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Sila-Peterson Reaction of Cyclic Silanides

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ABSTRACT: Sila-Peterson type reactions of the 1,4,4-tris-(trimethylsilyl)-1-metallooctamethylcyclohexasilanes $(Me_3Si)_2Si_6Me_8(SiMe_3)M$ (**2a**, M = Li; **2b**, M = K) with various ketones were investigated. The obtained products strongly depend on the nature of the ketone component. With 2-adamantanone **2a,b** afforded the moderately stable silene **3**. **3** is the first example of an Apeloig−Ishikawa−Oehme-type silene with the tricoordinate silicon atom incorporated into a cyclopolysilane framework and could be characterized by NMR and UV spectroscopy as well as by trapping reactions with water, methanol, and MeLi. The reaction of **2b** with aromatic ketones also follows a sila-Peterson type mechanism with formation of carbanionic species. With 1,2-diphenylcyclopropenone **2b** reacted by conjugate 1,4-addition to give a spirocyclic carbanion. In most cases the underlying reaction mechanism could be elucidated by the isolation and characterization of unstable intermediates and final products after proper derivatization.
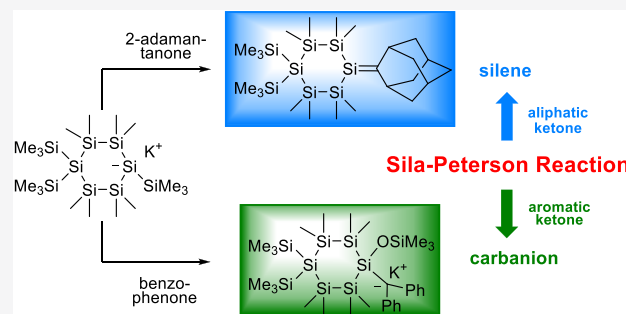
INTRODUCTION

The Peterson olefination reaction represents a useful methodology for the preparation of alkenes from α-silyl carbanions and carbonyl compounds.[1,2] A modified procedure, the sila-Peterson reaction, suitable for the preparation of silenes was established independently by Oehme,[3] Apeloig,[4] and Ishikawa.[5] The key step is a 1,2-elimination of silanolates from α-hydroxypolysilanes, made by the interaction of polysilyllithium compounds with aldehydes or ketones, under formation of silenes (Scheme 1).

Scheme 1. General Scheme of the Sila-Peterson Reaction
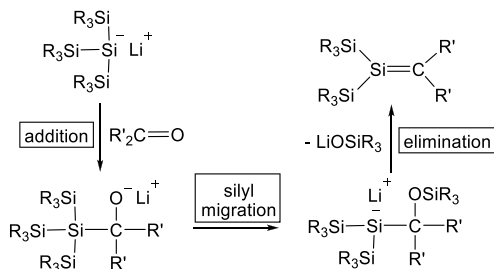
Most silenes formed by the sila-Peterson elimination mechanism (Apeloig−Ishikawa−Oehme-type silenes) are only transient species. They either can be trapped or undergo various types of subsequent decomposition reactions. For details on the synthesis and properties of silenes the reader is referred to the comprehensive review literature published on that topic.[6−12] In 1996 Apeloig et al. reported the synthesis of the persistent silene **I** (Chart 1) via a sila-Peterson type reaction from $(RMe_2Si)_3SiLi$ and 2-adamantanone.[13] Kira et al. applied the sila-Peterson reaction to prepare the first isolable silatriafulvene, **II**, showing reduced polarization of the Si−C double bond.[14] Related approaches were used later for the synthesis of the stable or metastable silenes **III−VI**.[15−18]

With only a few exceptions such as the sila-aromatic species[19,20] 1- and 2-silanaphthalene, 9-silaanthracene, 9-silaphenanthrene, and 1,2-disilabenzene or some three- and four-membered endocyclic silenes with Si−Si bonds,[21−24] most stable silenes described in the literature are acyclic molecules. Compounds with the coordinatively unsaturated silicon atoms incorporated into a cyclopolysilane ring were unknown before we reported the successful isolation and structural characterization of Brook-type methylenecyclohexasilanes **VII**[25] and endocyclic silenes **VIII** (Chart 2).[26,27]

In the course of our long-term studies of substituent effects on polysilane frameworks we now employed the sila-Peterson type reaction for the synthesis of methylenecyclohexasilanes structurally related to **VII**. In this paper we present the first successful synthesis of a moderately stable Apeloig−Ishikawa−Oehme-type silene with an exocyclic structure by the reaction of the cyclic silanides **2a,b** with 2-adamantanone. Furthermore,
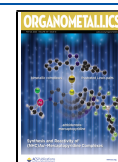
Chart 1. Stable or Metastable Silenes Prepared by Sila-Peterson Reactions

