ORGANOMETALLICS

Basic Reactivity Pattern of a Cyclic Disilylated Germylene

Małgorzata Walewska,[†] Johann Hlina,[†] Judith Baumgartner,*[‡] Thomas Müller,[§] and Christoph Marschner*[†]

[†]Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9, 8010 Graz, Austria
[‡]Institut für Chemie, Universität Graz, Stremayrgasse 9, 8010 Graz, Austria
[§]Institut für Chemie, Universität Oldenburg, Carl von Ossietzky-Strasse 1-3, 26211 Oldenburg, Federal Republic of Germany

S *Supporting Information*

ABSTRACT: In order to estimate the reactivity of disilylated germylene phosphine adducts, a cyclic version of this compound class was reacted with a number of different reagents. Reactions with the chalcogens sulfur, selenium, and tellurium led to dimers of the heavy ketone analogues. Reactions with water and ethyl bromide proceeded to give the respective oxidized germanol and germyl bromide. Two different reactions with alkynes were observed which led either to a germacyclopropene, by addition of tolane to the germylene, or to a silagermacyclobutene, likely formed by addition of the alkyne across a silagermene. Reaction via the silagermene was also observed in the reaction with benzophenone. Reaction of a germylene phosphine adduct with GeCl₂·(dioxane) provided insertion of the silylated germylene into a Ge—Cl bond, leading to a germylated chlorogermylene phosphine adduct.
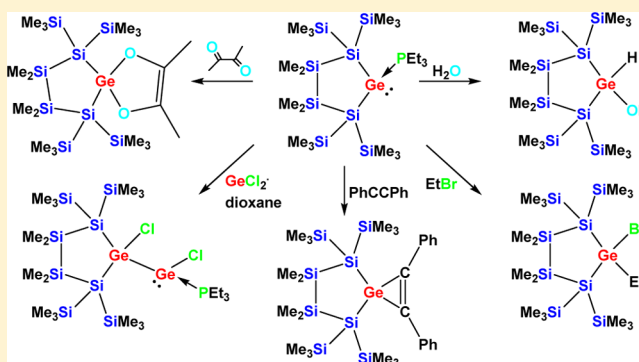
INTRODUCTION

The chemistry of higher carbene analogues (tetrylenes) is a very active field of research.[1−5] Most of the studied compounds bear amino substituents, which stabilize the coordinative unsaturation of the divalent group 14 element by π-donation of the nitrogen lone pairs into its empty p orbital. Compounds with σ-donating alkyl or aryl substituents, which lack this particular stabilization, are intrinsically more reactive and require bulky substituents to prevent di- or oligomerization.[5]

In the course of the last few years we have investigated the chemistry of tetrylenes with even more σ-donating oligosilanyl and germyl substituents.[6−14]

RESULTS AND DISCUSSION

Recently, we have described the synthesis of a cyclic germylene by reaction of an oligosilanyl-1,3-diide with GeCl₂·(dioxane).[12] The formed germylene was found to be unstable and dimerizes to an exocyclic digermene, which subsequently undergoes a rearrangement to form an endocyclic digermene.[12] While this reaction was found to be remarkably clean, attempts to carry out analogous reactions with oligosilanyl-1,4-diides **2a,b** turned out to be rather messy (Scheme 1). The only compounds that could be isolated from these reactions were **3a,b**, which contain extra trimethylsilyl groups in comparison to the starting material. While the reason for this is unclear, it should be mentioned that in the recent attempted synthesis of a related disilylated silylene by reducing the respective dichlorosilane,[15] also a compound with an additional trimethylsilyl group was

Scheme 1. Attempted Synthesis of Cyclic Germylenes 5a,b
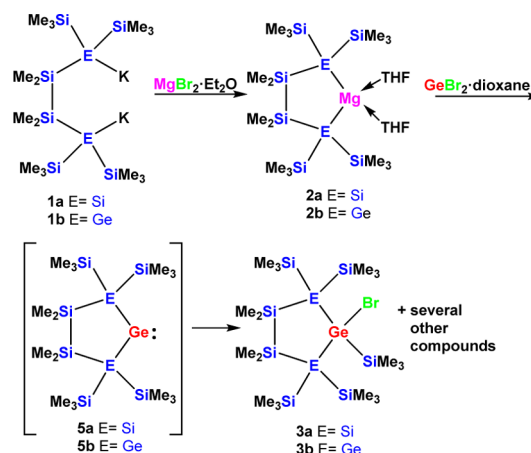
obtained and it thus seems not unlikely that **5a,b** were formed in the course of the reactions but are likely too reactive to be detected or isolated (Scheme 1).

This unfortunate situation was resolved carrying out the reaction of 1,4-silanediide **1a** with GeBr₂·(dioxane) in the presence of either PEt₃[10] or PMe₃. This way germylene **5a** is

trapped as a base adduct (**4a,b**) (Scheme 2) and cannot undergo a 1,2-silyl shift to yield a silagermene.[10]

Scheme 2. Synthesis of Phosphine Adducts 4a,b of the Five-Membered Cyclic Disilylated Germylene 5a
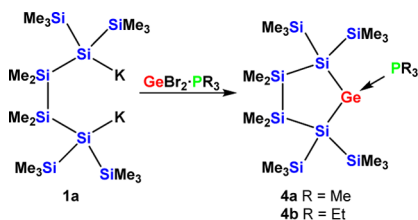
In order to study the principal reactivity of silylated germylene phosphine adducts, a number of addition reactions were carried out. Oxidation of divalent germanium compounds with elemental chalcogens formally causes the formation of heavy ketone analogues. However, due to the limited stability of double bonds between germanium and the heavier chalcogens, usually products of dimerization via head-to-tail [2 + 2] cycloadditions are observed. This was reported for cyclic[16−20] and acyclic[21−23] germylenes with sulfur,[16−22,24] selenium,[16,17,21−23] and tellurium.[16,21−23] For very bulky germylenes Tokitoh and co-workers have shown that stable thianones and selenones can be isolated.[25,26]

For the case of phosphine adduct **4b**, in the reactions with 2 mol equiv of either sulfur or selenium and with 1 equiv of tellurium clean conversion was observed to yield compounds **7a−c**, in addition to the respective oxidized phosphines SPEt$_3$ and SePEt$_3$ for the S and Se cases (Scheme 3). The formation

Scheme 3. Reactions of Germylene Phosphine Adduct 4b with Heavy Chalcogens
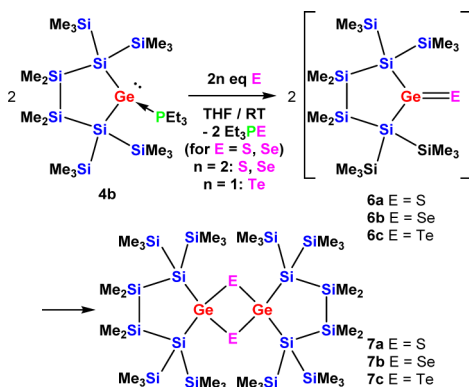
of the dimeric compounds clearly shows that the steric bulk exercised by the trimethylsilyl groups at the silicon atoms in a position α to the germylene is by no means sufficient to inhibit head-to-tail dimerization processes of the presumably initially formed heavy ketone analogues **6a−c** (Scheme 3).

Also of interest were addition reactions of the germylene with polar reagents and unsaturated organic compounds. The first group of reagents is expected to test for nucleophilic reactivity, whereas the second group is more likely to indicate electrophilic reactivity of the tetrylene.

While reactions of germylenes with water have received some theoretical attention,[27] the number of actual examples of clean reactions is surprisingly small. A reason for this lack seems to be facile follow-up reactions. For instance, exposure of Lappert's

Ge[CH(SiMe$_3$)$_2$]$_2$ to atmospheric conditions caused hydrolyses to give HGe[CH(SiMe$_3$)$_2$][CH(SiMe$_3$)(SiMe$_2$O)].[28] While Power and co-workers found that reactions of the divalent germylene Ge(ArMe^6)$_2$ (ArMe^6 = C$_6$H$_3$-2,6-{C$_6$H$_2$-2,4,6-(CH$_3$)$_3$}$_2$) with water gave the Ge(IV) insertion product (ArMe^6)$_2$Ge(H)-OH, the analogous stannylene Sn(ArMe^6)$_2$ reacted to give the Sn(II) species {ArMe^{6}Sn(μ-OH)}$_2$ with elimination of ArMe^{6}H.[29] Related compounds containing the R$_2$Ge(H)OH structural motif were obtained upon hydrolysis of Tamao's spectacular germanone (Eind)$_2$GeO (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl)[30] and presumably in the hydrolysis of a germylated germylene.[31]

In any case reaction of **4b** with water was found to occur cleanly by insertion of the germylene into the O−H bond, yielding germanol **8** (Scheme 4).

