Synthesis of Stable Dianionic Cyclic Silenolates and Germenolates
Tanja Wiesner, Mario Leypold, Anja Steinmaurer, Dominik Schnalzer, Roland C. Fischer, Ana Torvisco, and Michael Haas*

ABSTRACT: In this contribution a convenient synthetic method to obtain the previously unknown dianionic cyclic silenolates and germenolates 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 ClSiIP₃ to give new examples of polysilanes and polygermanes with exocyclic double bonds. The reaction of 2b with ClSiMe₅SiMe₅Cl 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 ClSiMe₃ showed that the outcome of the reaction was strongly influenced by the substituent at the carbonyl moiety. 2a reacted with 1 equiv of ClSiMe₃ to give the corresponding cyclic silenolate 5a, which demonstrated that the silyl anion is more nuclophilic than the silenolate with attached aromatic groups. 2b, on the other hand, reacted with 1 equiv of ClSiMe₃ to give the bicyclic compound 11 via an intramolecular sila-Peteron alkene 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.

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 or Lewis acid catalyzed rearrangement reactions. 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 multi-functionalized starting materials such as α,ω-dianions. Gilman and Hengge were pioneers in this area and developed the cleavage of strained cyclosilanes to obtain dianions. Sekiguchi, Tokitoh, Kira, and Apeloig 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. Recently, Klausen and co-workers established new phenyl-substituted dianions. These dianions were used as building blocks for the formation of defined polysilanes as well as for the synthesis of heteroatom substituted polysilanes. 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. 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). 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

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

**RESULTS AND DISCUSSION**

**Synthesis of Dianionic Silenolates.** The reaction of the acyclocyclohexasilanes 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, Et₂O, 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,ω-oligosilyl diions by Marschner et al., 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 S1a,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 Et₂O/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 °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.

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. Furthermore, we could show that the reaction of these enolates with chlorosilanes ClSiR₃ allowed straightforward access to silenes and germenes with exocyclic structures. 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.
adopt chair conformations. Additionally, 2a shows short Si(2)−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 Si−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 Et2O/18-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 germyl anion (keto form) with a Ge−C single bond, a C=O double bond, and markedly pyramidal central Ge(1) and 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 13C chemical shifts were observed for the carbonyl C atom of the two compounds 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 SiMe2 resonance lines in the 29Si NMR, which clearly suggest free rotation around the Si(1)−C(1) bond (Table 3). It was not possible to use THF-d8 for 2b and 4b because a detectable degradation was found within minutes at room temperature.

Table 1. Selected Bond Lengths d (Å) and Sum of Valence Angles \( \sum \alpha \) (deg) for 2a,b

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

Table 2. Selected Bond Lengths d (Å) and Sum of Valence Angles \( \sum \alpha \) (deg) for 4b

|      |      |
|------|------|
| \( d(Ge(1)−C(1)) \)  | 2.047 |
| \( d(Ge(1)−K(1)) \)  | 3.427 |
| \( d(C(1)−K(1)) \)  | 3.335 |
| \( d(C(1)−O(1)) \)  | 1.248 |
| \( d(K(1)−O(1)) \)  | 2.760 |
| \( d(Ge(2)−K(2)) \)  | 3.635 |
| \( d(Ge(1)−K(2)) \)  | 6.671 |
| \( \sum \alpha Ge(1) \) | 314.5° |
| \( \sum \alpha Ge(2) \) | 298.2° |
| \( \sum \alpha C(1) \) | 359.6° |
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.\textsuperscript{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.\textsuperscript{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 S1a,b and germenolates S2a,b.\textsuperscript{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 pπ 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 pπ 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 pπ 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.

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

\[
\begin{array}{cccc|cccc}
\hline
 & \text{2} & \text{3} & \text{4} & \text{5} & \text{6} & \text{7} & \text{8} \\
\hline
\delta_{\text{C(=O)}}(\text{C=O}) & 266.63 & 273.96 & 281.01 & 280.92 & 260.39 & 269.76 & 277.79 \\
\delta_{\text{Si(Me2)}}(\text{SiMe2}) & 0.05 & -1.14 & 0.93 & 0.36 & 2.24 & 3.37 & 4.50 \\
\delta_{\text{Si(SiMe2)}}(\text{SiMe2}) & -27.69 & -26.48 & -27.69 & -23.45 & -25.40 & -25.40 & -25.40 \\
\delta_{\text{Si(Si)}}(\text{Si}) & -67.70 & -87.33 & -29.35 & -27.69 & -25.40 & -25.40 & -25.40 \\
\delta_{\text{Si(O)}}(\text{O}) & -189.08 & -192.42 & -25.40 & -23.45 & -25.40 & -25.40 & -25.40 \\
\hline
\end{array}
\]

\(a,b\) values relative to external TMS. \(b\) In THF-d8 at 25 °C. \(c\) In C6D6 at 25 °C.

