, 127.57, 127.32, 125.66 (ArCH), 127.09, 126.23 (NCCN), 123.37, 123.14, 122.97, 122.57, 122.42, 122.22 (PhCH), 54.16, 52.39 (CH(CH₃)₂ of NHC), 38.65, 36.59, 36.27, 35.98, 35.86, 34.72, 34.65, 31.13 (CH(CH₃)₂ of Tip), 28.51, 27.48, 26.69, 26.40, 26.26, 25.80, 25.41, 25.36, 24.68, 24.54, 24.21, 24.18, 24.13, 24.06, 24.04, 23.77, 23.52, 21.59, 21.19, 20.60 (CH(CH₃)₂ of Tip and NHC), 34.46, 22.72, 14.28 (CH₃ and CH₂ of cocrystallized pentane), 10.59, 10.01 (CH₃ of NHC) ppm. ²⁹Si NMR (59.62 MHz, C₆D₆, 300 K, TMS) δ = -1.10 (SiTip₂), -19.16 (SiTipPh) ppm. UV/vis (hexane) λ_{max} = 425 nm (ε = 5500 L mol⁻¹cm⁻¹). Anal. Calcd

for C₇₀H₁₀₀GeN₂Si₂·0.25 C₅H₁₂ (1116.4): C, 76.65; H, 9.3, N, 2.51. Found: C, 76.65; H, 8.93; N, 2.48.

(E)-2-(1,3-Diisopropyl-4,5-dimethyl-1H-imidazol-3-ium-2-yl)-4-((2,6-dimethylphenyl)imino)-1-phenyl-1,3,3-tris(2,4,6-triisopropylphenyl)-1,3,2-disilagermetan-2-ide (12). At -20 °C a solution of 75 mg xylyl isocyanide (0.572 mmol) in 1 mL toluene is added by syringe to a solution of 542 mg **5b** (0.568 mmol) in 3 mL toluene. The color changes immediately from deep red to deep purple. The reaction mixture is allowed to warm to room temperature and stirred for 2 h. The solvent is evaporated to dryness in vacuum and the residue is digested with 40 mL hexane. After filtration, the hexane is concentrated to about 3 mL. After 24 h purple needles of **12** were obtained (103 mg). Storing the mother liquor at room temperature for 2 days afforded again purple needles (157 mg). The total yield of **12** (2 crops) is 0.26 g (41%). Dissolving the purple solid in toluene (concentrated solution, ca. 1.3 mL) afforded purple crystals of **12** suitable for X-ray diffraction. mp. 163–165 °C (dec.). ¹H NMR (300.13 MHz, C₆D₆, 300 K, TMS) δ = 7.73 (br, 1H, CH(CH₃)₂ of NHC), 7.29–7.19 (m, 3H, PhH and TipH), 7.03–6.68 (m, 10H, TipH, PhH and XylH), 6.56 (br, 1H, CH(CH₃)₂ of Tip), 6.41 (d, 1H, ArH), 5.16 (br, 1H, CH(CH₃)₂ of NHC), 4.36 (br, 1H, CH(CH₃)₂ of Tip), 4.09–4.01 (m, 2H, CH(CH₃)₂ of Tip), 3.70 (br, 1H, CH(CH₃)₂ of Tip), 3.52 (br, 1H, CH(CH₃)₂ of Tip), 3.29 (impurity: t, n-dibutyl ether from **5b**), 2.86–2.66 (m, 4H, CH(CH₃)₂ of Tip), 2.60 (s, 3H, CH₃ of Xyl), 1.86–1.60 (m, 22H, CH(CH₃)₂ of Tip, CH(CH₃)₂ of NHC and CH₃ of NHC), 1.39–1.12 (m, 54H, CH(CH₃)₂ of Tip, CH(CH₃)₂ of NHC, CH₃ of NHC and cocrystallized *n*-hexane), 0.92–0.79 (m, 13H, CH(CH₃)₂ of Tip and cocrystallized *n*-hexane), 0.53–0.24 (m, 21H, CH(CH₃)₂ of Tip) ppm. ¹³C NMR (75.56 MHz, C₆D₆, 300 K, TMS) δ = 169.33 (NCN), 156.68, 155.63, 154.85, 153.68, 152.16 (br), 148.70, 148.46, 144.62, 141.49 (br), 139.18, 138.75 (ArC_{quart} and XylN = C), 128.44, 128.20, 122.90, 122.51, 121.93, 120.75 (ArCH), 127.70, 127.01 (NCCN), 57.07, 53.13 (CH(CH₃)₂ of NHC), 36.14, 35.36, 34.60 (br), 34.44, 33.22, 32.78, 30.39 (CH(CH₃)₂ of Tip), 28.68, 26.78 (br), 25.57, 24.21 (br), 20.61, 18.61 (CH(CH₃)₂ of Tip and NHC), 21.19, 19.72 (CH₃ of Xyl), 31.97, 23.05, 14.35 (CH₂ and CH₃ of cocrystallized hexane), 10.36, 10.09 (CH₃ of NHC) ppm. ²⁹Si NMR (59.62 MHz, C₆D₆, 300 K, TMS) δ = -1.74 (SiTip₂), -3.92 (SiTipPh) ppm. UV/vis (hexane) λ_{max} = 290–320 (br sh) nm. Anal. Calcd for C₇₁H₁₀₃GeN₃Si₂·0.25 C₆H₁₄ (1148.9): C, 75.79; H, 9.34; N, 3.66. Found: C, 75.41; H, 9.27; N, 3.63.