The situation for reactions of germylenes with alkyl halides is somewhat similar. Again only a few clear-cut examples have been reported. Baines and co-workers found that NHC adducts of several germylenes with alkyl iodides led mainly to the alkylation of the germylene lone pair and upon further reaction with CDCl$_3$ provided the oxidation product Mes$_2$Ge(Cl)R.[32] Conversely, reaction of Lappert's Ge[CH(SiMe$_3$)$_2$]$_2$ with methyl iodide gave Me(I)Ge[CH(SiMe$_3$)$_2$]$_2$.[33] It is likely that such reactions involve the transient formation of germyl radicals. Banaszak Holl and co-workers have been able to exploit this reactivity for facile C−H activation chemistry.[34] In order to probe the reactivity of **4b** against alkyl halides, a reaction with ethyl bromide was carried out, leading cleanly to the ethylated germyl bromide **9**, which is the product of oxidative addition of **5a** (Scheme 4).

Although we are not aware of reactions of germylenes with α-diketones, it was reported that (^{t}Bu$_2$MeSi)$_2$Ge=Ge-(SiMe^{t}Bu$_2$)$_2$ reacts with 3,5-di-*tert*-butyl-1,2-benzoquinone as a masked germylene.[35,36] Related reactions with transient silylenes were studied by Ando et al. and were found to lead to 1,3-dioxa-2-silacyclopent-4-enes.[37] An analogous product was obtained in the reaction of **4b** with diacetyl (2,3-butanedione), which led to the respective 4,5-dimethyl-1,3-dioxa-2-germacyclopent-4-ene **10** (Scheme 4).

Addition of an alkyne to disilylated germylenes was achieved by Sekiguchi and co-workers, who reacted disilylated dichlorogermanes with molten potassium, in the presence of bis(trimethylsilyl)acetylene without a solvent, to obtain the corresponding germacyclopropenes after 19 h at reflux.[38] The related reaction of **4b** with tolane occurred under less drastic conditions and provided germacyclopropene **11** in a yield of 86% (Scheme 4). As the reaction of **4b** with tolane can be considered to be analogous to the addition of bis-(trimethylsilyl)acetylene to titanocene[39] or zirconocene,[40] we wondered whether the reaction of **4b** with 1,4-bis-(trimethylsilyl)butadiyne would also mimic the respective reaction with titanocene.[41] However, instead of addition to the germylene to give either a cumulene or an alkynyl-substituted germacyclopropene, the diyne underwent [2 + 2] cycloaddition to the silagermene isomer of **5a**,[10] yielding a mixture of the two regioisomers **12a,b** (Scheme 4). Addition of phenylacetylene across silagermenes was observed previously in a similar way by Baines[42] and Sekiguchi.[43,44] Scheschkewitz's [2 + 2] cycloaddition of phenylacetylene to a NHC-stabilized silagermenylidene constitutes another related precedent.[45]

The formation of **12a,b** seems to indicate that in solution **4b** is in equilibrium with **5a** (Scheme 1) and its silagermene isomer. Although we have found that the silagermene can

Scheme 4. Reactions of Germylene Phosphine Adduct 4b with a Number of Small Molecules
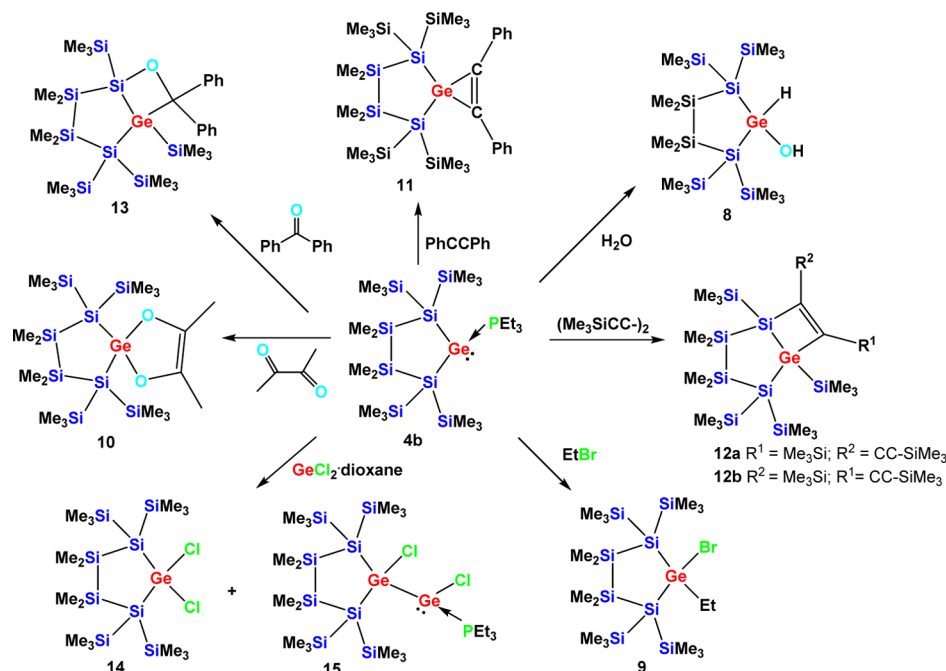
Table 1. Selected NMR Spectroscopic Data (Chemical Shifts in ppm) of Germylene Derivatives 4a,b, 7a−c, 8−11, 14, and 15, Sharing the 1-Germa-2,2,5,5-tetrakis(trimethylsilyl)tetramethylcyclopentasilane Backbone

compd	^{1}H SiMe$_3$	SiMe$_2$	^{13}C SiMe$_3$	SiMe$_2$	^{29}Si SiMe$_3$	SiMe$_2$	Si$_q$	other
3a					−3.4	−24.3	−105.2	^{29}Si: 0.6 (GeSiMe$_3$)
4a	0.41	0.44	4.3/2.8	−1.1 to −1.6	−7.8	−22.3 (d, $^3J_{Si-P}$ = 10 Hz)	−126.0 (d, $^2J_{Si-P}$ = 16 Hz)	^{31}P: −20.0
					−4.3			
		0.32			−8.5			
4b[a]	0.43	0.51	3.8	−1.2	−7.9	−22.7 (d, $^3J_{Si-P}$ = 10 Hz)	−127.1 (d, $^2J_{Si-P}$ = 15 Hz)	^{31}P: +14.8
7a	0.54	0.41	5.0	−1.2	−5.4	−30.1	−90.8	
7b	0.55	0.39	4.4	−1.8	−4.7	−30.5	−92.6	
7c	0.57	0.35	4.1	−2.2	−3.2	−30.4	−99.4	
8	0.34	0.39	3.0	−2.1	−4.7	−25.5	−113.9	^{1}H: 6.38 (d, $^3J_{H-H}$ = 1.6 Hz, 1 H, Ge−H), −0.44 (d, $^3J_{H-H}$ = 1.7 Hz, 1H, OH)
	0.27	0.28	2.1		−7.3			
9	0.25	0.35	3.5	−2.2	−4.1	−25.9	−111.5	^{1}H: 1.46 (t, 3H, CH$_3$), 1.60 (m, 2H, Ge-CH$_2$)
	0.48	0.44	3.6	−1.8	−8.1			^{13}C: 12.5 (CH$_3$), 19.4 (Ge-CH$_2$)
10	0.38	0.40	2.9	−2.3	−6.1	−30.4	−117.0	^{1}H: 1.96 (s, 6 H, CMe)
								^{13}C: 131.6 (CO), 14.9 (CMe)
11	0.32	0.50	3.6	−1.8	−7.3	−30.3	−120.1	
14					−7.6		−96.7	
15					−3.9		−102.5 (d, $^3J_{Si-P}$ = 6.0 Hz)	^{31}P: +10.5
					−4.3			

[a]Values taken from ref 10.

undergo dimerization via a head-to-tail [2 + 2] cycloaddition,[10] the addition of an alkyne to the Ge−Si double bond seems to be energetically much more facile. The presence of a silagermene isomer was further substantiated by the reaction of **4b** with benzophenone.[46] Again, addition across the Si−Ge double bond was observed in a regioselective manner to form Si−O and Ge−C bonds in compound **13** (Scheme 4). This behavior is consistent with earlier studies by Baines and co-workers.[47−49]

Reaction of **4b** with GeCl$_2$·(dioxane) provides another interesting insertion reaction where the silylated germylene inserts into a Ge−Cl bond. In this way the germylated chlorogermylene adduct **15** forms. The dioxane which served as the Lewis base in GeCl$_2$·(dioxane) is replaced by PEt$_3$. The reaction is not completely selective, and in addition to compound **15** also a similar amount of dichlorogermane **14** forms (Scheme 4). Repeating the reaction at different

temperatures and concentrations did not have an influence on the amount of formation of **14**.

Recently, there have been reports of reactions of carbenes[50,51] and other low-valent main-group compounds with hydrogen[52,53] and carbon monoxide.[54] We have therefore attempted reactions of these two small molecules with **4b**, but no reaction was observed. This lack of reactivity may be explained by the fact that despite it being very electrophilic, germylene **5a** released from **4b** is not nucleophilic enough to participate in carbonylation or hydrogenation reactions.