**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.\textsuperscript{15,16,23,28,29} Thus, 2b with an alkyl group attached to the carbonyl moiety reacted with an equimolar amount of tetramethyldichlorodisilane (C8SiMe2Cl2) 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 acylosilane 6 exhibits two 29Si resonance lines for the SiMe2.
observed for germenate and germyl anions.24,31 The chlorosilanes was investigated and parallels that previously reasoned that ClSi$_2$ and gave also rise to an undefined polymer. Therefore, we reasoned that ClSiP$_3$ is too sterically demanding to allow $M$–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 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 $9$a were obtained as cis/trans mixtures. The silicon atoms of $9$a,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 silane is more nucleophilic, the silyl anion or the silenolates. Therefore, we

| Compound | $\lambda_{\text{max}, \exp}$ (nm) | $\varepsilon$ (1 mol$^{-1}$ cm$^{-1}$) | $\lambda_{\text{max}, \text{calc}}$ (nm) | $f$ |
|----------|----------------------------------|-----------------------------------|-----------------------------------|-----|
| 2a       | 450                              | 6602                             | 441                               | 0.2102 |
| 2b       | 433                              | 3730                             | 428                               | 0.1131 |
| 4a       | 447                              | 5753                             | 435                               | 0.1591 |
| 4b       | 420                              | 2178                             | 418                               | 0.0858 |

* $\lambda_{\text{max, calc}}$ values are corrected by a factor of 5% due to a consistent overestimation of excitation energies with CAM-B3LYP.
reacted 2a,b with 1 equiv of trimethylchlorosilane (ClSiMe$_3$) at $-30$ °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 equivmolar amount of ClSiMe$_3$ to form the cyclic silanol 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 carbamion 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. Analitical 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$_3$

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**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 germanenolates 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 ClSiPh$_2$ to give new examples of a polysilylaine and a polygermanene with an exocyclic double bond. The reaction of 2b with ClSiMe$_5$SiMeCl 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 alkylaation reactions at the negatively charged silicon and germaunium 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.

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**EXPERIMENTAL SECTION**

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system. ClSiMe$_3$ (99%), KOtBu (>98%), CICOMes (99%), CICOAd (98%) and 18-cr-6 (99%), were used without any further purification. $^1$H, $^{13}$C, and $^{29}$Si NMR spectra were recorded on a Varian INOVA 300 spectrometer in CD$_2$Cl$_2$ or CDCl$_3$ solutions and were referenced versus TMS using the internal $^1$H peak 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 apparatus. UV absorption spectra were recorded on a PerkinElmer Lambda 5 spectrometer.

**Synthesis of 2a.** A 500 mg portion of acyclocyclohexasilane 1a (0.76 mmol) and 423 mg of 18-cr-6 (1.60 mmol) were dissolved in 20 mL of Et$_2$O. The solution was then cooled to $-70$ °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$_2$O (3 × 5 mL). The yellow 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.

**Synthesis of 2b.** A 500 mg portion of acyclocyclohexasilane 1b (0.74 mmol) and 413 mg of 18-cr-6 (1.60 mmol) were dissolved in 20 mL of Et$_2$O. The solution was then cooled to $-70$ °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$_2$O (3 × 5 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.

