

Synthesis of Stable Dianionic Cyclic Silenolates and Germanolates

Tanja Wiesner, Mario Leypold, Anja Steinmaurer, Dominik Schnalzer, Roland C. Fischer, Ana Torvisco, and Michael Haas*

Cite This: *Organometallics* 2020, 39, 2878–2887

Read Online

ACCESS |

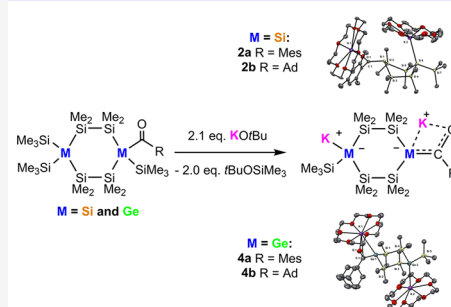
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: In this contribution a convenient synthetic method to obtain the previously unknown dianionic cyclic silenolates and germanolates is described. These dianions **2a,b** and **4a,b** are easily accessible *via* a one-pot synthetic protocol in high yields. Their structural properties were analyzed by a combination of NMR, single-crystal X-ray crystallography, and DFT quantum mechanical calculations. Moreover, the reactivity of **2a,b** and **4a,b** with selected examples of electrophiles was investigated. **2a** and **4a** were reacted with ClSiMe_3 to give new examples of polysilanes and polygermanes with exocyclic double bonds. The reaction of **2b** with $\text{ClSiMe}_2\text{SiMe}_2\text{Cl}$ led to the formation of the acyl bicyclo[2.2.2]octasilane **6**. Moreover, the reaction of **2a,b** and **4a,b** with MeI , as an example of a carbon-centered electrophile, led to selective alkylation reactions at the negatively charged silicon and germanium atoms. The corresponding methylated structures **9a,b** and **10a,b** were formed in nearly quantitative yields. The competitive reactivity of the silyl and silenolate anion toward 1 equiv of ClSiMe_3 showed that the outcome of the reaction was strongly influenced by the substituent at the carbonyl moiety. **2a** reacted with 1 equiv of ClSiMe_3 to give the corresponding cyclic silenolate **S_{1a}**, which demonstrated that the silyl anion is more nucleophilic than the silenolate with attached aromatic groups. **2b**, on the other hand, reacted with 1 equiv of ClSiMe_3 to give the bicyclic compound **11** *via* an intramolecular silyl-Peterson alkenation reaction. These findings clearly showed that the alkyl-substituted silenolate is more nucleophilic than the silyl anion. This paper demonstrates that **2a,b** and **4a,b** have the potential to be used as unique building blocks for complex polysilane and polygermane frameworks.

Unique Building Blocks for complex Polysilane and Polygermane Frameworks.



INTRODUCTION

The synthesis of defined polysilanes in which more than five silicon atoms are connected is challenging. The standard approaches for such polysilanes are Wurtz-type coupling^{1–3} or Lewis acid catalyzed rearrangement reactions.⁴ These two methods generally give rise to structurally simple polysilanes with a low set of functionalities for further derivatization, which prevent the construction of molecules of even moderate complexity.

A potent strategy for the construction of structurally more challenging silicon frameworks is the use of di- or multifunctionalized starting materials such as α,ω -dianions. Gilman^{5,6} and Hengge^{7,8} were pioneers in this area and developed the cleavage of strained cyclosilanes to obtain dianions. Sekiguchi,⁹ Tokitoh,¹⁰ Kira,¹¹ and Apeloig¹² also contributed with their groups to this research field and prepared some previously unknown 1,1-, 1,2-, and 1,4-dilithiooligosilanes. Marschner and Baumgartner, who introduced KOtBu into the field of polysilane chemistry, achieved a milestone in polysilane synthesis. Consequently, the construction of relative complex polysilanes could be accomplished in a straightforward way.^{13–16} Recently, Klausen and co-workers established new phenyl-substituted dianions.¹⁷ These dianions were used as building blocks for the formation of defined polysilanes as well

as for the synthesis of heteroelement substituted polysilanes.^{18–20} Scheschkewitz et al. treated their hexasilabenzene with lithium naphthalenide and obtained a novel dianionic silicon cluster. This dianion turned out to be a valuable synthon for the generation of unprecedented molecular heterosiliconoids with boron and phosphorus directly incorporated into the cluster scaffold.²¹ In addition, we just published a paper about the synthesis of a mixed substituted dianion, which allows straightforward access to a hitherto unknown tricyclic polysilane (see Chart 1).²² Nevertheless, the synthesis of mixed functionalized disilanides has not been reported so far, although these substances would represent ideal building blocks for highly complex silicon frameworks.

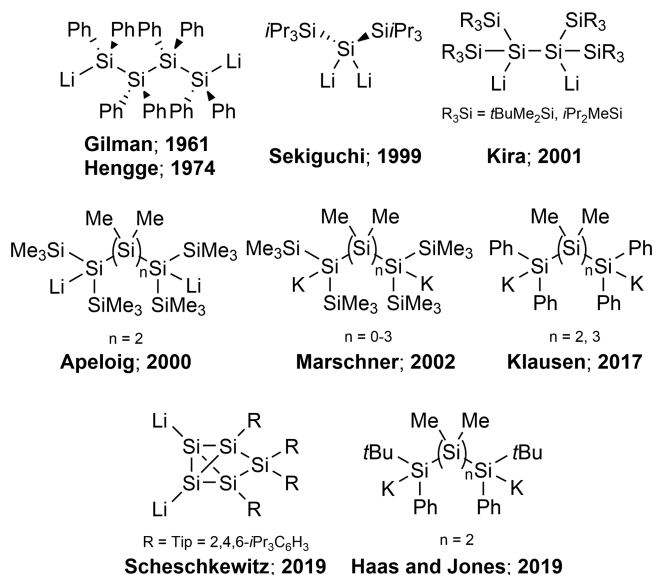
As we have reported earlier, it is possible to synthesize and characterize cyclic silenolates as well as cyclic germanolates and convert them with suitable electrophiles in order to gain a

Received: June 5, 2020

Published: July 17, 2020

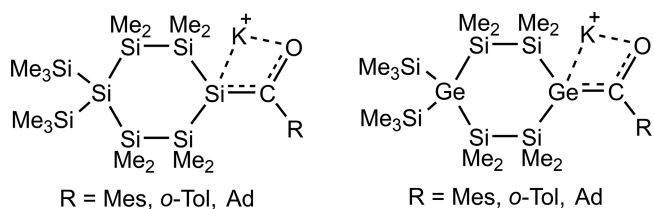


Chart 1



new set of differently substituted acylsilanes as well as acylgermanes (see Chart 2).

Chart 2

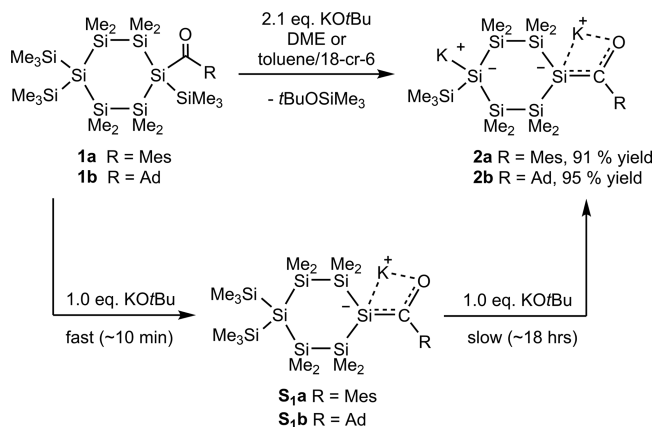


Furthermore, we could show that the reaction of these enolates with chlorosilanes $ClSiR_3$ allowed straightforward access to silenes and germenenes with exocyclic structures.^{23,24} Due to the straightforward accessibility of these cyclic enolates, we saw the potential to investigate their chemical behavior in greater depth. In this context, we have established a novel synthetic strategy for the synthesis of previously unknown dianionic cyclic silenolates and germenolates. The aim of this work is to investigate the spectroscopic properties and the reactivity of these new types of dianions with selected examples of electrophiles.

RESULTS AND DISCUSSION

Synthesis of Dianionic Silenolates. The reaction of the acylcyclohexasilanes **1a,b** with 2 equiv of $KOtBu$ led to the formation of compounds **2a,b**, whereby two different functionalized anionic silicon atoms were incorporated into one molecule (Scheme 1).

To the best of our knowledge, **2a,b** represent the first examples of dianionic polysilanes bearing a silyl anion and a silenolate fragment in one molecule. The dianionic compounds **2a,b** were formed in the same fashion as previously described for the corresponding silenolates. Two major differences are worth mentioning. First, the use of an appropriate solvent is highly important. We observed the formation of **2a,b** only in DME, Et_2O , and toluene. In the case of THF, no product was formed, probably due to the reaction of **2a,b** with THF leading to degradation. This was also described in the case of α -*o*-

Scheme 1. Synthesis of Dianionic Compounds **2a,b**

oligosilyl dianions by Marschner et al.,¹⁴ who observed that stable dianionic species were only formed with the use of DME or benzene/toluene with the addition of crown ethers. Second, the reaction is characterized by a two-step reaction sequence. The first 1 equiv of $KOtBu$ is consumed immediately (approximately 10 min), yielding the silenolates **S_{1a,b}**. The second abstraction of the trimethylsilyl group is much slower and takes place within approximately 18 h. For isolation, **2a,b** were crystallized from $Et_2O/18-cr-6$ at room temperature to give orange crystals of the 1:2 $18-cr-6$ adducts, which were obtained in isolated yields of >90%. After filtration, the crystals can be stored at $-30\text{ }^\circ\text{C}$ in the absence of air even for prolonged periods. **2a,b** afforded crystals of sufficient quality for single-crystal X-ray crystallography. The molecular structures are depicted in Figures 1 and 2; selected bond lengths and the sums of valence angles are summarized in Table 1.