NMR Spectroscopy. The NMR spectroscopic characterization of the magnesium germanide **2b** is not as straightforward as it is for **2a**, where the typical upfield-shifted ^{29}Si resonances of metalated silicon atoms around −170 ppm are very characteristic.[55] The ^{29}Si NMR spectrum of **2b** displays only the SiMe$_3$ and SiMe$_2$ signals at −3.4 and −23.7 ppm, respectively, which are slightly shifted toward low field; this is common for germanium-connected silyl groups. The same is observed in the ^{29}Si NMR spectrum of **3a**, where the trimethylsilyl group attached to germanium is found at 0.6 ppm. The other ^{29}Si signals of **3a** are two SiMe$_3$ resonances for the two different ring sides at −3.4 and −7.8 ppm and the SiMe$_2$ (−24.3 ppm) and *Si*(SiMe$_3$) (−105.2 ppm) resonances with rather ordinary chemical shifts.

The reactions of **4b** can be conveniently monitored using ^{29}Si NMR spectroscopy. The chemical shifts of the ^{1}H (and to some extent also the ^{13}C) resonances of the formed products are very similar and do not cover a vast spectral region. Thus, these signals are not very indicative. Nevertheless, the number and intensity of observed ^{1}H and ^{13}C resonances provide straightforward insight into the molecular symmetry. Compounds **4a,b** (Table 1) are interesting compounds, as ^{1}H, ^{13}C, and ^{29}Si spectra taken at ambient temperature show different rates for the inversion of the coordination sphere around the low-valent germanium center. For **4a** two different signals for the trimethylsilyl groups were observed in the ^{1}H, ^{13}C, and ^{29}Si spectra (Table 1). Although this means that the inversion process at germanium is slow on the NMR time scale, the observed signals are broad, indicating that the coalescence temperature is close to ambient temperature. $^2J_{Si−P}$ and $^3J_{Si−P}$ couplings to the germylated silicon atom and the SiMe$_2$ unit can be observed with values of 16 and 10 Hz, respectively. For **4b** the slightly diminished degree of interaction between the germylene and the phosphine leads to an increased rate of inversion of germanium. The signals for the trimethylsilyl groups at the two different sides of the ring therefore coalesce at room temperature and are only visible as broad singlets. The signals for the *Si*(SiMe$_3$)$_2$ (−127.1 ppm) and *Si*Me$_2$ (−22.7 ppm) atoms are not affected by the inversion process and appear as sharp doublets due to the coupling to ^{31}P with $^2J_{Si−P}$ and $^3J_{Si−P}$ coupling constants very similar to those observed for **4a**.[10]

The reactions of **4b** with elemental chalcogens to give the structurally related compounds **7a–c** result, as expected, in rather similar ^{29}Si spectra. The signals of the trimethylsilyl groups and of the germylated silicon atoms resonate at unusually low field at −5.4, −90.8 (**7a**), −4.7, −92.6 (**7b**), and −3.2, −99.4 (**7c**) ppm (Table 1). As the resonances of the SiMe$_2$ groups around −30 ppm are rather conventional, the downfield shift can likely be assigned to the proximity of the chalcogen atoms. In this context it should be noted that both selenium and tellurium possess spin 1/2 nuclei with abundances of 7.58% for ^{77}Se and 6.99% for ^{125}Te. Despite

the fact that $^3J_{P−Si}$ coupling was clearly visible for **4b**, no satellite signals were observed for $^3J_{Se−Si}$ or $^3J_{Te−Si}$ coupling in **7b** or **7c**, respectively. The structure of the dichlorogermane **14** is actually rather similar to those of **7a–c**, and accordingly the ^{29}Si NMR spectrum of **14** is similar to the signals of the SiMe$_3$ groups and of the germylated silicon atoms at −4.3 and −96.7 ppm (Table 1).

While the spectra of germirene **11** are unremarkable, compound **15** is more interesting. As observed for **7a–c** and **14**, the attachment of heavy atoms to germanium causes the aforementioned downfield shift of the SiMe$_3$ and SiGe resonances to −3.9/−4.3 and −102.5 ppm for **15** (Table 1). The presence of the PEt$_3$ is visible by a $^3J_{Si−P}$ coupling of 6.0 Hz to the germylated silicon atoms. The spectroscopic appearance of compound **15** suggests C_s symmetry. This leads to the conclusion that the germylene atom cannot be configuratively stable and at ambient temperature the inversion process must be fast on the NMR time scale. The ^{31}P resonance at 10.5 ppm indicates a diminished degree of interaction in comparison to that in **4b**, where the ^{31}P resonance of PEt$_3$ was observed at 14.8 ppm. The ^{29}Si NMR spectra of compound **10** are similar to those of **14** without the strong deshielding effect on the SiMe$_3$ and SiGe groups. Spectra of compounds **8** and **9** are similar to those of **15**, indicating side differentiation of the five-membered ring. ^{29}Si NMR chemical shifts of **8** and **9** are comparable and completely lie within the range of expected values (Table 1). Like compound **14**, **10** also has C_{2v} symmetry, giving similar spectra. However, the two oxygen atoms attached to germanium in **10** do not cause the same downfield shift behavior as observed for **7a–c**, **14**, and **15** (Table 1). The C_1-symmetric silagermene addition products **12a,b** and **13** are more interesting with respect to their ^{29}Si NMR spectra.

Isomeric compounds **12a,b** were formed in a 1:1 ratio and could not be separated. Therefore, a ^{29}Si NMR spectrum with each silicon atom giving rise to two signals was observed. Nevertheless, a tentative assignment of resonances is possible. The trimethylsilyl groups at germanium appear around −3.5 ppm, and four trimethylsilyl resonances were found between −7.4 and −12.6 ppm which can be assigned to the three silyl-substituted and the vinylated SiMe$_3$ groups. Two signals between −22.1 and −28.4 ppm can be associated with SiMe$_2$ units, and that around −37 ppm corresponds to the silicon atom which is part of the silagermabutene ring with a strong downfield shift, as expected for four-membered rings. The signal at −112.5 ppm is in the typical region for tetrasilylated silicon atoms.[56] The ^{29}Si NMR spectrum of **13** is much like that of **12a,b** but is less complicated. The oxygenate silicon incorporated into the four-membered ring resonates at 40.3 ppm. Again the trimethylsilyl group at germanium is shifted downfield (−2.1 ppm), and the other SiMe$_3$ groups are found at −7.9, −8.5, and −14.0 ppm. The signals for the two SiMe$_2$ groups at −25.3 and −37.2 (SiMe$_2$) and the tetrasilylated silicon atom at −104.7 ppm complete the spectrum.

X-ray Crystallography. Compounds **2b** (Figure 1), **3b** (Figure S1 in the Supporting Information), **4a** (Figure 2), **7a** (Figure 3), **7b** (Figure S2 in the Supporting Information), **7c** (Figure S3 in the Supporting Information), **8** (Figure 4), **9** (Figure S4 in the Supporting Information), **10** (Figure 5), **11** (Figure S5 in the Supporting Information), **12a** (Figure 6), **13** (Figure 7), **14** (Figure S6 in the Supporting Information), and **15** (Figure 8) reported in this study were subjected to single-crystal X-ray diffraction analysis (Table 2 and Tables S1–S3 in the Supporting Information). The cyclic 1,4-digermyl magne-
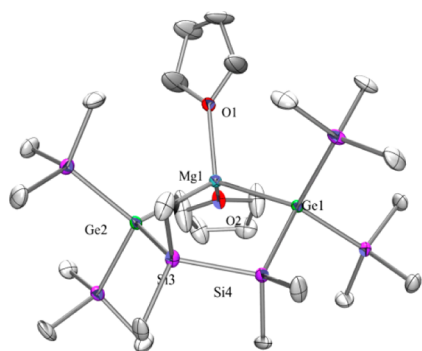
Figure 1. Molecular structure of **2b** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) 2.041(5), Mg(1)−O(2) 2.052(5), Mg(1)−Ge(1) 2.636(2), Mg(1)−Ge(2) 2.637(2), Ge(1)−Si(5) 2.373(2), Ge(1)−Si(6) 2.3770(19), Ge(1)−Si(4) 2.3919(18), Ge(2)−Si(1) 2.371(2), Ge(2)−Si(2) 2.374(2), Ge(2)−Si(3) 2.3970(19), Si(3)−Si(4) 2.337(3); O(1)−Mg(1)−O(2) 92.0(2), O(1)−Mg(1)−Ge(1) 114.62(15), Ge(1)−Mg(1)−Ge(2) 109.37(7), Si(5)−Ge(1)−Si(6) 104.34(8), Si(5)−Ge(1)−Si(4) 106.44(7).