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(−CH₂(CH₃O−)₂)−; 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-crown-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 KOBu 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 × 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 °C. Anal. Calc. for C₉₅H₂₈Ge₂O₆Si: C, 44.85; H, 7.70. Found: C, 44.96; H, 7.96. ²Si NMR (THF-δ, TMS, ppm): −0.93 (SiMe₃); −27.69, −29.35 (SiMe₆). ¹³C NMR (THF-δ, TMS, ppm): 281.01 (C=O); 154.14, 133.42, 121.23, 129.20, 128.57 (Ar); 71.19 (−CH₂(CH₃O−)₂); 21.35, 21.16 (Aryl-H); 8.86 (Si(CH₃)₃); 4.54, 1.93 (Si(CH₃)₂). ³¹P NMR (THF-δ, TMS, ppm): 5.34 (δ, 2H, Mes-H); 3.52 (s, 48H, −(−CH₂(CH₃O−)₂); 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-crown-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 KOBu 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 × 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 °C. Anal. Calc. for C₇₂H₂₀Ge₂O₄Si₂: C, 45.25; H, 7.92. Found: C, 45.30; H, 7.77. ²Si NMR (CD₂, TMS, ppm): 0.36 (SiMe₂); −23.45, −25.40 (SiMe₆). ¹³C NMR (CD₂, TMS, ppm): 280.92 (C=O); 70.16 ((−CH₂(CH₃O−)₂); 52.11 (Ad−C=O); 39.78, 38.43 (Ad−CH₂); 30.66 (Ad−H); 9.74 (−CH₂); 7.24 (−CH₃); 5.96, 4.23, 2.35 (Si(CH₃)₂). ³¹P NMR (CD₂, TMS, ppm): 3.35 (δ, 48H, −(−CH₂(CH₃O−)₂); 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 KOBu 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 Cl₂SiP₃ 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 °C. Anal. Calc. for C₃₀H₂₂Ge₂O₆Si₂: C, 56.86; H, 10.52. Found: C, 56.90; H, 10.25. ²⁹Si NMR (CD₂, TMS, ppm): 32.83 (Si=C); 13.15 (Si(Pr)); −9.07 (SiMe₆); −33.90, −34.19, −35.68, −35.84 (SiMe₂); −128.70 (Si(SiMe₆)(SiPr)). ¹³C NMR (CD₂, TMS, ppm): 199.38 (C=Si); 143.16, 137.21, 137.09, 136.92, 128.85 (Aryl-C); 21.50, 21.21 (Aryl-CH₂); 20.83, 18.54 (CH₂); 15.48, 14.18 (CH₃); 5.35 (Si(CH₃)₂); 0.95, 0.50, 0.36, −0.77, −0.92, −2.03, −2.36 (Si(CH₃)₃). ³¹P NMR (CD₂, 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)); 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 (cm⁻¹). HRMS: calc for [C₆H₄O₂Si₂]⁺ (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 KOBu 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 Cl₂SiMe₃SiMe₂Cl 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 KOBu 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 Cl₂SiMe₃SiMe₂Cl 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.
showed that the dianionic species 2b was completely formed. Subsequently, the reaction mixture was cooled to $-30\, ^\circ\text{C}$ and 287 mg (1.49 mmol) of C3SiPr5 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 4c.** A 500 mg portion (0.66 mmol) of 3b was dissolved in 20 mL of DME and cooled to $-30\, ^\circ\text{C}$, and 155 mg (1.38 mmol) of KOButBu 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 $-30\, ^\circ\text{C}$ and 267 mg (1.38 mmol) of ClSiPr2 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 9a.** A 500 mg portion (0.76 mmol) of 1a was dissolved in 20 mL of DME and cooled to $-30\, ^\circ\text{C}$, and 180 mg (1.60 mmol) of KOButBu 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 $-30\, ^\circ\text{C}$ 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 Na2SO4 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 acetonitrile, 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: 124–126 °C. Anal. Calc for C28H50O6Si7: C, 55.03; H, 9.35. Found: C, 55.07; H, 9.41. 29Si NMR (CDCl3, TMS, ppm): 6.78 (s, 2H, O-Mes); 11.78 (Si(CH3)2); 0.30, 0.15 (3H each, Si(C2H5)); HRMS: calcld for [C28H50O6Si7]+ (M+) 554.2560; found, 554.2560.