I
Apeloig 1996

II
Kira 2002

III
Apeloig 2003

IV
West 2004

V
Sekiguchi 2007

VI
Iwamoto 2014
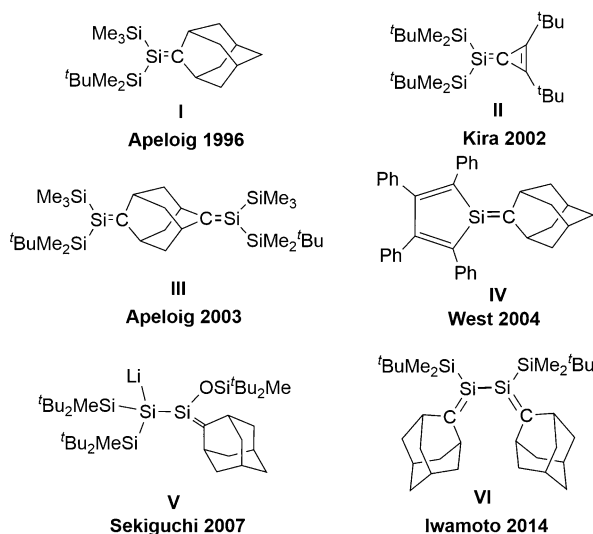
Chart 2. Stable Cyclopolysilanes with Exo- and Endocyclic Si−C Double Bonds (R = Mesityl, o-Tolyl, 1-Adamantyl)

VII

VIII

Stueger, Haas 2014, 2017
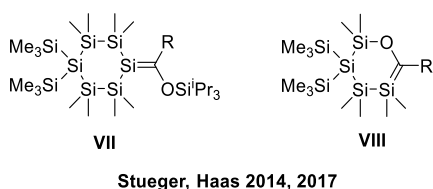
the effect of the substituents attached to the carbonyl function of the ketone on the course of the sila-Peterson reaction was studied and a significant effect of the substituents on the observed product distribution and reaction mechanisms was found.

■ RESULTS AND DISCUSSION

Synthesis and Reactivity of Silene 3. Scheme 2 summarizes the synthesis approach leading to the formation

of **3** along with the proposed synthetic intermediates and selected trapping reactions. The reaction of the cyclohexasilane **1** with either MeLi in THF (**2a**) or KO^{t}Bu in DME (**2b**) afforded the cyclic silanides **2a,b** in almost quantitative conversions. Analytical data obtained for the previously unknown **2a** (see the Experimental Section for details) are in accordance with the data published earlier for **2b**.[28] A strongly high field shifted ^{29}Si resonance signal for the anionic silicon at −184.4 ppm was found, confirming formation of the Li silanide **2a** (compare: $\delta(^{29}$Si) −186.3 ppm for the [K(18-crown-6)] complex of **2b**).

When **2a** and **2b**, dissolved in toluene, were slowly added to an equimolar amount of 2-adamantanone, orange solutions were obtained. NMR analysis performed after addition of Me$_3$SiCl to remove the formed MOSiMe$_3$ and filtration of the resulting MCl showed the exclusive formation of the silene **3**. The solvent exchange from THF or DME to toluene after the synthesis of the silanide played a crucial role in the outcome of the reaction. Otherwise, only unidentified decomposition products were formed. Surprisingly, no significant influence of the cation was found on the course of the reaction. Therefore, the slightly more easily accessible K-silanide **2b** was preferably used for the investigations presented below.