Figure 3. Molecular structure of **7a** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−S(1A) 2.2888(17), Ge(1)−S(1) 2.2906(17), Ge(1)−Si(1) 2.4448(19), Ge(1)−Si(4) 2.4798(19), S(1)−Ge(1A) 2.2889(17), Si(1)−Si(2) 2.348(2), Si(2)−C(1) 1.887(7); S(1A)−Ge(1)−S(1) 92.42(6), S-(1A)−Ge(1)−Si(1) 110.44(7), S(1)−Ge(1)−Si(1) 111.15(6), S-(1A)−Ge(1)−Si(4) 120.61(6), S(1)−Ge(1)−Si(4) 114.66(6), Si(1)−Ge(1)−Si(4) 107.00(7), Ge(1A)−S(1)−Ge(1) 87.58(6).
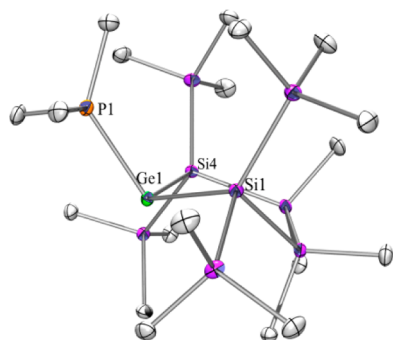

Figure 2. Molecular structure of **4a** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−P(1) 2.3484(6), Ge(1)−Si(1) 2.4533(6), Ge(1)−Si(4) 2.4589(5), P(1)−C(17) 1.8182(16), Si(1)−Si(2) 2.3504(6), Si(2)−C(1) 1.8914(15); P(1)−Ge(1)−Si(1) 102.163(19), P(1)−Ge(1)−Si(4) 105.239(18), Si(1)−Ge(1)−Si(4) 102.70(2).
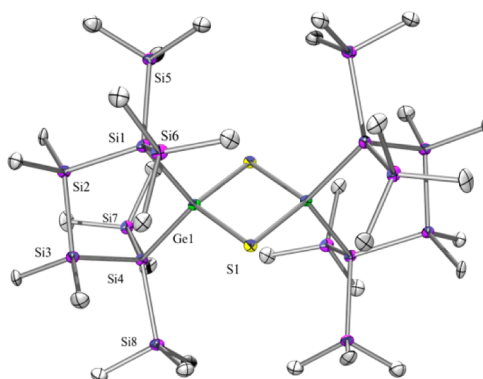

Figure 4. Molecular structure of **8** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−O(1) 1.788(4), Ge(1)−H(90) 1.3807(2), Ge(1)−Si(1) 2.3929(7), Si(1)−Si(2) 2.3563(6), Si(2)−C(1) 1.8814(16); O(1)−Ge(1)−Si(1) 113.46(12), Si(1A)−Ge(1)−Si(1) 110.55(3).

sium compound **2b** (Figure 1) crystallizes in the orthorhombic space group $P2_12_12_1$, isotypic with the previously characterized 1,4-disilyl magnesium compound **2a**.[55]

While the structural features of **2a,b** are essentially the same, it is interesting to note that the Ge−Mg distances of 2.637(2) Å in **2b** are slightly shorter than the analogous interactions in **2a**.[55] The structure of 2-bromo-1,2,3-trigerma-1,1,2,3,3-pentakis(trimethylsilyl)tetramethylcyclopentasilane **3b** (Figure S1), which crystallizes in the triclinic space group $P\bar{1}$, is somewhat unusual. The five-membered ring exhibits a rather flat envelope conformation with the trimethylsilyl group attached to germanium in an equatorial position with the bromine atom in the sterically less demanding axial position. Ge−Ge (2.453(1)/2.4623(9) Å), Ge−Si (2.389(1)−2.402(1) Å), and Ge−Br (2.4080(8) Å) distances of **3b** are within the expected ranges.

The solid-state structure of germylene phosphine adduct **4a** (Figure 2) is quite similar to those of **4b** and a related digermylated PEt₃ adduct.[10] The ring exhibits an envelope conformation with one of the Si(SiMe₃)₂ units out of plane. The PMe₃ coordinates in an orthogonal fashion to the

germylene atom ($d_{\text{P−Si}}$ = 2.3484(6) Å) with the angle between the SiGeSi plane and the phosphine of 112.3° similar to the 113.6° of **4b**. As found for other disilylated germylene base adducts, the Si−Ge distances of **4a** are elongated to 2.4589(5) and 2.4533(6) Å. Si−Ge distances of compounds with an analogous ring skeleton but tetravalent germanium atoms are typically close to 2.40 Å (see below).

Compounds **7a** (Figure 3), **7b** (Figure S2 in the Supporting Information), and **7c** (Figure S3 in the Supporting Information) are structurally much alike, and it was therefore expected that these compounds would exhibit similar structures in the solid state. However, **7a** was found to crystallize in the monoclinic space group $C2/c$ together with a disordered pentane molecule, whereas **7b,c** crystallized in the triclinic space group $P\bar{1}$. Nevertheless, the molecular structures of **7a−c** in the crystal form are analogous. In all molecules planar Ge−E−Ge−E (E = S, Se, Te) units are found.

The 1-germa-2,2,5,5-tetrakis(trimethylsilyl)-tetramethylcyclopentasilane units of **7a−c**, which over the germanium atoms have a spirocyclic connection to the Ge−E−Ge−E rings, all show the five-membered rings in envelope
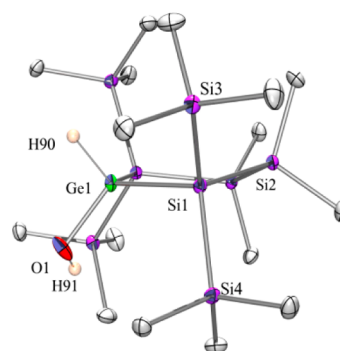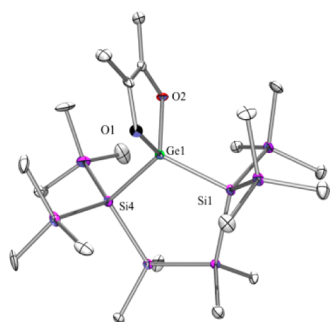
Figure 5. Molecular structure of **10** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−O(1) 1.833(4), Ge(1)−O(2) 1.839(4), Ge(1)−Si(1) 2.396(2), Ge(1)−Si(4) 2.400(2), Si(2)−Si(1) 2.364(3), Si(3)−C(7) 1.889(7), O(1)−C(2) 1.390(8), O(2)−C(3) 1.399(8), C(2)−C(3) 1.315(9), C(2)−C(1) 1.498(9); O(1)−Ge(1)−O(2) 91.1(2), O(1)−Ge(1)−Si(1) 113.91(16), O(2)−Ge(1)−Si(1) 112.98(15), O(1)−Ge(1)−Si(4) 109.70(15), O(2)−Ge(1)−Si(4) 112.48(16), Si(1)−Ge(1)−Si(4) 114.44(7), C(2)−O(1)−Ge(1) 106.1(4), C(3)−O(2)−Ge(1) 106.4(4), C(3)−C(2)−O(1) 118.8(6), O(1)−C(2)−C(1) 112.3(6), C(2)−C(3)−O(2) 117.1(6).

Figure 6. Molecular structure of **12a** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−C(18) 2.011(3), Ge(1)−Si(1) 2.3885(8), Ge(1)−Si(5) 2.4022(8), Ge(1)−Si(2) 2.4100(9), Si(1)−C(1) 1.871(3), Si(2)−C(17) 1.907(3), Si(2)−Si(3) 2.3368(10), Si(9)−C(18) 1.871(3), Si(10)−C(23) 1.829(3), C(17)−C(18) 1.364(4), C(17)−C(22) 1.428(4), C(22)−C(23) 1.210(4); C(18)−Ge(1)−Si(1) 109.96(7), C(18)−Ge(1)−Si(5) 115.90(7), Si(1)−Ge(1)−Si(5) 123.68(3), C(18)−Ge(1)−Si(2) 73.63(8), Si(1)−Ge(1)−Si(2) 116.86(3), Si(5)−Ge(1)−Si(2) 106.25(3), Si(9)−C(18)−Ge(1) 131.43(15).

conformations with one of the a SiMe$_2$ units serving as the flap extending about 0.9−1.0 Å from the (SiGeSiSi) ring plane.