**Synthesis of 10a.** A 500 mg portion (0.66 mmol) of 3a was dissolved in 20 mL of DME and cooled to $-30\, ^\circ\text{C}$, and 158 mg (1.41 mmol) of KOButBu 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 $-30\, ^\circ\text{C}$ 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 Na2SO4 and the solvent was stripped off with a rotary evaporator. Drying under vacuum afforded 392 mg (93%) of the analytically pure cyclic acylsilane 10a as a cis/trans mixture. Yield: 103 mg (28%) of analytically pure 10a (isomer 1). 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: 173–178 °C. Anal. Calc for C28H50O6Si7: C, 55.03; H, 9.35. Found: C, 55.07; H, 9.41. 29Si NMR (CDCl3, TMS, ppm): –9.70 (SiMe3); –38.87 to –39.75 (SiMe3); –43.96 (Si(OEt)); –83.27 (Si(OMe)); 13C NMR (CDCl3, TMS, ppm): 249.15 (C=O); 51.94 (Ad-C-CH); 36.95, 36.80 (Ad-CH2); 28.17 (Ad-CH); 1.08 (Si(CH3)); –3.40, –4.42, –4.39, –4.57 (Si(CH3)); –4.02, –11.21 (Si(CH3)). 1H NMR (CDCl3, TMS, ppm): 2.04, 1.71, 1.70 (15H, Ad-H); 0.29 (6H each, Si(CH3)); 0.19, 0.17, 0.15, 0.13 (24H, s, Si(CH3)2 and Si(CH3)); 0.55, 0.11 (s, 3H each, Si(CH3)). HRMS: calcld for [C28H50O6Si7]+ (M+) 554.2560; found, 554.2560.
30H each, Si(CH₃)₃, Si(CH₂)₃, and Ge(CH₃)) and 1H NMR. HRMS: calcld for [C₂₇H₄₄Ge₂O₂Si₂]⁺ (M⁺), 646.1445; found, 644.1442.

For 10b (isomer 2) are as follows. Anal. Calcld for C₄₇H₇₄Ge₂O₂Si₅: 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=C) 52.57 (Ad-C=O); 37.42, 37.37 (Ad-CH₃); 28.65 (Ad-CH); 2.21 (Si(CH₃)); 0.26, 0.24, 0.23 (19H, m). ¹¹B NMR (CDCl₃, TMS, ppm): 2.06, 1.70 (15H, Ad-H), 0.49 (3H, s, Ge(CH₃)); 3.02, 2.87, 2.86, 2.85, 2.84 (16H, m). ¹³C NMR (CDCl₃, TMS, ppm): 151.90, 132.71, 131.65, 127.38 (Aryl-C); 20.13, 20.10 (Aryl-CH₃); 3.42 (Si(CH₃)); 0.26, −1.17 (Si(CH₃)); ¹⁹F NMR (THF-de, TMS, ppm): 0.02 (s, 7H, Mes-H); 2.35 (s, 6H, Mes-CH₃); 2.16 (s, 3H, Mes-CH₃); 0.22 (18H, s, Si(CH₃)); 0.11, 0.10, 0.07, 0.05, 0.04 (24H, m, Si(CH₃)).

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 KOBu 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 NMR showed that the cyclic silenolate 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 2a was completely formed.

Data for 2a are as follows. ²⁹Si NMR (THF-de, TMS, ppm): −9.00 (SiMe₃); −29.61 to −36.72 (SiMe₂); −78.00 (Si=C=O); −131.17 (Si(q)). ¹³C NMR (THF-de, TMS, ppm): 263.96 (C=C) 151.90, 132.71, 131.65, 127.38 (Aryl-C); 20.13, 20.10 (Aryl-CH₃); 3.42 (Si(CH₃)); −0.26, −1.17 (Si(CH₃)); ¹¹B NMR (THF-de, TMS, ppm): 0.02 (s, 7H, Mes-H); 2.35 (s, 6H, Mes-CH₃); 2.16 (s, 3H, Mes-CH₃); 0.22 (18H, s, Si(CH₃)); 0.11, 0.10, 0.07, 0.05, 0.04 (24H, m, Si(CH₃)).

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 KOBu 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 the cyclic silenolate 2b was completely formed.

Data for 2b are as follows. Mp: 218–222 °C. Anal. Calcld for C₃₄H₇₂Ge₂O₂Si₅: C, 49.09; H, 9.75. Found: C, 50.17; H, 9.66. ²⁹Si NMR (CD₂Cl₂, TMS, ppm): 8.57 (OSiMe₃); 6.81 (Siq-OSiMe₃); −7.36, −16.85 (SiMe₃); −39.43, −43.33, −48.13 (SiMe₂); −79.34 (Siq). ¹³C NMR (CD₂Cl₂, TMS, ppm): 47.01, 37.53, 36.50, 29.49 (Ad-C); 35.34 (CH-Ad); 2.91, 0.32 (Si(CH₃)); 3.15, 2.55, −1.25, −2.27, −2.34; −2.70, −5.52, −6.55 (Si(CH₃)); ¹¹B 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)); 0.34, 0.32 (s, 9H each, Si(CH₃)). HRMS: calcld for [C₂₇H₄₄Ge₂O₂Si₂]⁺ (M⁺), 646.1445; found, 644.1442.

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

Notes

The authors declare no competing financial interest.

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