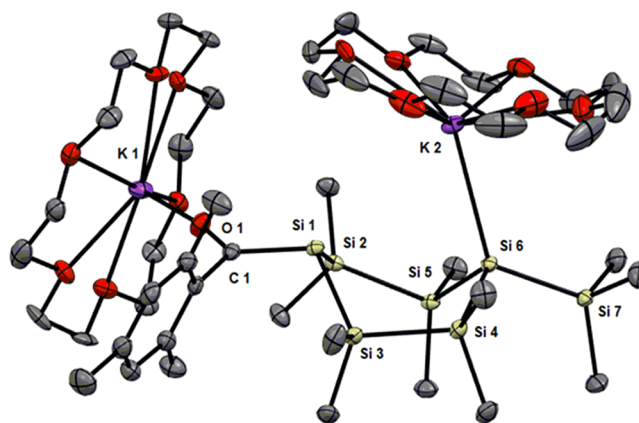


Figure 1. ORTEP diagram for compound **2a** (1:2 adduct with $18-cr-6$). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

On the basis of the observed structural features, **2a,b** are best described as acyl silyl anions (keto form) with $Si-C$ single bonds, $C=O$ double bonds, and markedly pyramidal central $Si_{(1)}$ atoms. Interestingly in **2a** the $K_{(2)}^+$ cation coordinates simultaneously to $Si_{(1)}$ and $Si_{(6)}$. This is probably caused by a packing phenomenon. Furthermore, this simultaneous coordination is also the reason for **2a** to adopt the half-boat conformation, while **2b** and **4b** (**4b** is the dianionic germenolate and will be introduced in the next section)

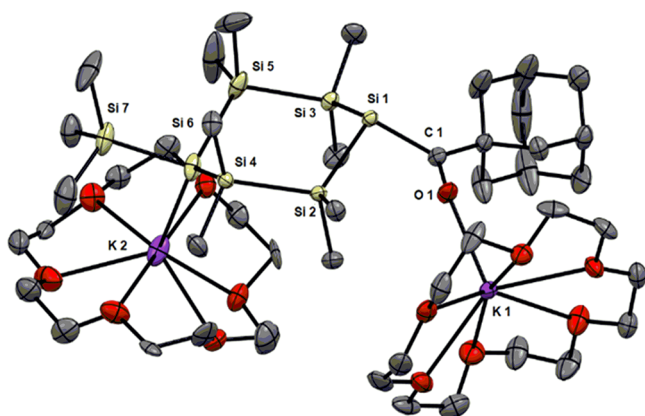


Figure 2. ORTEP diagram for compound **2b** (1:2 adduct with 18-cr-6). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths d (Å) and Sum of Valence Angles $\sum\alpha\text{Si}_{(1)}$, $\sum\alpha\text{Si}_{(6)}$, and $\sum\alpha\text{C}_{(1)}$ (deg) for **2a,b**

	2a	2b
$d(\text{Si}_{(1)}-\text{C}_{(1)})$	1.892	1.916
$d(\text{Si}_{(1)}-\text{K}_{(1)})$	5.102	5.215
$d(\text{C}_{(1)}-\text{K}_{(1)})$	3.843	3.672
$d(\text{C}_{(1)}-\text{O}_{(1)})$	1.254	1.254
$d(\text{K}_{(1)}-\text{O}_{(1)})$	2.614	2.579
$d(\text{Si}_{(6)}-\text{K}_{(2)})$	3.441	3.458
$d(\text{Si}_{(1)}-\text{K}_{(2)})$	4.143	7.361
$\sum\alpha\text{Si}_{(1)}$	312.5	314.4
$\sum\alpha\text{Si}_{(6)}$	307.8	306.1
$\sum\alpha\text{C}_{(1)}$	359.7	360.0

adopt chair conformations. Additionally **2a** shows short $\text{Si}_{(2)}-\text{CH}$ contacts which are less than the van der Waals radii of silicon and hydrogen. This can also explain its half-boat coordination. A similar result in terms of $\text{Si}-\text{CH}$ contacts was obtained by the Klausen group.¹⁷

Synthesis of Dianionic Germenolates. The straightforward synthesis of **2a,b** encouraged us to expand our new methodology to other starting materials. As we have reported previously, it is possible to synthesize cyclic acylgermanes **3a,b**.²⁴ The reaction of these cyclic acylgermanes with 2 equiv of KOtBu led to the formation of dianionic germenolates **4a,b** (Scheme 2). Again, the reaction is characterized by a two-step reaction sequence with reaction rates similar to those of the corresponding acylsilanes.

For isolation, **4a,b** were crystallized from $\text{Et}_2\text{O}/18\text{-cr-6}$ at room temperature to give orange crystals of the 1:2 18-cr-6 adducts, which can be stored after filtration at -30°C in the absence of air even for prolonged periods. **4b** afforded crystals of sufficient quality for single-crystal X-ray crystallography. The molecular structure is depicted in Figure 3; selected bond lengths and the sums of valence angles are summarized in Table 2.

On the basis of the observed structural features, **4b** is best described as an acyl germynyl anion (keto form) with a $\text{Ge}-\text{C}$ single bond, a $\text{C}=\text{O}$ double bond, and markedly pyramidal central $\text{Ge}_{(1)}$ and $\text{Ge}_{(2)}$ atoms.

NMR Spectroscopy of 2a,b and 4a,b. NMR data also supported that the dominant structure of **2a,b** and **4a,b** in solution is the keto form. Very similar ^{13}C chemical shifts were observed for the carbonyl C atom of the two compounds

Scheme 2. Synthesis of Dianionic Germenolates **4a,b**

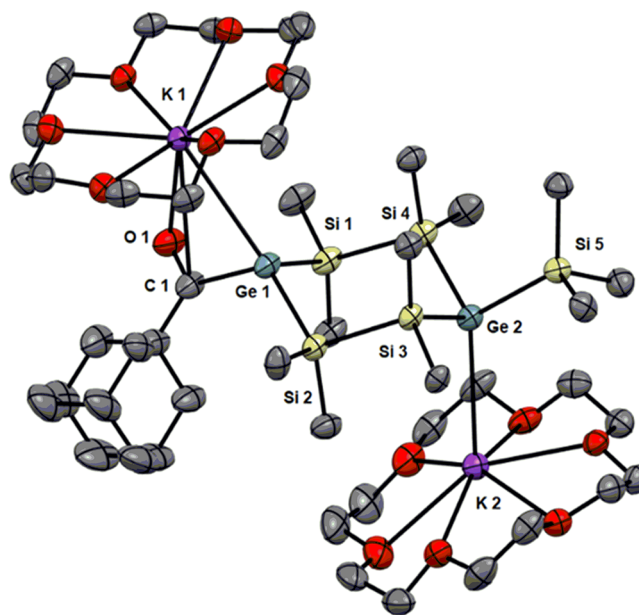
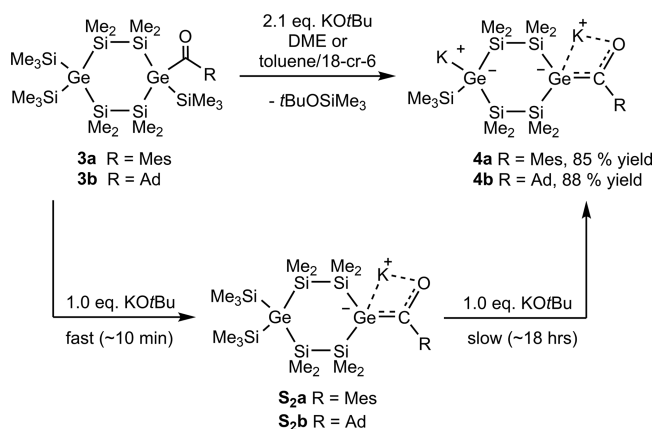


Figure 3. ORTEP diagram for compound **4b** (1:2 adduct with 18-cr-6). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths d (Å) and Sum of Valence Angles $\sum\alpha(\text{Ge}_1)$, $\sum\alpha(\text{Ge}_2)$, and $\sum\alpha(\text{C}_1)$ (deg) for **4b**

$d(\text{Ge}_{(1)}-\text{C}_{(1)})$	2.047
$d(\text{Ge}_{(1)}-\text{K}_{(1)})$	3.427
$d(\text{C}_{(1)}-\text{K}_{(1)})$	3.335
$d(\text{C}_{(1)}-\text{O}_{(1)})$	1.248
$d(\text{K}_{(1)}-\text{O}_{(1)})$	2.760
$d(\text{Ge}_{(2)}-\text{K}_{(2)})$	3.635
$d(\text{Ge}_{(1)}-\text{K}_{(2)})$	6.671
$\sum\alpha\text{Ge}_{(1)}$	314.5°
$\sum\alpha\text{Ge}_{(2)}$	298.2°
$\sum\alpha\text{C}_{(1)}$	359.6°

between δ 266.6 and 280.9 ppm in a typical range for carbonyl groups. Furthermore, **2a,b** and **4a,b** exhibit only two sharp SiMe_2 resonance lines in the ^{29}Si NMR, which clearly suggest free rotation around the $\text{Si}_{(1)}-\text{C}_{(1)}$ bond (Table 3). It was not possible to use $\text{THF-}d_8$ for **2b** and **4b** because a detectable degradation was found within minutes at room temperature.

Table 3. Selected ^{13}C and ^{29}Si NMR Chemical Shifts for the Silenolates **2a,b** and **4a,b**^a

	2 (ppm)		4 (ppm)	
	a, Mes ^b	b, Ad ^c	a, Mes ^b	b, Ad ^c
$\delta^{13}\text{C}(\text{C}=\text{O})$	266.63	273.96	281.01	280.92
$\delta^{29}\text{Si}(\text{SiMe}_3)$	0.05	-1.14	0.93	0.36
$\delta^{29}\text{Si}(\text{SiMe}_2)$	-27.69	-26.48	-27.69	-23.45
	-32.37	-31.31	-29.35	-25.40
$\delta^{29}\text{Si}(\text{Siq})$	-67.70	-87.33		
	-189.08	-192.42		

^a δ values relative to external TMS. ^bIn THF-*d*₈ at 25 °C. ^cIn C₆D₆ at 25 °C.

UV–Vis Spectroscopy and TDDFT-PCM Calculations.