All Si−Si distances and angles of these five-membered rings are rather similar (Table 2). The two rings of the spirocyclic arrangement are situated almost orthogonally to each other (angles between planes between 87.8 and 89.5°). The arguably most unusual structural property of compounds **7a−c** is the Ge−Si distance. In previous studies we have noticed that this particular bond is sensitive to the germanium oxidation state. The Si−Ge distances of PR$_3$ adducts of disilylated germylene are typically around 2.47 Å, whereas Si−Ge distances of tetravalent germanes are close to 2.40 Å.[14] The respective distances in **7a−c** are between 2.44 and 2.48 Å (Table 2), indicating at least some degree of unsaturation at germanium. The number of dimeric structures of higher germanones which
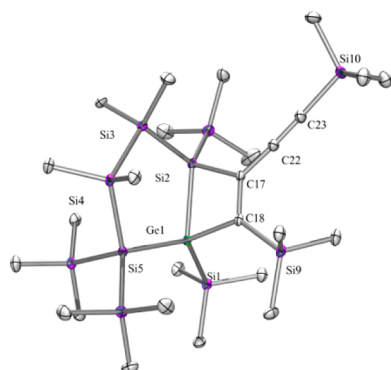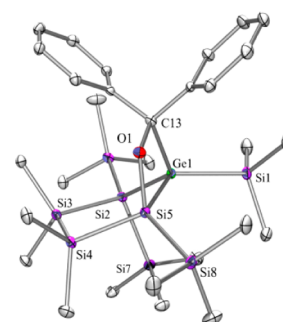

Figure 7. Molecular structure of **13** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−C(13) 2.118(2), Ge(1)−Si(5) 2.3824(7), Ge(1)−Si(1) 2.4050(8), Ge(1)−Si(2) 2.4307(8), Si(1)−C(14) 1.870(3), Si(2)−Si(3) 2.3683(10), Si(5)−O(1) 1.6998(17), O(1)−C(13) 1.446(3); C(13)−Ge(1)−Si(5) 69.34(6), C(13)−Ge(1)−Si(1) 116.32(6), Si(5)−Ge(1)−Si(1) 121.39(3), C(13)−Ge(1)−Si(2) 119.77(6), Si(5)−Ge(1)−Si(2) 105.36(2), Si(1)−Ge(1)−Si(2) 116.04(3), O(1)−Si(5)−Ge(1) 82.45(6), O(1)−C(13)−Ge(1) 98.70(13).
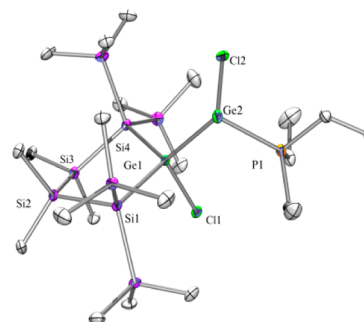

Figure 8. Molecular structure of **15** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(2)−Cl(2) 2.3192(16), Ge(2)−P(1) 2.4421(15), Ge(2)−Ge(1) 2.5289(8), Ge(1)−Cl(1) 2.2831(14), Ge(1)−Si(4) 2.4224(14), Ge(1)−Si(1) 2.4304(15), P(1)−C(19) 1.816(5), Si(1)−Si(2) 2.3536(18), Si(2)−C(1) 1.885(5); Cl(2)−Ge(2)−P(1) 93.17(5), Cl(2)−Ge(2)−Ge(1) 98.53(5), P(1)−Ge(2)−Ge(1) 98.34(4), Cl(1)−Ge(1)−Si(4) 102.11(5), Cl(1)−Ge(1)−Si(1) 100.77(5), Si(4)−Ge(1)−Si(1) 107.57(5), Cl(1)−Ge(1)−Ge(2) 111.76(4), Si(4)−Ge(1)−Ge(2) 120.61(4), Si(1)−Ge(1)−Ge(2) 111.86(4).

have been subjected to structural analysis in the solid state is small.

The CCDC database[57] lists 26 examples comparable to compound **7a** featuring four-membered rings with alternating Ge and S atoms. The Ge−S distances are in a narrow range between 2.209 and 2.258 Å with a mean value of 2.235 Å. The corresponding Ge−S distance in compound **7a** is 2.291(1) Å and thus is considerably longer. This is most likely caused by a combination of the bulky silanylene substituents of the germylene unit and its stronger electron-donating character. CCDC examples[57] of four-membered rings with alternating Ge and Se atoms comparable to **7b** exhibit Ge−Se distances in a range between 2.350 and 2.433 Å, with most compounds exhibiting Ge−Se distances at the lower limit. The compound with the longest distance ((TbtMesGeSe)$_2$)[25] features very large substituents at germanium and a folded asymmetric ring. All other compounds contain perfectly planar SeGeSeGe rings with two equivalent Ge−Se distances. Due to its lower

Table 2. Compilation of Structural Data of Germylene Derivatives 4a, 7a−c, 8−11, 14, and 15, sharing the 1-Germa-2,2,5,5-tetrakis(trimethylsilyl)tetramethylcyclopentasilane Backbone

compd	d_{Ge-E} (Å)	d_{Ge-Si} (Å)	$d_{Si-SiMe_3}$ (Å)	$d_{Si-SiMe_2}$ (Å)	∠SiGeSi (deg)
4a	2.3484(6) (E = P)	2.4589(5), 2.4533(6)	2.3493(6)− 2.3598(6)	2.3605(7), 2.3504(6)	102.70(1)
7a	2.291(2) (E = S)	2.445(2) 2.480(2)	2.360(2)− 2.391(2)	2.348(2)− 2.385(3)	107.00(6)
7b	2.412(2)−2.423(2) (E = Se)	2.444(4)− 2.483(3)	2.361(4)−2.392(5)	2.349(4)−2.374(4)	106.3(1), 106.4(1)
7c	2.632(1) (E = Te)	2.454(2), 2.451(3)	2.345(3)−2.367(3)		
8	1.788(4) (E = O)	2.3929(7)	2.342(1), 2.3433(9)	2.3564(6)	110.55(3)
9	2.3672(9) (E = Br), 1.973(12) (E = C)	2.411(1), 2.408(1)	2.347(2)−2.357(2)	2.358(2), 2.353(2)	110.86(4)
10	1.834(4), 1.839(5) (E = O)	2.396(2), 2.400(2)	2.334(4)−2.356(3),	2.364(3), 2.343(3)	114.43(7)
11	1.958(2) (E = C)	2.3861(8)	2.346(1), 2.338(1)	2.349(1)	113.88(4)
14	2.1961(9) (E = Cl)	2.3874(8)	2.338(1), 2.344(1)	2.358(1)	114.88(4)
15	2.5290(9) (E = Ge), 2.283(1) (E = Cl)	2.431(2), 2.422(1)	2.351(2)−2.370(2)	2.354(2), 2.354(2)	107.57(5)

molecular symmetry, compound **7b** exhibits several Ge−Se distances which lie between 2.412(2) and 2.423(2) Å. Despite these values being on the longer side of those for known compounds, the SeGeSeGe rings of **7b** are planar.

The CCDC database lists only five examples of Ge−Te comparable to **7c**. These compounds again feature planar four-membered GeTeGeTe rings and Ge−Te distances between 2.56 and 2.602 A. For compound **7c** with a planar ring the Ge−Te distances were found to be 2.632(1) Å. Much like **7a−c**, also compounds **11** (Figure S5 in the Supporting Information) and **10** (Figure 5) feature spirocyclic structures. The germacyclopentasilane rings of the latter also engage in envelope conformations which, however, are substantially flatter than those of **7a−c**.

In addition, the Ge−Si distances of **11** (2.38 Å) and **10** (2.40 Å) (Table 2) are shorter and are more in the expected range for fully saturated compounds. The germacyclopentasilane ring units of the structures of compounds **14** (Figure S6 in the Supporting Information), **8** (Figure 4), and **9** (Figure S4 in the Supporting Information) are similar to those of **11** and **10** in the sense that they all exhibit envelope conformations with the flap being one of the SiMe$_2$ units.

The Si−Si bond lengths are within the expected ranges, and the Si−Ge distances remain below or at least very close to 2.40 Å. Although the number of structurally characterized germacyclopropenes[14,38,58−61] is rather small, the range of Ge−C bond lengths is surprisingly broad, ranging from 1.915[60] to 2.005 Å.[38] The value found for compound **11** is 1.958(2) Å, which is a rather typical Ge−C distance and is comparable to that of the related bis[tris(trimethylsilyl)silyl]germirene reported recently.[14] The Ge−Cl distance of dichlorogermane **14** (2.1961(9) Å), the Ge−OH distance of germanol **8** (1.788(4) Å), the Ge-OC distance of **10** (1.834(4) Å), and the Ge−Br distance of **9** (2.3672(9) Å) are all somewhat shorter than the values typically found but are still completely within the ranges of what is expected.

The germylene adduct **15** (Figure 8), however, exhibits a rather long Ge−Ge distance of 2.5290(9) Å, which is quite long but is likely a consequence of the fact that one of the two Ge atoms involved is in the divalent state. This is further reflected by the Ge−Cl distance in compound **15**. The bond to the tetravalent Ge atom is, at 2.283(1) Å, shorter than the respective bond to the divalent Ge atom (2.319(2) Å). In addition to **7a−c** compound **15** is also the only other structure displaying significantly elongated Si−Ge bond lengths (2.422(1) and 2.431(2) Å).