(Z)-3-(1,3-Diisopropyl-4,5-dimethyl-1H-imidazol-3-ium-2-yl)-4-((2,6-dimethylphenyl)imino)-1-phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)-1,2,3-disilagermetan-3-ide (13). A solution of 503 mg **6b** (0.505 mmol) and 99 mg xylyl isocyanide (0.755 mmol) in 4 mL of toluene is heated to 75 °C for 6 h. All volatiles are removed under reduced pressure and a red solid remains. The product is dissolved in 20 mL of hexane and filtered. All volatiles are evaporated in high vacuum (8 h, 6 × 10⁻⁶ mbar). The solid residue is dissolved in 1.5 mL of pentane by gentle heating. Red single crystals of **13** (0.21 g, 36%) suitable for X-ray diffraction were obtained after 16 h at room temperature. mp. 145–148 °C (full conversion into **6b**). ¹H NMR (300.13 MHz, C₆D₆, 300 K, TMS) δ = 8.44 (br, 2H, PhH), 7.34–7.29 (m, 3H, TipH), 7.18–7.14 (br, 1H, TipH, overlap with C₆D₆), 7.10–7.05 (m, 3H, XylH), 6.93–6.88 (m, 2H, TipH and PhH), 6.79–6.70 (m, 3H, TipH and PhH), 6.43 (sept, 1H, CH(CH₃)₂ of NHC), 5.68 (sept, 1H, CH(CH₃)₂ of Tip), 5.15 (sept, 1H, CH(CH₃)₂ of Tip), 4.31–4.19 (m, 2H,