Toluene was used as a solvent to determine the charge transfer behavior for the longest wavelength absorption band.²⁵ Figure 4 depicts the measured UV–vis spectra of **2a,b** and **4a,b** in toluene together with their calculated frontier Kohn–Sham orbitals.

In order to examine the differences between aromatic and saturated substituents at the carbonyl moiety, the mesityl- and adamantyl-substituted derivatives **2a,b** and **4a,b** were investigated. All UV–vis calculations were performed on the geometry-optimized X-ray crystal structures *via* TDDFT-PCM in toluene at the CAM-B3LYP/6-31+G(d,p) level of theory.²⁶ Noteworthy, CAM-B3LYP achieved a better consistency for dianions **2a,b** and **4a,b** in calculated vertical excitations in comparison to B3LYP, which was previously applied to UV–vis calculations on silenolates **S_{1a,b}** and germenolates **S_{2a,b}**.^{24,27} The silenolates **2a,b** exhibit intense absorption maxima in the range between 433 and 450 nm, which are red-shifted in the order **2b** → **2a**. The same bathochromic trend **4b** → **4a** also applies to the germenolates **4a,b** with absorption maxima between 420 and 447 nm. The acyl substituent (aryl vs alkyl) significantly affects the HOMO orbital density and hence its shape, which ultimately leads to different reaction centers in conversion with electrophiles (see section below). The HOMO-1 and HOMO of **2a** (Figure 4) correspond to the *p_z* orbital of the silenolate with a significant part of the corresponding silanide mixed in, respectively. This contribution makes the silanide equally nucleophilic regarding reactions of cyclic silenolates with aromatic acyl substituents. In contrast, the HOMO of **2b** only exhibits the *p_z* character of the silenolate, whereas the HOMO-1 of **2b** shows the silanide orbital alone, allowing a site-specific functionalization. In addition, the energy difference between the HOMO-1 and the HOMO is in **2a** significantly larger than in **2b** (0.28 eV vs 0.09 eV). Similar observations were made with the dianionic germenolates **4a,b**. Upon excitation, electron density is displaced into the π^* orbital of the corresponding carbonyl orbitals. In the corresponding LUMOs of the aryl-substituted species **2a** and **4a**, our calculations additionally showed considerable conjugation of the carbonyl group and the aromatic π systems, which is not possible for the alkyl-substituted silenolate **2b** and germanolate **4b**. As a consequence of this, the empty orbitals are energetically stabilized in the order **2b** → **2a**. This stabilization results in smaller excitation energies and in the observed bathochromic shifts of the corresponding absorption bands. The obtained experimental and computational data are summarized in Table 4 and show reasonable agreement.

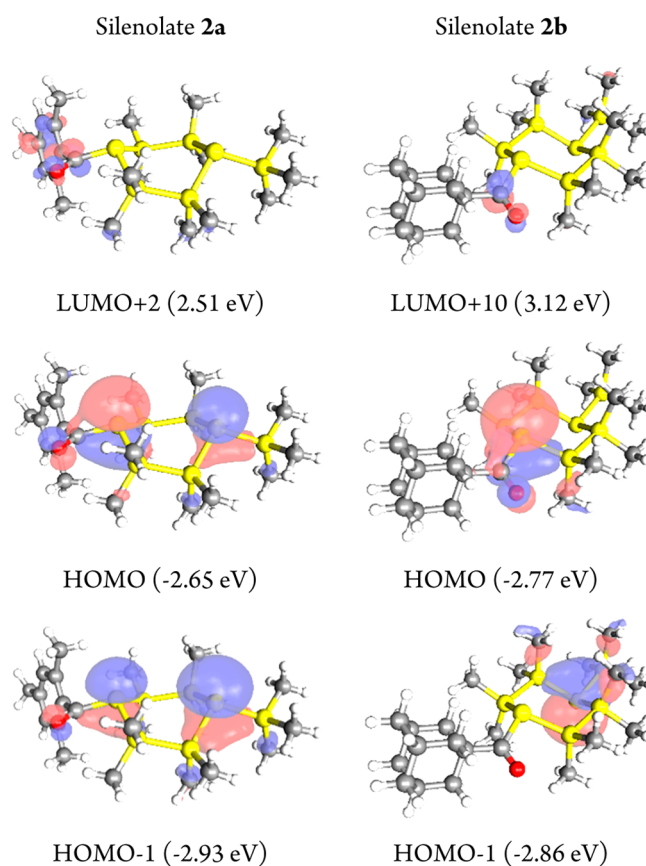
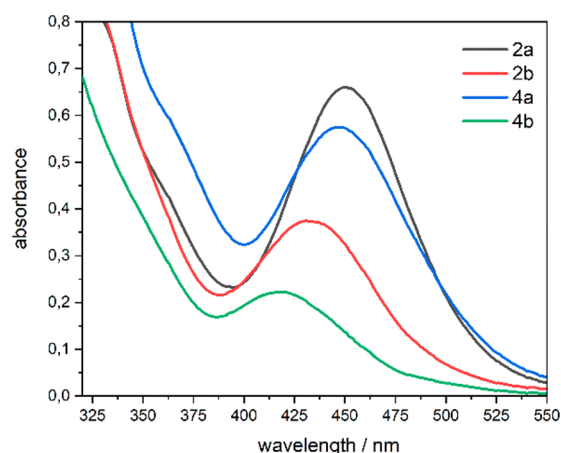


Figure 4. Measured UV–vis spectra of **2a,b** and **4a,b** in toluene (1×10^{-4} mol L⁻¹), and the calculated frontier Kohn–Sham orbitals of **2a,b** at the TDDFT-PCM(toluene) CAM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory. Kohn–Sham orbitals of **4a,b** are similar in shape and energy (see the Supporting Information).

Reactivity of **2a,b versus Selected Examples of Chlorosilanes.** The reactivity of **2a,b** versus chlorosilanes parallels the observed reactivities for silenolates and silyl anions. The same reactivity was found by Ohshita and Ishikawa, by Marschner et al., and by our group.^{13–15,23,28,29}

Thus, **2b** with an alkyl group attached to the carbonyl moiety reacted with an equimolar amount of tetramethyldichlorodisilane (ClSiMe₂SiMe₂Cl) at 0 °C in THF with formation of the acyl bicyclo[2.2.2]octasilane **6**. **6** was obtained in nearly quantitative yield (95% yield). The asymmetrically substituted acylsilane **6** exhibits two ^{29}Si resonance lines for the SiMe₂

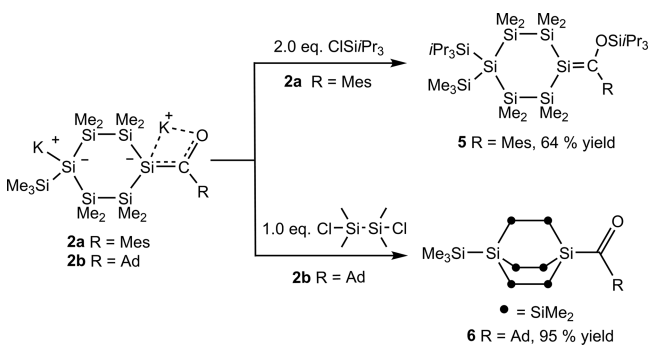
Table 4. Experimental and TDDFT-PCM(toluene) CAM-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) Calculated Absorption Bands λ in Toluene and Extinction Coefficients ϵ with Respect to Oscillator Strengths f for **2a,b** and **4a,b**

	$\lambda_{\text{max,exp}}$ (nm)	ϵ (L mol ⁻¹ cm ⁻¹)	$\lambda_{\text{max,calc}}^a$ (nm)	f	assignment
2a	450	6602	441	0.2102	$p_z \rightarrow \pi^*(\text{CO/aryl})$
2b	433	3730	428	0.1131	$p_z \rightarrow \pi^*(\text{CO})$
4a	447	5753	435	0.1591	$p_z \rightarrow \pi^*(\text{CO/aryl})$
4b	420	2178	418	0.0858	$p_z \rightarrow \pi^*(\text{CO})$

^a $\lambda_{\text{max,calc}}$ values are corrected by a factor of 5% due to a consistent overestimation of excitation energies with CAM-B3LYP.

groups near -37 ppm, which are not significantly influenced by the nature of the adamantoyl group. The two δ_{Si} values for the bridgehead Si atoms were measured near -131 ppm (characteristic for tetrasilyl-substituted silanes) and -77 ppm (characteristic for acyl-substituted quaternary silanes). The same tendencies were found earlier by Stueger et al. during the synthesis of a series of substituted bicyclo[2.2.2]octasilanes.³⁰ The aryl-substituted compound **2a** exclusively afforded the *O*-silylated silene **5** under the same conditions (compare Scheme 3). NMR spectral data of **5** (see the Experimental Section) are

Scheme 3. Reactivity of Dianionic Compounds **2a,b** toward Chlorosilanes

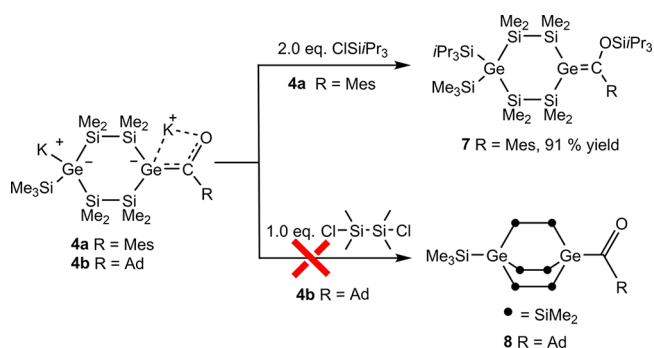


also typical for a Brook-type silene. ¹³C and ²⁹Si signals characteristic for Si=C were observed at δ_{Si} 32.8 ppm and δ_{C} 198.9 ppm, respectively. **5** was obtained in a good yield (64% yield).