The structures of **12a** (Figure 6) and **13** (Figure 7) do not possess a 1-germa-2,2,5,5-tetrakis(trimethylsilyl)- tetramethylcyclopentasilane substructure but a 1-germa-1,2,5,5-tetrakis(trimethylsilyl)tetramethylcyclopentasilane unit where one of the trimethylsilyl groups is shifted to germanium. This is caused by the fact that both compounds are formed by a [2 + 2] cycloaddition across the silagermene formed by a 1,2-trimethylsilyl shift of the germylene derived from **4b**. The compounds thus both possess a bicyclo[3.2.0]heptane structure with the tetrahedral coordination environment of the bridge-head atoms being severely distorted. Apart from a slightly elongated Ge−Si bond length of 2.4306(9) in **13**, the Si−Si and Si−Ge distances in **12a** and **13** are within the expected range.

■ CONCLUSION

Recently reports of small-molecule activation of carbenes and other low-valent main-group compounds have attracted considerable attention. The main reasons these compounds exhibit such interesting reactivity are the coordinative unsaturation, small singlet−triplet gaps, and fitting orbital energies. In order to investigate the question of whether the recently introduced class of silylated germylene phosphine adducts is also capable of small-molecule activation, we studied the reactions of a cyclic disilylated germylene phosphine adduct with a number of small molecules including elemental chalcogens, water, alkyl halides, alkynes, ketones, and α-diketones. All these reagents reacted in a defined way with the germylene or its silagermene isomer in a manner that can be considered as oxidation of the germylene or the silagermene isomer. Further attempted reactions with carbon monoxide and hydrogen, however, did not proceed.

It has been pointed out conclusively that the range of the small singlet−triplet gap energy (ΔE_{ST}) of a low-valent main-group compound can be considered as an inverse measure of its electrophilicity and further that the orbital energy of the HOMO (lone pair) is proportional to its nucleophilicity.[5,50] A qualitative comparison of the values for ΔE_{ST} and HOMO of **5a**[12] reveals a small ΔE_{ST} of 86 kJ/mol,[12] consistent with it having highly electrophilic behavior, whereas the HOMO energy of −6.46 eV,[11,62] indicating low basicity, explains the lacking nucleophilic properties. This picture is fully consistent with the facile addition chemistry and the reactions with polar reagents, and it also clarifies the reluctant behavior in the attempted hydrogenation and carbonylation reactions.

■ EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents were dried using a column-based solvent purification system.[63] Chemicals were

2734

obtained from different suppliers and used without further purification. Compounds **1a**,[64,65] **1b**,[66] **2a**,[55] **4b**,[10] GeBr$_2$·(dioxane),[67] and MgBr$_2$·Et$_2$O[68] were prepared by following reported procedures.

^{1}H (300 MHz), ^{13}C (75.4 MHz), ^{29}Si (59.3 MHz), and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer and are referenced to Me$_4$Si (^{1}H, ^{13}C, ^{29}Si) and 85% H$_3$PO$_4$ (^{31}P). If not noted otherwise, the solvent of the samples was C$_6$D$_6$. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence was used for the amplification of the signal.[69,70] Elementary analysis was carried out using a Heraeus VARIO ELEMENTAR instrument. For a number of compounds no good elemental analysis values could be obtained, which is a typical problem for these compounds caused by silicon carbide formation during the combustion process. High-resolution (HR) electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Thermo Scientific Orbitrap LTQ XL mass spectrometer and the raw data evaluated using the Xcalibur computer program.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers. Data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[71] and SADABS,[72,73] respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).[74] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as CCDC supplementary publication nos. 1473871 (**2b**), 1473872 (**3b**), 1473861 (**4a**), 1473868 (**7a**), 1473866 (**7b**), 1473869 (**7c**), 1473870 (**8**), 1473864 (**9**), 1473863 (**10**), 1450269 (**11**), 1473865 (**12a**), 1473867 (**13**), 1473860 (**14**), and 1473862 (**15**). Copies of data can be obtained free of charge at: http://www.ccdc.cam.ac.uk/products/csd/request/. Figures of solid-state molecular structures were generated using Ortep-3 as implemented in WINGX[75] and rendered using POV-Ray 3.6.[76]

1,3-Digerma-2-magnesa-1,1,3,3-tetrakis(trimethylsilyl)-tetramethylcyclopentasilane·2THF (2b). A solution of **1b** (0.285 mmol) in THF (2 mL) was added to MgBr$_2$·Et$_2$O (0.145 mmol) in THF (4 mL), and the obtained white suspension was stirred for 1 h after which it could be used for further reactions. For characterization purposes the solution was filtered and the filtrate volume reduced to ca. 3 mL. After cooling to −35 °C, colorless crystals of **2b** (152 mg, 74%) were obtained. NMR (δ in ppm): ^{1}H, 3.60 (m, 8H, THF), 1.26 (m, 8H, THF), 0.72 (s, 12H, SiMe$_2$), 0.52 (s, 36H, SiMe$_3$); ^{13}C, 69.8 (THF), 25.2 (THF), 6.8 (SiMe$_3$), 1.0 (SiMe$_2$); ^{29}Si, −3.4 (SiMe$_3$); −23.7 (SiMe$_2$).

2-Bromo-2-germa-1,1,2,3,3-pentakis(trimethylsilyl)-4,4,5,5-tetramethylcyclopentasilane (3a). A pentane solution of **2a** (0.491 mmol, prepared in DME) was added dropwise to a suspension of GeBr$_2$·(dioxane) (165 mg, 0.515 mmol) in pentane at −70 °C. The mixture was then slowly warmed to ambient temperature and was stirred for another 12 h. All volatiles were evaporated, and the dark red residue was extracted with pentane. After filtration the dark solution was evaporated to dryness, leaving a dark red residue. From the mixture of products only the title compound **3a** could be crystallized, identified by X-ray crystallography and subsequently associated with the following NMR resonances: ^{29}Si NMR (δ ppm) 0.6 (GeSiMe$_3$), −3.4 (Si*Si*Me$_3$), −7.8 (Si*Si*Me$_3$), −24.3 (SiMe$_2$), −105.2 (*Si*SiMe$_3$).

2-Germa-1,1,3,3-tetrakis(trimethylsilyl)-2,2,3,3-tetramethyl-cyclopentasilan-2-ylidene Trimethylphosphine Adduct (4a). A solution of **1a** (0.33 mmol) in DME (2 mL) was slowly added dropwise to a stirred solution of GeCl$_2$·(dioxane) (91 mg, 0.39 mmol) and PMe$_3$ (30 mg, 0.39 mmol) in THF (4 mL) at −30 °C. After 4 h the solvent was evaporated and the product was extracted with pentane (3 × 5 mL). The solvent was removed to yield **4a** as an orange solid (160 mg, 80%). Crystallization from pentane at −35 °C provided orange crystals suitable for X-ray diffraction. Mp: 161−162 °C. NMR (δ in ppm): ^{1}H, 1.11 (d, 9H, PMe$_3$, $^2J_{H-P}$ = 9.9 Hz), 0.44 (s,

12H, SiMe$_2$), 0.41 (s, 18H, SiMe$_3$), 0.32 (s, 18H, SiMe$_3$); ^{13}C, 18.3 (d, PMe$_3$, $^1J_{C-P}$ = 23 Hz), 4.3 (SiMe$_3$), 2.8 (SiMe$_3$), −1.1 (SiMe$_2$), −1.6 (SiMe$_2$); ^{29}Si, −4.3 (br, SiMe$_3$), −8.5 (br, SiMe$_3$), −22.3 (d, SiMe$_2$, $^3J_{Si-P}$ = 10 Hz), −126.0 (d, *Si*(SiMe$_3$)$_3$, $^3J_{Si-P}$ = 16 Hz); ^{31}P, −20.0 (PMe$_3$). Anal. Calcd for C$_{19}$H$_{57}$GePSi$_8$ (613.95): C, 37.17; H, 9.36. Found: C, 36.83; H, 9.12.

Reactions of Germylene Adduct 4b. *Reaction with Sulfur (7a).* A mixture of **4b** (33 mg, 0.05 mmol) and S$_8$ (3 mg, 0.013 mmol) was stirred in THF (1 mL) for 18 h at room temperature. The solvent was removed under reduced pressure, and the product was extracted with pentane (3 × 5 mL). The solution was concentrated to give an inseparable mixture of yellow crystals of **7a** and white crystals of SPEt$_3$. NMR (δ in ppm): ^{1}H, 0.54 (s, 72H, Me$_3$Si), 0.41 (s, 24H, Me$_2$Si); ^{13}C, 5.0 (SiMe$_3$), −1.2 (SiMe$_2$); ^{29}Si, −5.4 (SiMe$_3$), −30.1 (SiMe$_2$), −90.8 (*Si*(SiMe$_3$)).