NMR analysis of the crude product showed only minor impurities (see Figures S4−S6 in the Supporting Information). Five resonance lines are present in the ^{29}Si NMR spectrum. The signals at $\delta(^{29}$Si) −131.7, −37.8, −37.6, and −8.7 ppm are easily assigned to the cyclohexasilane moiety by comparison with the corresponding values measured for compound **VII**.[25] ^{13}C and ^{29}Si signals characteristic of Si═C were observed at $\delta(^{29}$Si) 51.9 ppm and $\delta(^{13}$C) 197.7 ppm. These values excellently agree with those reported for Apeloig's acyclic silene **I** ($\delta(^{29}$Si) for Si═C 51.7 ppm/$\delta(^{13}$C{^{1}H}) for Si═C 196.8 ppm).[13] Relative to the Brook-type methylenecyclohexasilanes **VII** the chemical shifts of the tricoordinate carbon in **3** appears at considerably higher field by about 20 ppm, while the ^{29}Si resonance line of the unsaturated Si atom exhibits a downfield shift of 14.5 ppm. As pointed out earlier by Brook,[29] the siloxy group at the Si═C carbon of compound **VII** can be expected to contribute to deshielding of ^{13}C and shielding of
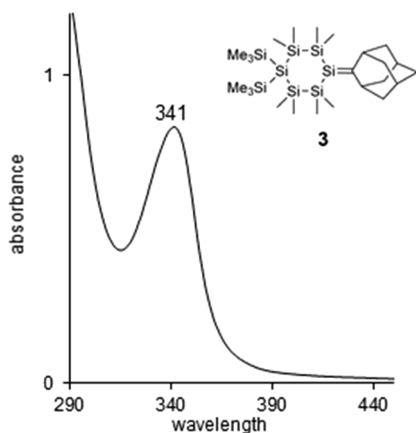
Scheme 2. Synthesis, Proposed Synthetic Intermediates, and Reactions of the Exocyclic Apeloig-Type Silene 3
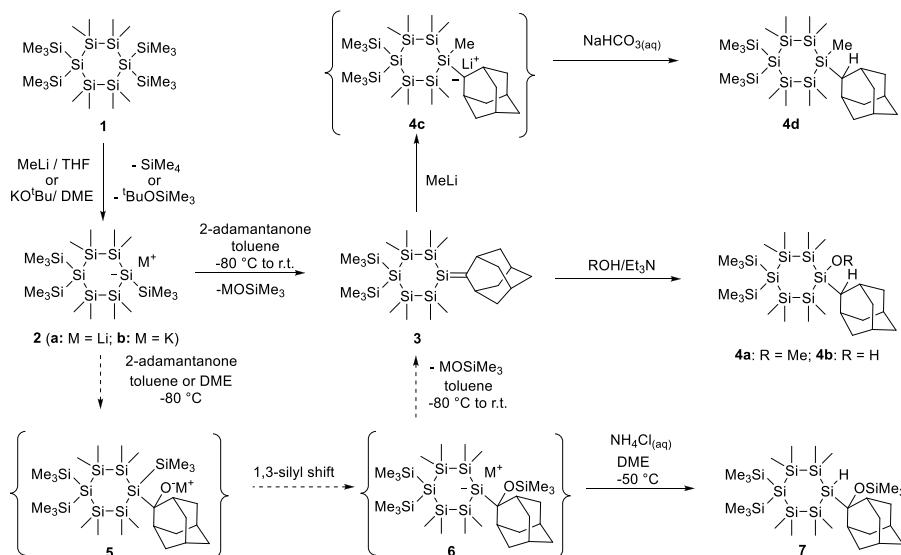
^{29}Si signals, if resonance contributions of the types shown in Chart 3 are important.

Chart 3. Possible Resonance Structures of Brook-Type Silenes
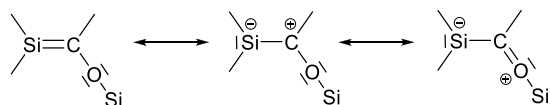
UV/vis measurements of silene **3** showed an absorption band centered at 341 nm (Figure 1), consistent with a $\pi-\pi^*$

Figure 1. UV−vis absorption spectrum of crude **3** (toluene, $c \approx 5 \times 10^{-4}$ mol L^{-1}).

transition of the Si=C double bond. This band is considerably red shifted with respect to the corresponding acyclic silene **I** (322 nm).[13] An analogous trend was observed in recent studies for the Brook-type silene $(Me_3Si)_2Si=C(O)Ad$ (339 nm)[30] and the related cyclic compound **VII** (362 nm)[31] and interpreted in terms of enhanced $\sigma(Si-Si)$ conjugation within the cyclic systems.[32]

Silene **3** is thermally only marginally stable. Storage of toluene or pentane solutions under inert gas at −70 °C for periods >12 h resulted in the formation of increasing amounts of unidentified polymeric material possibly due to incomplete steric protection of the Si=C double bond (compare Figure S7 in the Supporting Information). Attempts to isolate crystals of pure **3** at low temperature were also unsuccessful. It is interesting to note that there is no evidence for the formation of head-to-head dimers arising from thermally induced 2 + 2 cycloaddition reactions of **3** as observed by Apeloig et al. for the acyclic silene **I** (R = Me).[4] We assume that the cyclic structure of the polysilane backbone effectively inhibits dimerization of **3**.