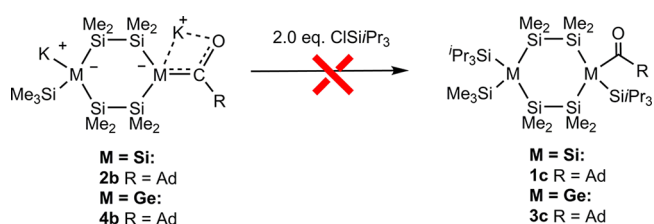
Reactivity of 4a,b versus Selected Examples of Chlorosilanes. Furthermore, the reactivity of **4a,b** versus chlorosilanes was investigated and parallels that previously observed for germenolates and germyl anions.^{24,31} The reaction of **4a** with 2 equiv of ClSiPr₃ afforded the formation of the *O*-silylated germene **7** in excellent yields (compare Scheme 4). NMR spectral data of **7** (see the Experimental Section) are again typical for a Brook-type germene. A ¹³C signal characteristic for Ge=C was observed at δ_{C} 210.17 ppm. Interestingly, the reaction of **4b** with an equimolar amount of ClSiMe₂SiMe₂Cl did not lead to the formation of the expected product **8**; instead, an undefined polymeric material was formed.

The unsuccessful derivatization of **4b** with ClSiMe₂SiMe₂Cl encouraged us to investigate the reactivity of **4b** with 2 equiv of ClSiPr₃. Again, no expected product formation was observed (Scheme 5). The same experiment was further repeated with **2b** and gave also rise to an undefined polymer. Therefore, we reasoned that ClSiPr₃ is too sterically demanding to allow M–

Scheme 4. Reactivity of Dianionic Compounds **4a,b** toward Chlorosilanes



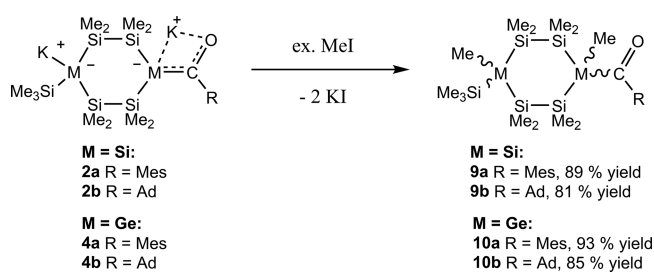
Scheme 5. Reactivity of Dianionic Compounds **2b** and **4b** toward ClSiPr₃



Si (M = Si for **2b** and M = Ge for **4b**) bond formation in the presence of an adamantoyl group.

Reactivity of 2a,b and 4a,b versus Carbon-Centered Electrophiles. We selected MeI as a carbon-centered electrophile, because it represents a benchmark reagent with numerous examples found in the literature.^{27,29,32} In the reaction of **2a,b** and **4a,b** with MeI, the same reactivities in terms of reaction sites were observed. In all cases, alkylation of the negatively charged silicon as well as germanium atoms were found in nearly quantitative yields (Scheme 6). Again, the

Scheme 6. Reactivity of Dianionic Compounds **2a,b** and **4a,b** toward MeI

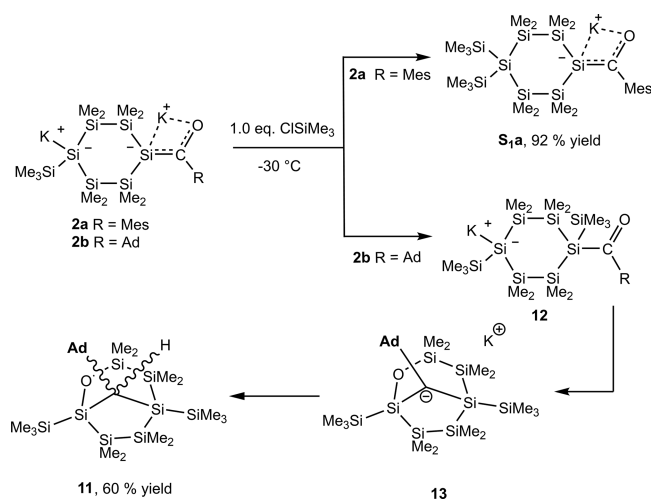


same tendency was reported in the case of acyclic silenolates and silanides by Ohshita, Ottosson, and Marschner earlier.^{14,15,28,29,32} The methylated silicon derivatives **9a,b** and germanium derivatives **10a,b** were obtained as *cis/trans* mixtures. The silicon atoms of **9a,b** undergo a significant low-field shift from -70 to 45 ppm (in the case of the acyl-substituted silicon atom) and from -131 to -84 ppm (for the silyl-substituted silicon atom). This is caused by the lower shielding of the methyl group in comparison to the trimethylsilyl group (see the Experimental Section).

Competitive Reactivity of the Silyl Anion and the Silenolate. Finally, we investigated which silanide is more nucleophilic, the silyl anion or the silenolates. Therefore, we

reacted **2a,b** with 1 equiv of trimethylchlorosilane (ClSiMe_3) at $-30\text{ }^\circ\text{C}$. The outcome of the reaction was again strongly dependent on the substituent at the carbonyl moiety and reflected our predictions from the computational analyses. **2a** with an aryl group attached to the carbonyl moiety reacted with an equimolar amount of ClSiMe_3 to form the cyclic silenolate **S_{1a}**, making the silanide the more nucleophilic reaction center. **2b**, on the other hand, reacted with an equimolar amount of ClSiMe_3 to give the bicyclic oxahexasilabicyclo[3.2.1]octan-8-ide **11**, which clearly showed that the silenolate is more nucleophilic than the silyl anion in the case of an alkyl substitution. The formation of **11** can be rationalized by assuming the intermediate formation of the silanide **12**, which subsequently rearranged to give the bicyclic carbanion **13** by an intramolecular sila-Peterson alkenation. Apparently, **13** is very unstable, losing its intense red color within minutes, presumably by the abstraction of one proton from the surrounding media to give **11** as the final product. Analytical and spectroscopic data (see the [Experimental Section](#)) clearly supported the bicyclic structure of **11** (see [Scheme 7](#)). Moreover, this compound was obtained by a previous study by our group.²⁷

Scheme 7. Competitive Reactivity of Silyl Anion and Silenolate toward 1 Equiv of ClSiMe_3



CONCLUSION

In summary, we synthesized the first examples of mixed functionalized compounds **2a,b** and **4a,b**, which represent ideal building blocks for highly complex silicon frameworks. These dianions are easily accessible, can be isolated, and were fully characterized. Silenolates **2a,b** as well as the germenolates **4a,b** adopt the keto form in solution, irrespective of the nature of the R group attached to the carbonyl moiety. Furthermore, the reactivity of **2a,b** and **4a,b** versus chlorosilanes was investigated as an example of a silicon-centered electrophile. **2a** and **4a** reacted with ClSiPr_3 to give new examples of a polysilane and a polygermane with an exocyclic double bond. The reaction of **2b** with $\text{ClSiMe}_2\text{SiMe}_2\text{Cl}$ led to the formation of the acyl bicyclo[2.2.2]octasilane **6**. Moreover, the reaction of **2a,b** and **4a,b** with MeI , as a carbon-centered electrophile, led to selective alkylation reactions at the negatively charged silicon and germanium atoms. The methylated structures **9a,b** and **10a,b** were formed in nearly quantitative yields. Finally, we

examined the competitive reactivity of the silyl anion and the silenolate toward 1 equiv of ClSiMe_3 . The outcome of the reaction was strongly influenced by the substituent at the carbonyl moiety, which was in alignment with our computational analysis. **2a** reacted with 1 equiv of ClSiMe_3 to give the corresponding cyclic silenolate **S_{1a}** and demonstrated that the silyl anion is more nucleophilic than the silenolate. In contrast to that, **2b** reacted with 1 equiv of ClSiMe_3 to give the bicyclic compound **11** via an intramolecular sila-Peterson alkenation reaction. This observation clearly showed that the alkyl-substituted silenolate is more nucleophilic than the silyl anion. Further studies to probe the scope of these new dianions are currently in progress.

EXPERIMENTAL SECTION

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system.³³ ClSiMe_3 (95%), KOtBu (>98%), ClCOMes (99%), ClCOAd (98%) and 18-cr-6 (99%), were used without any further purification. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Varian INOVA 300 spectrometer in C_6D_6 , $\text{THF-}d_8$, or CDCl_3 solutions and were referenced versus TMS using the internal ^2H -lock signal of the solvent. HRMS spectra were obtained on a Kratos Profile mass spectrometer. Infrared spectra were obtained on a Bruker Alpha-P Diamond ATR spectrometer from the solid sample. Melting points were determined using a Stuart SMP50 apparatus and are uncorrected. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus. UV absorption spectra were recorded on a PerkinElmer Lambda 5 spectrometer.

Synthesis of 2a. A 500 mg portion of acylcyclohexasilane **1a** (0.76 mmol) and 423 mg of 18-cr-6 (1.60 mmol) were dissolved in 20 mL of Et_2O . The solution was then cooled to $-70\text{ }^\circ\text{C}$, and 180 mg (1.60 mmol) of KOtBu was added. During the addition, the reaction mixture turned from yellow to dark orange and an orange precipitate began to form. The reaction mixture was warmed to room temperature and stirred overnight for 15 h. The orange precipitate was isolated and washed with Et_2O ($3 \times 5\text{ mL}$). The orange powder was dried under vacuum (not longer than 5 min; otherwise a slow degradation process occurs) to give **2a**. Yield: 775 mg (91%) of analytically pure **2a** as an orange powder.