Reaction with Selenium (7b). A mixture of Se (32 mg, 0.40 mmol) and **4b** (131 mg, 0.20 mmol) was stirred in THF (1 mL) at −30 °C for 30 min and was then allowed warmed to room temperature with the stirring continued for another 3 h. The same workup procedure as for **7a** gave an inseparable mixture of yellow crystals of **7b** and white crystals of SePEt$_3$. NMR (δ in ppm): ^{1}H, 0.55 (s, 72H, Me$_3$Si), 0.39 (s, 24H, Me$_2$Si); ^{13}C, 4.4 (SiMe$_3$), −1.8 (SiMe$_2$); ^{29}Si, −4.7 (SiMe$_3$), −30.5 (SiMe$_2$), −92.6 (*Si*(SiMe$_3$)). HR ESI-MS: calcd for C$_{16}$H$_{47}$GeSeSi$_8$, m/z 617.02; found, m/z 617.04.

Reaction with Tellurium (7c). A mixture of Te (26 mg, 0.20 mmol) and **4b** (131 mg, 0.2 mmol) was stirred in THF (2 mL) at room temperature for 18 h. The same workup procedure as for **7a** gave orange crystals of **7c** (61 mg, 46%). Mp: 248−249 °C. NMR (δ in ppm): ^{1}H, 0.57 (s, 72 H, SiMe$_3$), 0.35 (s, 24 H, SiMe$_2$); ^{13}C, 4.1 (SiMe$_3$), −2.2 (SiMe$_2$); ^{29}Si, −3.2 (SiMe$_3$), −30.4 (SiMe$_2$), −99.4 (*Si*(SiMe$_3$)). Anal. Calcd for C$_{32}$H$_{96}$Ge$_2$Si$_{16}$Te$_2$ (1330.95): C, 28.88; H, 7.27. Found: C, 30.21; H, 6.52.

Addition of Water (8). Degassed H$_2$O (1.8 μL, 0.1 mmol) was added to a stirred solution of **4b** (65 mg, 0.1 mmol) in THF (1 mL) for 18 h at room temperature. The solvent was removed under reduced pressure, and from the residue the product was extracted with pentane (3 × 5 mL). The solvent was removed again, and the residue was dissolved in a minimum amount of toluene to give yellowish crystals of **8** (50 mg, 90%). Mp: 123−125 °C. NMR (δ in ppm): ^{1}H, 6.38 (d, $^3J_{H-H}$ = 1.6 Hz, 1 H, Ge−H), 0.39 (s, 6 H, SiMe$_2$), 0.34 (s, 18 H, SiMe$_3$), 0.28 (s, 6 H, SiMe$_2$), 0.27 (s, 18 H, SiMe$_3$), −0.44 (d, $^3J_{H-H}$ = 1.7 Hz, 1H, OH); ^{13}C, 3.0 (SiMe$_3$), 2.1 (SiMe$_3$), −2.1(SiMe$_2$); ^{29}Si, −4.7 (SiMe$_3$), −7.3 (SiMe$_3$), −25.5 (SiMe$_2$), −113.9 (*Si*(SiMe$_3$)). Anal. Calcd for C$_{16}$H$_{50}$GeOSi$_8$ (555.89): C, 34.57; H, 9.07. Found: C, 34.23; H, 9.10.

Addition of Ethyl Bromide (9). Ethyl bromide (5 mg, 0.05 mmol) and **4b** (33 mg, 0.05 mmol) were stirred in THF (2 mL) for 2 h at room temperature. The same workup procedure as for **7a** gave colorless crystals of **9** (29 mg, 91%). Mp: 136−138 °C. NMR (δ in ppm): ^{1}H, 0.25 (s, 18 H, SiMe$_3$), 0.35 (s, 6 H, SiMe$_2$), 0.44 (s, 6 H, SiMe$_2$), 0.48 (s, 18 H, SiMe$_3$), 1.46 (t, 3H, CH$_3$), 1.60 (m, 2H, Ge-CH$_2$); ^{13}C, −2.2 (SiMe$_2$), −1.8 (SiMe$_2$), 3.5 (SiMe$_3$), 3.6 (SiMe$_3$), 12.5 (CH$_3$), 19.4 (Ge-CH$_2$); ^{29}Si, −4.1 (SiMe$_3$), −8.1 (SiMe$_3$), −25.9 (SiMe$_2$), −111.5 (*Si*(SiMe$_3$)).

Addition of Diacetyl (10). A mixture of diacetyl (5 mg, 0.05 mmol) and **4b** (33 mg, 0.05 mmol) was stirred in THF (2 mL) for 24 h at room temperature. The same workup procedure as for **7a** gave yellow crystals of **10** (31 mg, 98%). Mp: 153−155 °C. NMR (δ in ppm): ^{1}H, 1.96 (s, 6 H, CMe), 0.40 (s, 12 H, SiMe$_2$), 0.38 (s. 36 H, SiMe$_3$); ^{13}C, 131.6 (CO), 14.9 (CMe), 2.9 (SiMe$_3$), −2.3 (SiMe$_2$); ^{29}Si, −6.1 (SiMe$_3$), −30.4 (SiMe$_2$), −117.0 (*Si*(SiMe$_3$)).

Addition of Tolane (11). A mixture of tolane (18 mg, 0.1 mmol) and **4b** (65 mg, 0.1 mmol) was stirred in THF (2 mL) for 24 h at room temperature. The same workup procedure as for **8** gave colorless crystals of **11** (62 mg, 86%) at −35 °C. Mp: 167−169 °C. NMR (δ in ppm): ^{1}H, 7.86 (m, 4H), 7.23 (m, 4H), 7.04 (m, 2H), 0.50 (s, 12 H, SiMe$_2$), 0.32 (s, 36 H, SiMe$_3$); ^{13}C, 148.1, 135.7, 131.9, 129.2, 128.6, 3.6 (SiMe$_3$), −1.8 (SiMe$_2$); ^{29}Si, −7.3 (SiMe$_3$), −30.3 (SiMe$_2$), −120.1 (*Si*(SiMe$_3$)).

Addition of 1,4-Bis(trimethylsilyl)-1,3-butadiyne (12a,b). 1,4-Bis(trimethylsilyl)-1,3-butadiyne (8 mg, 0.05 mmol) was added to a stirred solution of **4b** (33 mg, 0.05 mmol) in THF (1 mL). The same workup procedure as for **8** gave an inseparable mixture of colorless crystals of **12a** and **12b**. NMR (δ in ppm, D_2O capillary): ^{29}Si, −3.5, −3.8, −7.4, −7.7, −8.0, −8.5, −10.8, −11.2, −12.6, −16.5, −18.9, −19.0, −22.1, −24.6, −26.7, −28.4, −35.9, −38.0, −112.4, −113.0. Anal. Calcd for $C_{26}H_{66}GeSi_{10}$ (732.29): C, 42.64; H, 9.08. Found: C, 42.22; H, 9.01.

Addition of Benzophenone (13). Benzophenone (10 mg, 0.05 mmol) and **4b** (33 mg, 0.05 mmol) were stirred in THF (2 mL) for 18 h at room temperature. The solvent was removed under reduced pressure, and the product was extracted with pentane (3 × 5 mL). The solution was concentrated and gave at −35 °C colorless crystals of **13** (35 mg, 97%). NMR (δ in ppm): ^{1}H, 7.79 (m, 2 H), 7.68 (m, 2 H), 7.19 (m, 4 H), 7.10 (m, 2 H), 0.62 (s, 3 H, SiMe$_2$), 0.56 (s, 18 H, SiMe$_3$), 0.41 (s, 6 H, SiMe$_2$), 0.29 (s, 9 H, SiMe$_3$), 0.22 (s, 9 H, SiMe$_3$), 0.38 (s, 3 H, SiMe$_2$); ^{13}C, 152.5, 151.6, 138.2, 132.0, 130.2, 126.3, 125.5, 124.7, 98.0, 4.5, 4.4, 2.8, 0.7, −0.2, −2.6, −4.3, −5.3; ^{29}Si, 40.3 (Si−O), −2.1 (SiMe$_3$), −7.9 (SiMe$_3$), −8.5 (SiMe$_3$), −14.0 (SiMe$_3$), −25.3 (SiMe$_2$), −37.2 (SiMe$_2$), −104.7 (*Si*(SiMe$_3$)).

Addition of GeCl$_2$·dioxane (14, 15). A mixture of GeCl$_2$·(dioxane) (22 mg, 0.1 mmol) and **4b** (65 mg, 0.10 mmol) was stirred in THF (1 mL) for 10 min at −30 °C. The same workup procedure as for **8** gave an inseparable mixture of yellow crystals of **14** and colorless **15**. NMR (δ in ppm): ^{29}Si, −3.9 (**15**, SiMe$_3$), −4.3 (**15**, SiMe$_3$), −7.6 (**14**, SiMe$_3$), −22.8 and −24.6 (both SiMe$_2$), −96.7 (**14**, *Si*(SiMe$_3$)), −102.5 (**15**, d, *Si*(SiMe$_3$), $^2J_{Si−P}$ = 6 Hz); ^{31}P (in THF with D_2O cap.), + 10.5.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00482.