To further prove the structural integrity of **3**, trapping experiments were performed. Addition of water or methanol, to which a trace of Et_3N had been added, to toluene solutions of **3** afforded the expected 1,2-adducts in form of the derivatives **4a,b** (Scheme 2). MeLi also adds to the Si=C bond in **3**. In this case the primary carbanionic addition product **4c** cleanly gave the methylcyclohexasilane **4d** after hydrolysis with an aqueous solution of $NaHCO_3$. In general, organolithium reagents add regiospecifically across Si=C double bonds, yielding a carbanion which subsequently can be protonated by hydrolysis.[33] All trapping products could be

isolated and completely characterized (compare the Experimental Section).

When the reaction of **2b** with 2-adamantanone was performed in DME at −80 °C and quenched by the addition of an aqueous NH_4Cl solution prior to warming to room temperature, compound **7** was obtained as the quenching product of the silanide **6** (Scheme 2). The structure of **7** was verified by spectroscopic analysis (see the Experimental Section). The ^{29}Si NMR spectrum shows a characteristic resonance line at 7.0 ppm typical for the formed $OSiMe_3$ moiety. The Si−H signal in the proton spectrum appears at $\delta(^1H)$ 3.89 ppm. Compound **3** thus, is formed through intermediate **5**, which immediately rearranges by a fast 1,3-Si→ O shift of a $SiMe_3$ group to give **6**. In the absence of proton sources the silanide **6** finally decomposes upon warming to room temperature to give $KOSiMe_3$ and the silene **3**. An analogous mechanism for the sila-Peterson reaction was described by Oehme et al., who investigated the reaction of $(Me_3Si)_3Li$ with aliphatic ketones.[34]

Reaction of 2b with Acetone. To evaluate the scope of the reaction, we performed a more systematic study with several alternative ketones. The reaction of $(Me_3Si)_3SiLi$ with acetone was studied before, and it has been found that the observed product distribution strongly depends on the experimental performance of the synthesis (Scheme 3).[34]

Scheme 3. Influence of the Addition Mode on the Reaction of $(Me_3Si)_3SiLi$ with Acetone[34]
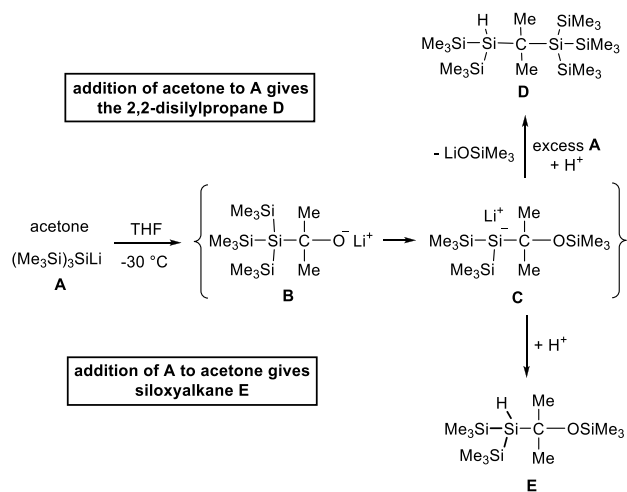
When THF solutions of the silanide were added to acetone at −30 °C, primarily the siloxyalkane **E** was formed. Alternatively, the addition of acetone to the silanide solution at low temperature afforded the 2,2-disilylpropane **D** as the major product, which has been interpreted as the result of a surprisingly fast substitution of the siloxy group in the intermediate **B** by a second equivalent of the silanide **A**.
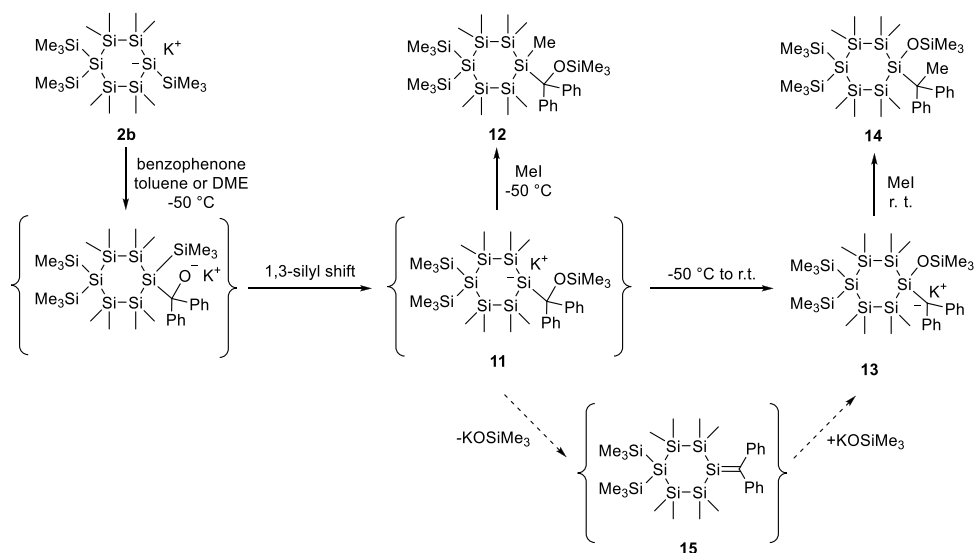
Apparently, in case of the sterically much more encumbered cyclic silanide **2b** this second substitution step is not possible. Thus, compound **8** was obtained after the addition of acetone to toluene or DME solutions of **2b** at −80 °C after hydrolytic workup (Scheme 4). Products originating from an intermediate silene could not be detected. Structural proof of **8** was obtained by the characteristic NMR chemical shifts of the $OSiMe_3$ group ($\delta(^{29}Si)$ 8.8 ppm ($OSiMe_3$); $\delta(^1H)$ 3.73 ppm (Si−H)) and the characteristic IR absorption band at $\nu(Si-H)$ 2055 cm^{-1}.