Data for **2a** are as follows. Mp: $158\text{--}159\text{ }^\circ\text{C}$. Anal. Calcd for $\text{C}_{45}\text{H}_{92}\text{K}_2\text{O}_{13}\text{Si}_7$: C, 48.43; H, 8.31. Found: C, 48.68; H, 8.45. ^{29}Si NMR ($\text{THF-}d_8$, TMS, ppm): 0.05 (SiMe_3); -27.69 , -32.37 (SiMe_2); -67.70 (SiCOAryl); -189.08 ($\text{Si}(\text{SiMe}_3)$). ^{13}C NMR ($\text{THF-}d_8$, TMS, ppm): 266.63 ($\text{C}=\text{O}$); 154.00, 132.80, 132.50, 128.18 (Aryl-C); 71.03 ($(-\text{CH}_2\text{CH}_2\text{O}-)_6$); 21.61, 21.29 (Aryl- CH_3); 8.92 ($\text{Si}(\text{CH}_3)_3$); 4.33, 1.30 ($\text{Si}(\text{CH}_3)_2$). ^1H NMR ($\text{THF-}d_8$, TMS, ppm): 6.57 (s, 2H, Mes-H); 3.61 (s, 48H, $(-\text{CH}_2\text{CH}_2\text{O}-)_6$); 2.38 (s, 6H, Mes- CH_3); 2.15 (s, 3H, Mes- CH_3); 0.12, 0.05 (s, 33H, $\text{Si}(\text{CH}_3)_2$ and $\text{Si}(\text{CH}_3)_3$). UV-vis: λ [nm] (ϵ [$\text{L mol}^{-1}\text{ cm}^{-1}$]) 450 (6602).

Synthesis of 2b. A 500 mg portion of acylcyclohexasilane **1b** (0.74 mmol) and 413 mg of 18-cr-6 (1.60 mmol) were dissolved in 20 mL of Et_2O . The solution was then cooled to $-70\text{ }^\circ\text{C}$, and 175 mg (1.60 mmol) of KOtBu was added. During the addition, the reaction mixture turned from colorless to dark orange and a yellow precipitate began to form. The reaction mixture was warmed to room temperature and stirred overnight for 15 h. The yellow precipitate was isolated and washed with Et_2O ($3 \times 5\text{ mL}$). The yellow powder was dried under vacuum (not longer than 5 min; otherwise a slow degradation process occurs) to give **2b**. Yield: 801 mg (95%) of analytically pure **2b** as a yellow powder.

Data for **2b** are as follows. Mp: $155\text{--}157\text{ }^\circ\text{C}$. Anal. Calcd for $\text{C}_{46}\text{H}_{96}\text{K}_2\text{O}_{13}\text{Si}_7$: C, 48.81; H, 8.55. Found: C, 48.92; H, 8.63. ^{29}Si NMR (C_6D_6 , TMS, ppm): -1.14 (SiMe_3); -26.48 , -31.31 (SiMe_2); -87.33 (SiCOAryl); -192.42 ($\text{Si}(\text{SiMe}_3)$). ^{13}C NMR (C_6D_6 , TMS, ppm): 273.96 ($\text{C}=\text{O}$); 70.14 ($(-\text{CH}_2\text{CH}_2\text{O}-)_6$); 50.79 (Ad-C-CO); 40.36, 38.46 (Ad- CH_2); 30.17 (Ad-CH); 9.36 ($\text{Si}(\text{CH}_3)_3$); 5.21, 4.11, 2.50 ($\text{Si}(\text{CH}_3)_2$). ^1H NMR (C_6D_6 , TMS, ppm): 3.34 (s, 48H,

($-\text{CH}_2\text{CH}_2\text{O}-$)₆; 2.34, 2.05, 1.96 (bs, 15H Ad-H); 0.95, 0.86, 0.79 (bs, 33H, Si(CH₃)₂ and Si(CH₃)₃). UV-vis: λ [nm] (ϵ [L mol⁻¹ cm⁻¹]) 433 (3730).

Synthesis of 4a. A 500 mg portion of cyclic acylgermane **3a** (0.67 mmol) and 372 mg of 18-cr-6 (1.41 mmol) were dissolved in 20 mL of Et₂O. The solution was then cooled to -70°C , and 158 mg (1.41 mmol) of KOtBu was added. During the addition, the reaction mixture turned from yellow to dark orange and an orange precipitate began to form. The reaction mixture was warmed to room temperature and stirred overnight for 15 h. The orange precipitate was isolated and washed with Et₂O (3 \times 5 mL). The orange powder was dried under vacuum (not longer than 5 min; otherwise a slow degradation process occurs) to give **4a**. Yield: 688 mg (85%) of analytically pure **4a** as an orange powder.

Data for **4a** are as follows. Mp: 90–92 $^\circ\text{C}$. Anal. Calcd for C₄₅H₉₂Ge₂K₂O₁₃Si₅: C, 44.85; H, 7.70. Found: C, 44.96; H, 7.96. ²⁹Si NMR (THF-*d*₆, TMS, ppm): -0.93 (SiMe₃); -27.69 , -29.35 (SiMe₂). ¹³C NMR (THF-*d*₆, TMS, ppm): 281.01 (C=O); 154.14, 133.42, 131.23, 129.20, 128.57 (Aryl-C); 71.19 ($-\text{CH}_2\text{CH}_2\text{O}-$)₆; 21.35, 21.16 (Aryl-CH₃); 8.86 (Si(CH₃)₃); 4.54, 1.93 (Si(CH₃)₂). ¹H NMR (THF-*d*₆, TMS, ppm): 6.54 (s, 2H, Mes-H); 3.62 (s, 48H, ($-\text{CH}_2\text{CH}_2\text{O}-$)₆); 2.30 (s, 6H, Mes-CH₃); 2.14 (s, 3H, Mes-CH₃); 0.16 (s, 9H, Si(CH₃)₃); 0.08 (s, 24H, Si(CH₃)₂); UV-vis: λ [nm] (ϵ [L mol⁻¹ cm⁻¹]) = 447 (5753).

Synthesis of 4b. A 500 mg portion of cyclic acylgermane **3b** (0.66 mmol) and 365 mg of 18-cr-6 (1.38 mmol) were dissolved in 20 mL of Et₂O. The solution was then cooled to -70°C and 155 mg (1.38 mmol) of KOtBu was added. During the addition, the reaction mixture turned from colorless to dark orange and a yellow precipitate began to form. The reaction mixture was warmed to room temperature and stirred overnight for 15 h. The yellow precipitate was isolated and washed with Et₂O (3 \times 5 mL). The yellow powder was dried under vacuum (not longer than 5 min; otherwise a slow degradation process occurs) to give **4b**. Yield: 688 mg (88%) of analytically pure **4b** as yellow powder.

Data for **4b** are as follows. Mp: 190–192 $^\circ\text{C}$. Anal. Calcd for C₄₆H₉₆Ge₂K₂O₁₃Si₅: C, 45.25; H, 7.92. Found: C, 45.30; H, 7.77. ²⁹Si NMR (C₆D₆, TMS, ppm): 0.36 (SiMe₃); -23.45 , -25.40 (SiMe₂). ¹³C NMR (C₆D₆, TMS, ppm): 280.92 (C=O); 70.16 ($-\text{CH}_2\text{CH}_2\text{O}-$)₆; 52.11 (Ad-C-CO); 39.78, 38.43 (Ad-CH₂); 30.06 (Ad-CH); 9.74 (Si(CH₃)₃); 5.73, 5.64, 4.23, 2.35 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm): 3.35 (s, 48H, ($-\text{CH}_2\text{CH}_2\text{O}-$)₆); 2.30, 2.08, 1.95 (m, 15H Ad-H); 1.01, 0.90, (s, each 12H, Si(CH₃)₂); 0.83 (s, 9H, Si(CH₃)₃). UV-vis: λ [nm] (ϵ [L mol⁻¹ cm⁻¹]) 420 (2178).

Synthesis of 5. A 500 mg portion (0.76 mmol) of **1a** was dissolved in 20 mL DME and cooled to -30°C , and 180 mg (1.60 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ²⁹Si NMR showed that the dianionic species **2a** was completely formed. Subsequently, the reaction mixture was cooled to -30°C and 309 mg (1.60 mmol) of ClSiPr₃ was added dropwise. The red solution immediately turned yellow. After removal of the volatile components under vacuum, the remaining yellow solid was dissolved in heptane, the solution was filtered through dry Celite, and the solvent was stripped off again. Recrystallization from Et₂O afforded 405 mg (64%) of the analytically pure silene **5** as yellow crystals.

Data for **5** are as follows. Mp: 155–157 $^\circ\text{C}$. Anal. Calcd for C₃₉H₈₆O_{Si₉}: C, 56.86; H, 10.52. Found: C, 56.90; H, 10.25. ²⁹Si NMR (C₆D₆, TMS, ppm): 32.83 (Si=C); 13.15 (SiPr₃); -9.07 (SiMe₃); -33.90 , -34.19 , -35.68 , -35.84 (SiMe₂); -128.70 (Si(SiMe₃)(SiPr₃)). ¹³C NMR (C₆D₆, TMS, ppm): 199.38 (Si=C); 143.16, 137.21, 137.09, 136.92, 128.85 (Aryl-C); 21.50, 21.21 (Aryl-CH₃); 20.83, 18.54 (CH(CH₃)₂); 15.36, 14.18 (CH(CH₃)₂); 5.35 (Si(CH₃)₃); 0.95, 0.50, 0.36, -0.77 , -0.92 , -2.03 , -2.36 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm): 6.80 (s, 2 H, Mes-H); 2.61 (s, 6H, Mes-CH₃); 2.12 (s, 3H, Mes-CH₃); 1.25–1.07 (m, 42 H, CH(CH₃)₂); 0.78, 0.74 (s, 3H each, Si(CH₃)₂); 0.52 (s, 6H each, Si(CH₃)₂); 0.43–0.42 (s, 15H, Si(CH₃)₂ and Si(CH₃)₃); 0.07, 0.02

(s, 3H each, Si(CH₃)₂). IR (neat): ν (Si=C) 1159 (s) cm⁻¹. HRMS: calcd for [C₃₉H₈₆O_{Si₉}]⁺⁺ (M⁺), 822.4602; found, 822.4610.

Synthesis of 6. A 500 mg portion (0.74 mmol) of **1b** was dissolved in 20 mL of DME and cooled to -30°C , and 175 mg (1.60 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ²⁹Si NMR showed that the dianionic species **2b** was completely formed. Subsequently, the reaction mixture was cooled to -30°C and 146 mg (0.74 mmol) of ClSiMe₂SiMe₂Cl was added dropwise. The red solution immediately turned colorless. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na₂SO₄ and the solvent was stripped off with a rotary evaporator. Drying under vacuum and crystallization from acetone solution at -30°C afforded 454 mg (95%) of the analytically pure acylbicyclo[2.2.2]octasilane **6** as colorless crystals.