> ORTEP plots of compounds **3b**, **7b,c**, **9**, **11**, and **14**, ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra of compounds **2b**, **7a−c**, **9−11**, **12a/12b**, **13**, **14/15**, and HR ESI-MS of compound **7b** (PDF)
>
> Crystallographic data for all reported crystal structures (CIF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail for J.B.: baumgartner@tugraz.at.
*E-mail for C.M.: christoph.marschner@tugraz.at.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Blom, B.; Driess, M. In *Functional Molecular Silicon Compounds II*; Scheschkewitz, D., Ed.; Springer: Berlin, 2013; Vol. 156, pp 85−123.
(2) Brown, Z. D.; Power, P. P. *Inorg. Chem.* **2013**, *52*, 6248−6259.
(3) Kira, M.; Ishida, S.; Iwamoto, T. *Chem. Rec.* **2004**, *4*, 243−253.
(4) Driess, M. *Nat. Chem.* **2012**, *4*, 525−526.
(5) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479−3511.
(6) Arp, H.; Baumgartner, J.; Marschner, C.; Müller, T. *J. Am. Chem. Soc.* **2011**, *133*, 5632−5635.
(7) Arp, H.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. *J. Am. Chem. Soc.* **2012**, *134*, 6409−6415.
(8) Arp, H.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. *J. Am. Chem. Soc.* **2012**, *134*, 10864−10875.
(9) Arp, H.; Marschner, C.; Baumgartner, J.; Zark, P.; Müller, T. *J. Am. Chem. Soc.* **2013**, *135*, 7949−7959.
(10) Hlina, J.; Baumgartner, J.; Marschner, C.; Albers, L.; Müller, T. *Organometallics* **2013**, *32*, 3404−3410.
(11) Hlina, J.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. *Organometallics* **2013**, *32*, 3300−3308.
(12) Hlina, J.; Baumgartner, J.; Marschner, C.; Albers, L.; Müller, T.; Jouikov, V. *Chem. - Eur. J.* **2014**, *20*, 9357−9366.
(13) Hlina, J.; Arp, H.; Walewska, M.; Flörke, U.; Zangger, K.; Marschner, C.; Baumgartner, J. *Organometallics* **2014**, *33*, 7069−7077.
(14) Walewska, M.; Baumgartner, J.; Marschner, C. *Chem. Commun.* **2015**, *51*, 276−278.
(15) Xiao, X.-Q.; Zhao, H.; Xu, Z.; Lai, G.; He, X.-L.; Li, Z. *Chem. Commun.* **2013**, *49*, 2706−2708.
(16) Veith, M.; Noetzel, M.; Stahl, L.; Huch, V. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1264−1270.
(17) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162−11167.
(18) Al-Rafia, S. M. I.; Lummis, P. A.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Inorg. Chem.* **2010**, *49*, 9709−9717.
(19) Huang, M.; Kireenko, M. M.; Zaitsev, K. V.; Oprunenko, Y. F.; Churakov, A. V.; Howard, J. A. K.; Lermontova, E. K.; Sorokin, D.; Linder, T.; Sundermeyer, J.; Karlov, S. S.; Zaitseva, G. S. *Eur. J. Inorg. Chem.* **2012**, *2012*, 3712−3724.
(20) Liew, S. K.; Al-Rafia, S. M. I.; Goettel, J. T.; Lummis, P. A.; McDonald, S. M.; Miedema, L. J.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Inorg. Chem.* **2012**, *51*, 5471−5480.
(21) Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Leung, W.-P.; Rai, A. K.; Taylor, R. E. *Polyhedron* **1991**, *10*, 1203−1213.
(22) Wegner, G. L.; Jockisch, A.; Schier, A.; Schmidbaur, H. *Z. Naturforsch., B: J. Chem. Sci.* **2000**, *55b*, 347−351.
(23) Weidenbruch, M.; Hagedorn, A.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1996**, *129*, 401−404.
(24) Sasamori, T.; Sugiyama, Y.; Takeda, N.; Tokitoh, N. *Organometallics* **2005**, *24*, 3309−3314.
(25) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811−8824.
(26) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855−8856.
(27) Wu, C.-S.; Su, M.-D. *Dalton Trans.* **2012**, *41*, 3253−3265.
(28) Lappert, M. F. *Pure Appl. Chem.* **1978**, *50*, 703−708.
(29) Erickson, J. D.; Vasko, P.; Riparetti, R. D.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. *Organometallics* **2015**, *34*, 5785−5791.
(30) Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *Nat. Chem.* **2012**, *4*, 361−365.
(31) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2011**, *133*, 18622−18625.
(32) Rupar, P. A.; Staroverov, V. N.; Baines, K. M. *Organometallics* **2010**, *29*, 4871−4881.
(33) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480−482.
(34) Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 8986−8987.
(35) Lee, V. Y.; McNeice, K.; Ito, Y.; Sekiguchi, A. *Chem. Commun.* **2011**, *47*, 3272−3274.
(36) Lee, V. Y.; McNiece, K.; Ito, Y.; Sekiguchi, A.; Geinik, N.; Becker, J. Y. *Heteroat. Chem.* **2014**, *25*, 313−319.
(37) Ando, W.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1979**, *0*, 655−656.
(38) Sekiguchi, A.; Izumi, R.; Ihara, S.; Ichinohe, M.; Lee, V. Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 1598−1600.
(39) Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Y. T.; Shur, V. B.; Vol'pin, M. E.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1994**, *476*, 197−206.

(40) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **1993**, *105*, 1228−1230.

(41) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *J. Am. Chem. Soc.* **1999**, *121*, 8313−8323.

(42) Baines, K. M.; Dixon, C. E.; Langridge, J. M.; Liu, H. W.; Zhang, F. *Organometallics* **1999**, *18*, 2206−2209.

(43) Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2000**, *122*, 12604−12605.

(44) Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *J. Organomet. Chem.* **2001**, *636*, 41−48.

(45) Jana, A.; Huch, V.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 12179−12182.

(46) A reviewer of this paper pointed out that instead of reactions of 1,4-bis(trimethylsilyl)-1,3-butadiyne and benzophenone with the silagermene isomer also nucleophilic attack of the germylene **5a** across the diyne and benzophenone would be a plausible reaction pathway. We do not agree, as we think that the germylene nucleophilicity is likely not sufficient. However, nucleophilic attack of the diyne and benzophenone onto **5a** followed by 1,2-silyl migration also seems possible.

(47) Baines, K. M.; Cooke, J. A.; Vittal, J. J. *Heteroat. Chem.* **1994**, *5*, 293−303.

(48) Dixon, C. E.; Liu, H. W.; Vander Kant, C. M.; Baines, K. M. *Organometallics* **1996**, *15*, 5701−5705.

(49) Dixon, C. E.; Cooke, J. A.; Baines, K. M. *Organometallics* **1997**, *16*, 5437−5440.

(50) Siemeling, U. *Aust. J. Chem.* **2011**, *64*, 1109−1112.

(51) Song, H.; Kim, Y.; Park, J.; Kim, K.; Lee, E. *Synlett* **2016**, *27*, 477−485.

(52) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389−399.

(53) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232−12233.

(54) Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3488−3491.

(55) Gaderbauer, W.; Zirngast, M.; Baumgartner, J.; Marschner, C.; Tilley, T. D. *Organometallics* **2006**, *25*, 2599−2606.

(56) Krempner, C. *Polymers* **2012**, *4*, 408−447.

(57) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 389−397.

(58) Meiners, F.; Saak, W.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2821−2822.

(59) Fukaya, N.; Ichinohe, M.; Kabe, Y.; Sekiguchi, A. *Organometallics* **2001**, *20*, 3364−3366.

(60) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Y. T.; Antipin, M. Y.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27−C30.

(61) Tokitoh, N.; Kishikawa, K.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 827−828.

(62) In comparison to a HOMO energy of −6.23 eV reported in ref 11. This value was obtained by calculation at the M06-2X/6-311+G(d,p)(Si,C,H)def2tzvp(Ge) level.

(63) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(64) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723−3731.

(65) Kayser, C.; Kickelbick, G.; Marschner, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 989−992.

(66) Fischer, J.; Baumgartner, J.; Marschner, C. *Organometallics* **2005**, *24*, 1263−1268.

(67) Leigh, W. J.; Harrington, C. R.; Vargas-Baca, I. *J. Am. Chem. Soc.* **2004**, *126*, 16105−16116.

(68) Nützel, K. In *Houben-Weyl, Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme: Stuttgart, Germany, 1973; Vol. *13/2a*, p 76.

(69) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760−762.

(70) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877−879.

(71) *SAINTPLUS: Software Reference Manual, Version 6.45*; Bruker-AXS: Madison, WI, 1997−2003.

(72) Blessing, R. H. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1995**, *51*, 33−38.

(73) Sheldrick, G. M. *SADABS, Version 2.10*; Bruker AXS, Madison, WI, 2003.

(74) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

(75) Farrugia, L. J. *J. Appl. Crystallogr.* **2012**, *45*, 849−854.

(76) *POVRAY 3.6*; Persistence of Vision Pty. Ltd., 2004; retrieved from http://www.povray.org/download/.