CH(CH₃)₂ of Tip and CH(CH₃)₂ of NHC), 3.84 (sept, 1H, CH(CH₃)₂ of Tip), 3.72 (sept, 1H, CH(CH₃)₂ of Tip), 3.47 (sept, 1H, CH(CH₃)₂ of Tip), 2.86–2.62 (m, 3H, CH(CH₃)₂ of Tip), 2.48 (s, 3H, CH₃ of Xyl), 2.16–2.15 (m, 4H, CH(CH₃)₂ of NHC and CH₃ of Xyl), 1.75 (d, 3H, CH(CH₃)₂ of Tip), 1.66–1.62 (m, 6H, CH(CH₃)₂ of Tip), 1.57 (d, 3H, CH(CH₃)₂ of Tip), 1.48 (s, 3H, CH₃ of NHC), 1.45 (d, 3H, CH(CH₃)₂ of Tip), 1.37 (d, 3H, CH(CH₃)₂ of NHC), 1.34 (s, 3H, CH₃ of NHC), 1.26–1.34 (m, 24H, CH(CH₃)₂ of NHC, CH(CH₃)₂ of Tip and CH₂ of cocrystallized pentane), 1.04 (d, 3H, CH(CH₃)₂ of Tip), 0.88 (CH₃ of cocrystallized pentane), 0.70 (d, 3H, CH(CH₃)₂ of Tip), 0.66 (d, 3H, CH(CH₃)₂ of Tip), 0.48–0.34 (m, 12H, CH(CH₃)₂ of Tip), 0.08–0.02 (m, 6H, CH(CH₃)₂ of NHC). ¹³C NMR (75.56 MHz, C₆D₆, 300 K, TMS) δ = 214.58 (XylN = C), 169.56 (NCN), 156.67, 155.37, 155.20, 155.16, 153.85, 151.78, 150.80, 149.02, 148.66, 147.90, 146.16, 139.76, 137.31, 136.65, 133.18, 123.44 (ArC_{quart}), 139.55, 129.16, 128.36, 127.70, 127.38, 126.81 (ArCH), 127.15, 126.96 (NCCN), 123.75, 123.21, 122.93, 122.61, 122.41, 122.36, 122.31 (ArCH), 55.57, 52.51 (CH(CH₃)₂ of NHC), 38.95, 35.86, 35.48, 35.13, 34.66, 34.61, 33.84, 31.50 (CH(CH₃)₂ of Tip), 27.88, 27.79, 27.11, 26.26, 25.22, 25.06, 24.75, 24.61, 24.54, 24.44, 24.24, 24.21, 24.18, 24.05, 23.99, 23.55, 21.93, 21.33, 21.10, 20.78, 19.62, (CH(CH₃)₂ of Tip and NHC), 20.40 (CH₃ of Xyl), 34.43, 22.72, 14.28 (CH₂ and CH₃ of cocrystallized pentane), 10.23, 9.94 (CH₃ of NHC) ppm. ²⁹Si NMR (59.62 MHz, C₆D₆, 300 K, TMS) δ = -7.06 (SiTip₂), -45.21 (SiTipPh) ppm. UV/vis (hexane) λ_{\max} = 522 nm (ϵ = 3200 L mol⁻¹cm⁻¹), 442 nm (ϵ = 3400 L mol⁻¹cm⁻¹), 347 nm (ϵ = 16400 L mol⁻¹cm⁻¹). Anal. Calcd for C₇₁H₁₀₃GeN₃Si₂·0.25 C₅H₁₂ (1145.44): C, 75.87; H, 9.44; N, 3.61. Found: C, 75.49; H, 9.22; N, 3.62.

Computations. All theoretical calculations are carried out using the Gaussian09 suite of programs.²³ The proposed mechanisms and intermediates for the formation of **7**, **8**, and **12** were calculated using simplified model system with methyl groups instead of Tip, Ph, and ^tPr groups with methylacetylene and phenylacetylene (Figure S42–S52). The B3LYP/6-31G(d,p) was chosen as level of theory. Frequency analyses were performed to determine the character of optimized structures as minima or transition states. The relative Gibbs free energies are given in kcal mol⁻¹. The chemical reaction channels have been checked by the intrinsic reaction coordinate (IRC) method to verify the energy profiles at the B3LYP/6-31G(d,p) level of theory for the processes from transition states to intermediates, by using the second-order Gonzalez-Schlegel method.^{24,25} The electronic absorption spectra for **7-Me**, **8-Me**, **12-Me**, and **13-Me** were predicted with using the optimized geometry in the time-dependent density functional theory (TD-DFT) method in solution (heptane) at B3LYP/6-31+G(d,p) level of theory. The GaussView 5.0 program was employed for visualization of the final geometries of the optimized structures.²⁶

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07815.

Crystallographic data (CIF)

Plots of NMR spectra for new compounds, UV/vis spectra, and complete details of DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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NOTE ADDED IN PROOF

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