Data for **6** are as follows. Mp: 242–244 $^\circ\text{C}$. Anal. Calcd for C₂₆H₆₀O_{Si₉}: C, 48.68; H, 9.43. Found: C, 48.75; H, 9.55. ²⁹Si NMR (C₆D₆, TMS, ppm): -6.11 (SiMe₃); -37.79 – -38.37 (SiMe₂); -77.76 (SiC=O); -131.12 (Si(q)). ¹³C NMR (C₆D₆, TMS, ppm): 246.07 (C=O); 51.15 (Ad-C-CO); 37.43, 37.10 (Ad-CH₂); 28.57 (Ad-CH); 3.75 (Si(CH₃)₃); -0.79 , -1.31 (Si(CH₃)₂). ¹H NMR (CDCl₃, TMS, ppm): 1.95, 1.80, 1.64 (15H, Ad-H); 0.50, 0.39 (18H each, s, Si(CH₃)₂); 0.31 (9H, s, Si(CH₃)₃). IR (neat): ν (C=O) 1618 (m) cm⁻¹. HRMS: calcd for [C₂₆H₆₀O_{Si₉}]⁺⁺ (M⁺), 640.2568; found, 640.2590.

Synthesis of 7. A 500 mg portion (0.67 mmol) of **3a** was dissolved in 20 mL of DME and cooled to -30°C , and 158 mg (1.41 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ²⁹Si NMR showed that the dianionic species **4a** was completely formed. Subsequently, the reaction mixture was cooled to -30°C and 272 mg (1.41 mmol) of ClSiPr₃ was added dropwise. The red solution immediately turned yellow. After removal of the volatile components under vacuum, the remaining yellow solid was dissolved in heptane, the solution was filtered through dry Celite, and the solvent was stripped off again. Recrystallization from Et₂O afforded 558 mg (91%) of the analytically pure germene **7** as yellow crystals.

Data for **7** are as follows. Mp: 108–110 $^\circ\text{C}$. Anal. Calcd for C₃₉H₈₆Ge₂O_{Si₇}: C, 51.31; H, 9.50. Found: C, 51.45; H, 9.70. ²⁹Si NMR (C₆D₆, TMS, ppm): -4.38 (SiMe₃); -23.98 , -24.83 , -29.76 , -30.03 (SiMe₂). ¹³C NMR (C₆D₆, TMS, ppm): 210.17 (Ge=C); 145.26, 137.00, 135.80, 135.67, 128.82 (Aryl-C); 21.57, 21.53 (Aryl-CH₃); 20.75, 18.51 (CH(CH₃)₂); 15.63, 14.12 (CH(CH₃)₂); 5.74 (Si(CH₃)₃); 1.41, 1.14, 1.05, 1.00, 0.11, -1.34 , -1.36 , -1.51 (Si(CH₃)₂). ¹H NMR (C₆D₆, TMS, ppm): 6.79 (s, 2 H, Mes-H); 2.62 (s, 6H, Mes-CH₃); 2.13 (s, 3H, Mes-CH₃); 1.38–1.07 (m, 42H, CH(CH₃)₂); 0.84, 0.82 (s, 3H each, Si(CH₃)₂); 0.56 (s, 6H each, Si(CH₃)₂); 0.46–0.45 (s, 15H, Si(CH₃)₂ and Si(CH₃)₃); 0.14, 0.12 (s, 3H each, Si(CH₃)₂). IR (neat): ν (Si=C) 1245 (s) cm⁻¹. HRMS: calcd for [C₃₉H₈₆Ge₂O_{Si₇}]⁺⁺ (M⁺), 914.3503; found, 914.3509.

Synthesis of 8. A 500 mg portion (0.66 mmol) of **3b** was dissolved in 20 mL of DME and cooled to -30°C , and 155 mg (1.38 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ²⁹Si NMR showed that the dianionic species **4b** was completely formed. Subsequently, the reaction mixture was cooled to -30°C and 123 mg (0.66 mmol) of ClSiMe₂SiMe₂Cl was added dropwise. The red solution immediately turned colorless. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na₂SO₄ and the solvent was stripped off with a rotary evaporator. Drying under vacuum and subsequent NMR measurement showed complete degradation to an uncharacterizable polymer.

Synthesis of 1c. A 500 mg portion (0.74 mmol) of **1b** was dissolved in 20 mL of DME and cooled to -30°C , and 175 mg (1.60 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ²⁹Si NMR

showed that the dianionic species **2b** was completely formed. Subsequently, the reaction mixture was cooled to $-30\text{ }^{\circ}\text{C}$ and 287 mg (1.49 mmol) of ClSiPr_3 was added dropwise. The red solution immediately turned colorless. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na_2SO_4 and the solvent was stripped off with a rotary evaporator. Drying under vacuum and subsequent NMR measurement showed complete degradation to an uncharacterizable polymer.

Synthesis of 4c. A 500 mg portion (0.66 mmol) of **3b** was dissolved in 20 mL of DME and cooled to $-30\text{ }^{\circ}\text{C}$, and 155 mg (1.38 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ^{29}Si NMR showed that the dianionic species **4b** was completely formed. Subsequently, the reaction mixture was cooled to $-30\text{ }^{\circ}\text{C}$ and 267 mg (1.38 mmol) of ClSiPr_3 was added dropwise. The red solution immediately turned colorless. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na_2SO_4 and the solvent was stripped off with a rotary evaporator. Drying under vacuum and subsequent NMR measurement showed complete degradation to an uncharacterizable polymer.

Synthesis of 9a. A 500 mg portion (0.76 mmol) of **1a** was dissolved in 20 mL of DME and cooled to $-30\text{ }^{\circ}\text{C}$, and 180 mg (1.60 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ^{29}Si NMR showed that the dianionic species **2a** was completely formed. Subsequently, the reaction mixture was cooled to $-30\text{ }^{\circ}\text{C}$ and an excess of MeI was added dropwise. The red solution immediately turned yellow. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na_2SO_4 and the solvent was stripped off with a rotary evaporator. Drying under vacuum afforded 366 mg (89%) of the analytically pure cyclic acylsilane **9a** as a *cis/trans* mixture. The obtained product was recrystallized from acetone, giving yellow crystals of one isomer. Yield: 144 mg (35%) of analytically pure **9a** (isomer 1).

Data for **9a** (isomer 1) are as follows. Mp: $124\text{--}126\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{23}\text{H}_{50}\text{OSi}_7$: C, 51.23; H, 9.35. Found: C, 51.25; H, 9.45. ^{29}Si NMR (CDCl_3 , TMS, ppm): -11.81 (SiMe_3); -40.48 to -40.64 (SiMe_2); -46.77 ($\text{SiC}=\text{O}$); -84.85 ($\text{Si}(\text{Me})$). ^{13}C NMR (CDCl_3 , TMS, ppm): 251.92 ($\text{C}=\text{O}$); 144.75, 137.94, 131.65, 128.82 (Aryl-C); 21.21, 19.48 (Aryl- CH_3); 1.22 ($\text{Si}(\text{CH}_3)_3$); -3.00 , -4.07 , -4.87 , -5.67 ($\text{Si}(\text{CH}_3)_2$); -11.24 (SiCH_3). ^1H NMR (CDCl_3 , TMS, ppm): 6.78 (s, 2 H, Mes-H); 2.26 (s, 3H, Mes- CH_3); 2.14 (s, 6H, Mes- CH_3); 0.29, 0.24, 0.18, 0.17 (s, 6H each, $\text{Si}(\text{CH}_3)_2$); 0.19 (s, 9H each, $\text{Si}(\text{CH}_3)_3$); 0.30, 0.15 (s, 3H each, $\text{Si}(\text{CH}_3)_3$). HRMS: calcd for $[\text{C}_{23}\text{H}_{50}\text{OSi}_7]^{*+}$ (M^+), 538.2247; found, 538.2249.

Data for **9a** (isomer 2) are as follows. ^{29}Si NMR (C_6D_6 , TMS, ppm): -12.48 (SiMe_3); -41.59 to -42.55 (SiMe_2); -46.69 ($\text{SiC}=\text{O}$); -86.18 ($\text{Si}(\text{Me})$). ^{13}C NMR (CDCl_3 , TMS, ppm): 251.86 ($\text{C}=\text{O}$).

Synthesis of 9b. A 500 mg portion (0.74 mmol) of **1b** was dissolved in 20 mL of DME and cooled to $-30\text{ }^{\circ}\text{C}$, and 175 mg (1.60 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ^{29}Si NMR showed that the dianionic species **2b** was completely formed. Subsequently, the reaction mixture was cooled to $-30\text{ }^{\circ}\text{C}$ and an excess of MeI was added dropwise. The red solution immediately turned colorless. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na_2SO_4 and the solvent was stripped off with a rotary evaporator. Drying under vacuum afforded 335 mg (81%) of the analytically pure cyclic acylsilane **9b** as a *cis/trans* mixture. Finally, this mixture of isomers was chromatographed on a precoated TLC SIL G-200 UV₂₅₄ plate, with toluene/heptane (1/5) as eluent, to separate both isomers. Yield: 145 mg (35%) of analytically pure **9b** (isomer 1). Yield: 103 mg (25%) of analytically pure **9b** (isomer 2).

Data for **9b** (isomer 1) are as follows. Mp: $180\text{--}183\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{24}\text{H}_{54}\text{OSi}_7$: C, 51.91; H, 9.80. Found: C, 51.82; H, 9.85.

^{29}Si NMR (CDCl_3 , TMS, ppm): -9.70 (SiMe_3); -38.87 to -39.75 (SiMe_2); -43.96 ($\text{SiC}=\text{O}$); -83.27 ($\text{Si}(\text{Me})$). ^{13}C NMR (CDCl_3 , TMS, ppm): 249.15 ($\text{C}=\text{O}$); 51.93 (Ad-C-CO); 36.95, 36.80 (Ad- CH_2); 28.17 (Ad-CH); 1.08 ($\text{Si}(\text{CH}_3)_3$); -3.40 , -4.42 , -4.39 , -4.57 ($\text{Si}(\text{CH}_3)_2$); -4.02 , -11.21 (SiCH_3). ^1H NMR (CDCl_3 , TMS, ppm): 2.04, 1.71, 1.70 (15H, Ad-H); 0.29 (6H each, s, $\text{Si}(\text{CH}_3)_2$); 0.23, 0.19, 0.17, 0.15, 0.13 (24H, s, $\text{Si}(\text{CH}_3)_2$ and $\text{Si}(\text{CH}_3)_3$); 0.55, 0.11 (s, 3H each, $\text{Si}(\text{CH}_3)_3$). HRMS: calcd for $[\text{C}_{24}\text{H}_{54}\text{OSi}_7]^{*+}$ (M^+), 554.2560; found, 554.2566.

Data for **9b** (isomer 2) are as follows. Anal. Calcd for $\text{C}_{24}\text{H}_{54}\text{OSi}_7$: C, 51.91; H, 9.80. Found: C, 51.96; H, 9.89. ^{29}Si NMR (CDCl_3 , TMS, ppm): -9.70 (SiMe_3); -38.85 to -39.72 (SiMe_2); -43.93 ($\text{SiC}=\text{O}$); -83.21 ($\text{Si}(\text{Me})$). ^{13}C NMR (CDCl_3 , TMS, ppm): 249.12 ($\text{C}=\text{O}$); 51.94 (Ad-C-CO); 36.97, 36.82 (Ad- CH_2); 28.19 (Ad-CH); 1.08 ($\text{Si}(\text{CH}_3)_3$); -3.40 , -4.22 , -4.39 , -4.57 ($\text{Si}(\text{CH}_3)_2$); -4.00 , -11.21 (SiCH_3). ^1H NMR (CDCl_3 , TMS, ppm): 2.05, 1.70 (15H, Ad-H); 0.29 (6H each, s, $\text{Si}(\text{CH}_3)_2$); 0.19, 0.17, 0.15, 0.14 (27H, s, $\text{Si}(\text{CH}_3)_2$ and $\text{Si}(\text{CH}_3)_3$); 0.55, 0.11 (s, 3H each, $\text{Si}(\text{CH}_3)_3$). HRMS: calcd for $[\text{C}_{24}\text{H}_{54}\text{OSi}_7]^{*+}$ (M^+), 554.2560; found, 554.2568.

Synthesis of 10a. A 500 mg portion (0.67 mmol) of **3a** was dissolved in 20 mL of DME and cooled to $-30\text{ }^{\circ}\text{C}$, and 158 mg (1.41 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ^{29}Si NMR showed that the dianionic species **4a** was completely formed. Subsequently, the reaction mixture was cooled to $-30\text{ }^{\circ}\text{C}$ and an excess of MeI was added dropwise. The red solution immediately turned yellow. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na_2SO_4 and the solvent was stripped off with a rotary evaporator. Drying under vacuum afforded 392 mg (93%) of the analytically pure cyclic acylgermane **10a** as a *cis/trans* mixture.

Data for **10a** (*cis/trans* mixture) are as follows. Mp: $134\text{--}138\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{23}\text{H}_{50}\text{Ge}_2\text{OSi}_5$: C, 43.97; H, 8.02. Found: C, 43.85; H, 8.05. ^{29}Si NMR (CDCl_3 , TMS, ppm): -2.84 to -3.78 (SiMe_3); -29.19 to -31.29 to -30.96 , -32.06 (SiMe_2). ^{13}C NMR (CDCl_3 , TMS, ppm): 250.52 ($\text{C}=\text{O}$); 145.12/144.47, 137.75, 131.03/130.84, 128.71 (Aryl-C); 21.18, 19.30 (Aryl- CH_3); 1.95/1.74 ($\text{Si}(\text{CH}_3)_3$); -2.19 to -2.60 , -3.47 to -3.42 , -3.95 to -3.92 , -4.86 to -4.13 , ($\text{Si}(\text{CH}_3)_2$); -5.25 to -5.99 , -11.78 to -12.17 (GeCH_3). ^1H NMR (CDCl_3 , TMS, ppm): 6.78 (s, 2 H, Mes-H); 2.27 (s, 3H, Mes- CH_3); 2.15 (s, 6H, Mes- CH_3); 0.41, 0.39, 0.35, 0.32, 0.29, 0.27, 0.26, 0.25, 0.23 (s, 39H each, $\text{Si}(\text{CH}_3)_2$, $\text{Si}(\text{CH}_3)_3$ and $\text{Ge}(\text{CH}_3)$). HRMS: calcd for $[\text{C}_{23}\text{H}_{50}\text{Ge}_2\text{OSi}_5]^{*+}$ (M^+), 630.1132; found, 628.1140.

Synthesis of 10b. A 500 mg portion (0.66 mmol) of **3b** was dissolved in 20 mL of DME and cooled to $-30\text{ }^{\circ}\text{C}$, and 155 mg (1.38 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ^{29}Si NMR showed that the dianionic species **4b** was completely formed. Subsequently, the reaction mixture was cooled to $-30\text{ }^{\circ}\text{C}$ and an excess of MeI was added dropwise. The red solution immediately turned colorless. After aqueous workup with 10 mL of 3% sulfuric acid, the organic layer was separated and dried over Na_2SO_4 and the solvent was stripped off with a rotary evaporator. Drying under vacuum afforded 360 mg (85%) of the analytically pure cyclic acylgermane **10b** as a *cis/trans* mixture. Finally, this mixture of isomers was chromatographed on a precoated TLC SIL G-200 UV₂₅₄ plate, with toluene/heptane (1/5) as eluent, to separate both isomers. Yield: 80 mg (29%) of analytically pure **10b** (isomer 1). Yield: 60 mg (14%) of analytically pure **10b** (isomer 2).

Data for **10b** (isomer 1) are as follows. Mp: $173\text{--}178\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{24}\text{H}_{54}\text{Ge}_2\text{OSi}_5$: C, 44.74; H, 8.45. Found: C, 44.90; H, 8.52. ^{29}Si NMR (CDCl_3 , TMS, ppm): -3.63 (SiMe_3); -31.45 to -31.79 (SiMe_2). ^{13}C NMR (CDCl_3 , TMS, ppm): 247.31 ($\text{C}=\text{O}$); 52.14 (Ad-C-CO); 37.00, 36.95 (Ad- CH_2); 28.23 (Ad-CH); 1.78 ($\text{Si}(\text{CH}_3)_3$); -2.47 , -3.30 , -3.46 , -4.06 ($\text{Si}(\text{CH}_3)_2$); -3.99 , -12.05 (GeCH_3). ^1H NMR (CDCl_3 , TMS, ppm): 2.05, 1.69 (m, 15H, Ad-H); 0.60 (3H, s, $\text{Ge}(\text{CH}_3)$); 0.33 (6H, s, $\text{Si}(\text{CH}_3)_2$); 0.23, 0.21 (m,

30H each, Si(CH₃)₂, Si(CH₃)₃ and Ge(CH₃). HRMS: calcd for [C₂₄H₅₄Ge₂OSi₅]^{•+} (M⁺), 646.1445; found, 644.1452.

Data for **10b** (isomer 2) are as follows. Anal. Calcd for C₂₄H₅₄Ge₂OSi₅: C, 44.74; H, 8.45. Found: C, 44.97; H, 8.59. ²⁹Si NMR (CDCl₃, TMS, ppm): -2.86 (SiMe₃); -29.53, -30.96 (SiMe₂). ¹³C NMR (CDCl₃, TMS, ppm): 247.73 (C=O); 52.57 (Ad-C-CO); 37.42, 37.37 (Ad-CH₂); 28.65 (Ad-CH); 2.21 (Si(CH₃)₃); -2.04, -2.87, -3.03, -3.63 (Si(CH₃)₂); -3.57, -11.63 (GeCH₃). ¹H NMR (CDCl₃, TMS, ppm): 2.06, 1.70 (15H, Ad-H), 0.49 (3H, s, Ge(CH₃)); 0.32, 0.28, 0.26, 0.23, 0.21 (36H, m, Si(CH₃)₂, Si(CH₃)₃ and Ge(CH₃)). HRMS: calcd for [C₂₄H₅₄Ge₂OSi₅]^{•+} (M⁺), 646.1445; found, 644.1442.

Competitive Reactivity of 1a. A 500 mg portion (0.76 mmol) of **1a** was dissolved in 20 mL of DME and cooled to -30 °C, and 180 mg (1.60 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ²⁹Si NMR showed that the dianionic species **2a** was completely formed. Subsequently, the reaction mixture was cooled to -30 °C and 83 mg (0.76 mmol) of ClSiMe₃ was added dropwise. The reaction mixture was warmed to room temperature and stirred for an additional 30 min. At this time, reaction control by NMR showed that the cyclic silenolate **S_{1a}** was completely formed.

Data for **S_{1a}** are as follows. ²⁹Si NMR (THF-*d*₈, TMS, ppm): -9.00 (SiMe₃); -29.61 to -36.72 (SiMe₂); -78.00 (SiC=O); -131.17 (Si(q)). ¹³C NMR (THF-*d*₈, TMS, ppm): 263.96 (C=O); 151.90, 132.71, 131.65, 127.38 (Aryl-C); 20.13, 20.10 (Aryl-CH₃); 3.42 (Si(CH₃)₃); -0.26, -1.17 (Si(CH₃)₂). ¹H NMR (THF-*d*₈, TMS, ppm): 6.62 (s, 2 H, Mes-H); 2.35 (s, 6H, Mes-CH₃); 2.16 (s, 3H, Mes-CH₃); 0.22 (18H, s, Si(CH₃)₃), 0.11, 0.10, 0.07, 0.05, 0.04 (24H, m, Si(CH₃)₂).

Competitive Reactivity of 1b. A 500 mg portion (0.74 mmol) of **1b** was dissolved in 20 mL of DME and cooled to -30 °C, and 175 mg (1.60 mmol) of KOtBu was added. After it was stirred for an additional 30 min, the mixture was warmed to room temperature and finally stirred for an additional 14 h. At this time, reaction control by ²⁹Si NMR showed that the dianionic species **2b** was completely formed. Subsequently, the reaction mixture was cooled to -30 °C and 81 mg (0.74 mmol) of ClSiMe₃ was added dropwise. The reaction mixture was warmed to room temperature and stirred for an additional 30 min. At this time, reaction control by NMR showed that **9** was completely formed. After aqueous workup with 100 mL of 3% sulfuric acid, the organic layer was separated and dried over Na₂SO₄ and the solvent was stripped off on a rotary evaporator. Finally, the crude material was chromatographed on a precoated TLC SIL G-200 UV₂₅₄ plate, with with heptane as eluent, to give 268 mg (60%) of **11**.

Data for **11** are as follows. Mp: 218–222 °C. Anal. Calcd for C₂₅H₅₈OSi₈: C, 50.09; H, 9.75. Found: C, 50.17; H, 9.68. ²⁹Si NMR (C₆D₆, TMS, ppm): 8.57 (OSiMe₂); 6.81 (Siq-OSiMe₂); -7.36, -16.85 (SiMe₃); -39.43, -43.33, -48.13 (SiMe₂); -79.34 (Siq). ¹³C NMR (C₆D₆, TMS, ppm): 47.01, 37.53, 36.50, 29.49 (Ad-C); 35.34 (CH-Ad); 2.91, 0.32 (Si(CH₃)₃); 3.15, 2.55, -1.25, -2.27, -2.34, -2.70, -5.52, -6.55 (Si(CH₃)₂). ¹H NMR (CDCl₃, TMS, ppm): 1.97–1.58 (m, 16H, Ad-H and CH-Ad); 0.49, 0.42, 0.39, 0.36, 0.28, 0.26, 0.25, 0.17 (s, 3H each, Si(CH₃)₂); 0.34, 0.32 (s, 9H each, Si(CH₃)₃). HRMS: calcd for [C₂₅H₅₈OSi₈]^{•+} (M⁺), 598.2642; found, 598.2646.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00385>.

NMR spectra, crystallographic details, and computational section (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 1964268–1964270 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Michael Haas – Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria; orcid.org/0000-0002-9213-940X; Email: michael.haas@tugraz.at

Authors

Tanja Wiesner – Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria

Mario Leybold – Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria

Anja Steinmaurer – Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria

Dominik Schnalzer – Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria

Roland C. Fischer – Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria; orcid.org/0000-0001-9523-5010

Ana Torvisco – Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria; orcid.org/0000-0002-6203-7330

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00385>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the FWF (Wien, Austria) for financial support (project number P32606-N).

■ REFERENCES

- (1) Miller, R. D.; Michl, J. Polysilane high polymers. *Chem. Rev.* **1989**, *89*, 1359–1410.
- (2) West, R. The polysilane high polymers. *J. Organomet. Chem.* **1986**, *300*, 327–346.
- (3) West, R. Organopolysilanes. In *Comprehensive Organometallic Chemistry II*; Elsevier: 1995; pp 77–110.
- (4) Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. Aluminum chloride catalyzed skeletal rearrangement of permethylated acyclic polysilanes. *J. Am. Chem. Soc.* **1981**, *103*, 4845–4850.
- (5) Jarvie, A. W. P.; Winkler, H. J. S.; Peterson, D. J.; Gilman, H. Preparation and Characterization of Octaphenylcyclotetrasilane. *J. Am. Chem. Soc.* **1961**, *83*, 1921–1924.
- (6) Gilman, H.; Tomasi, R. A. Synthesis of a Nonasilane. *Chem. Ind.* **1963**, 954.
- (7) Hengge, E.; Wolfer, D. Darstellung und eigenschaften von heterocyclischen silanen des typs Si4X Mit X = B, N, O. *J. Organomet. Chem.* **1974**, *66*, 413–424.
- (8) Becker, G.; Hartmann, H.-M.; Hengge, E.; Schrank, F. Molekül- und Kristallstruktur des 1,4-Bis[tris(tetrahydrofuran)lithium]-octaphenyltetrasilans. *Z. Anorg. Allg. Chem.* **1989**, *572*, 63–74.
- (9) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. An Unexpected Reaction of Silacyclopropene To Form an Organodilithiosilane: Isolation and Characterization of a 1,1-Dilithiosilane Derivative. *J. Am. Chem. Soc.* **1999**, *121*, 10231–10232.

- (10) Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. Generation and Reactions of an Overcrowded Diaryldilithiosilane. *Chem. Lett.* **1999**, *28*, 931–932.
- (11) Kira, M.; Iwamoto, T.; Yin, D.; Maruyama, T.; Sakurai, H. Novel 1,2-Dilithiodisilanes Derived from Reduction of Stable Tetrakis(trialkylsilyl)disilenes with Lithium Metal. *Chem. Lett.* **2001**, *30*, 910–911.
- (12) Apeloig, Y.; Korogodsky, G.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. The Syntheses and Molecular Structure of a Branched Oligosilyl Anion with a Record of Nine Silicon Atoms and of the First Branched Oligosilyl Dianion. *Eur. J. Inorg. Chem.* **2000**, *2000*, 1091–1095.
- (13) Marschner, C. A New and Easy Route to Polysilylanylpotassium Compounds. *Eur. J. Inorg. Chem.* **1998**, *1998*, 221–226.
- (14) Kayser, C.; Kickelbick, G.; Marschner, C. Simple Synthesis of Oligosilyl- α,ω -dipotassium Compounds. *Angew. Chem., Int. Ed.* **2002**, *41*, 989–992.
- (15) Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. Tailor-made Oligosilyl Potassium Compounds. *Organometallics* **2002**, *21*, 1023–1030.
- (16) Fischer, R.; Konopa, T.; Ullly, S.; Baumgartner, J.; Marschner, C. Route Si6 revisited. *J. Organomet. Chem.* **2003**, *685*, 79–92.
- (17) Marro, E. A.; Press, E. M.; Purkait, T. K.; Jimenez, D.; Siegler, M. A.; Klausen, R. S. Cooperative Noncovalent Interactions Induce Ion Pair Separation in Diphenylsilanides. *Chem. - Eur. J.* **2017**, *23*, 15633–15637.
- (18) Press, E. M.; Marro, E. A.; Surampudi, S. K.; Siegler, M. A.; Tang, J. A.; Klausen, R. S. Synthesis of a Fragment of Crystalline Silicon: Poly(Cyclosilane). *Angew. Chem., Int. Ed.* **2017**, *56*, 568–572.
- (19) Purkait, T. K.; Press, E. M.; Marro, E. A.; Siegler, M. A.; Klausen, R. S. Low-Energy Electronic Transition in SiB Rings. *Organometallics* **2019**, *38*, 1688–1698.
- (20) Marro, E. A.; Folster, C. P.; Press, E. M.; Im, H.; Ferguson, J. T.; Siegler, M. A.; Klausen, R. S. Stereocontrolled Syntheses of Functionalized cis- and trans-Siladecalins. *J. Am. Chem. Soc.* **2019**, *141*, 17926–17936.
- (21) Heider, Y.; Willmes, P.; Huch, V.; Zimmer, M.; Scheschkewitz, D. Boron and Phosphorus Containing Heterosiliconoids: Stable p- and n-Doped Unsaturated Silicon Clusters. *J. Am. Chem. Soc.* **2019**, *141*, 19498–19504.
- (22) Haas, M.; Knoechl, A.; Wiesner, T.; Torvisco, A.; Fischer, R.; Jones, C. Attempted Synthesis of a Homocyclic Bis(silyl)silylene Leads to the Formation of a Tricyclo[3,1,1,1 2,4]octasilane. *Organometallics* **2019**, *38*, 4158–4170.
- (23) Haas, M.; Fischer, R.; Flock, M.; Mueller, S.; Rausch, M.; Saf, R.; Torvisco, A.; Stueger, H. Stable Silenolates and Brook-Type Silenes with Exocyclic Structures. *Organometallics* **2014**, *33*, 5956–5959.
- (24) Haas, M.; Leypold, M.; Schnalzer, D.; Torvisco, A.; Stueger, H. Stable Germenolates and Germenes with Exocyclic Structures. *Organometallics* **2015**, *34*, 5291–5297.
- (25) Reichardt, C.; Welton, T. *Solvents and solvent effects in organic chemistry*, 4th updated and enlarged ed.; Wiley-VCH: Weinheim, Germany, 2011.
- (26) A conformational analysis was performed on related silenolates and showed an energetic distribution: chair (60%) vs boat (40%). See ref 27.
- (27) Haas, M.; Leypold, M.; Schuh, L.; Fischer, R.; Torvisco, A.; Stueger, H. Reactivity of Cyclic Silenolates Revisited. *Organometallics* **2017**, *36*, 3765–3773.
- (28) Ohshita, J.; Masaoka, S.; Masaoka, Y.; Hasebe, H.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. Silicon–Carbon Unsaturated Compounds. 55. Synthesis and Reactions of Lithium Silenolates, Silicon Analogs of Lithium Enolates. *Organometallics* **1996**, *15*, 3136–3146.
- (29) Ohshita, J.; Masaoka, S.; Morimoto, Y.; Ishikawa, M. Reactions of Lithium Silenolates with Carbonyl Compounds. *Organometallics* **1997**, *16*, 910–917.
- (30) Stueger, H.; Hasken, B.; Gross, U.; Fischer, R.; Torvisco Gomez, A. Synthesis and Properties of Bridgehead-Functionalized Permethylbicyclo2.2.2octasilanes. *Organometallics* **2013**, *32*, 4490–4500.
- (31) Biltueva, I. S.; Bravo-Zhivotovskii, D. A.; Kalikhman, I. D.; Vitkovskii, V. Y.; Shevchenko, S. G.; Vyazankin, N. S.; Voronkov, M. G. Sila- and germa-enolate anions. The reaction of acylgermanes with triethylgermyllithium. *J. Organomet. Chem.* **1989**, *368*, 163–165.
- (32) Guliashvili, T.; El-Sayed, I.; Fischer, A.; Ottosson, H. The first isolable 2-silenolate. *Angew. Chem., Int. Ed.* **2003**, *42*, 1640–1642.
- (33) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.