Scheme 4. Reaction of 2b with Acetone
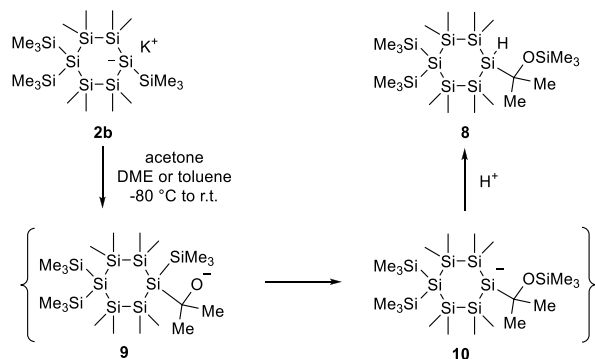
Reaction of 2b with Aromatic Ketones. It is well described in the literature that Peterson olefination reactions of $(Me_3Si)_3CLi$ with aromatic ketones such as benzophenone readily afford the corresponding 1,1-disilylalkenes.[35,36] To the best of our knowledge related sila-Peterson type reactions involving aromatic ketones have not been investigated so far. Oehme et al. even pointed out in 1988 that aromatic substrates cannot be used in these types of reactions because electron-transfer processes occur upon the interaction of the metal silanide with the aryl π-system, leading to deeply colored radical anion solutions.[34] In line with this statement we also obtained deep red solutions after the reaction of the silanide 2b with benzophenone in DME or toluene at low temperature. Careful analysis of the resulting mixture, however, showed the formation of products typical for a sila-Peterson-type reaction mechanism (Scheme 5). In close analogy to the behavior of adamantanone described above, the silanide 11 was obtained as the initial product after nucleophilic addition of 2b to the benzophenone C=O moiety followed by a fast 1,3-Si→O trimethylsilyl shift. 11 easily could be trapped by the addition of methyl iodide to the reaction solution at −50 °C. When the reaction mixture was warmed to room temperature in the absence of any trapping reagents, the silanide 11 rearranged spontaneously to the carbanion 13, which was detected as the predominant product by in situ NMR analysis of the reaction mixture (see Figures S26−S28 in the Supporting Information).

Subsequent addition of methyl iodide to the solution afforded the expected trapping product 14. The pure adducts 12 and 14 were isolated by crystallization from acetone and fully characterized. Analytical data including spectral assignment are included in the Experimental Section.

On the basis of earlier work it is conclusive that the carbanion 13 is formed via the silene intermediate 15 by readdition of the eliminated KOSiMe3 to the Si=C double bond (compare Scheme 5). Ishikawa et al. investigated the reaction of benzoyl(tristrimethylsilyl)silane with phenyllithium and explained the observed product distribution by the readdition of LiOSiMe3 to the intermediately formed silene $(Me_3Si)_2Si=CPh_2$.[37] Apparently, with aromatic ketones this process becomes energetically more favorable because the negative charge at the carbanionic center can be effectively delocalized within the aryl−C−aryl fragment. Thus, the carbanion 13 is formed as the final product instead of the silene or its dimerized derivatives.

The reaction of 2b with 9-fluorenone proceeds differently. Instead of the expected subsequent 1,3-Si→O trimethylsilyl shift the oxoanion 17 formed by the initial attack of 2b on the ketone rearranges by the migration of the complete cyclohexasilane fragment to oxygen to give the oxygen-bridged carbanion 18 (Scheme 6). Apparently, the propensity of the

Scheme 6. Reaction of 2b with 9-Fluorenone

**Scheme 5. Reaction of 2b with Benzophenone**
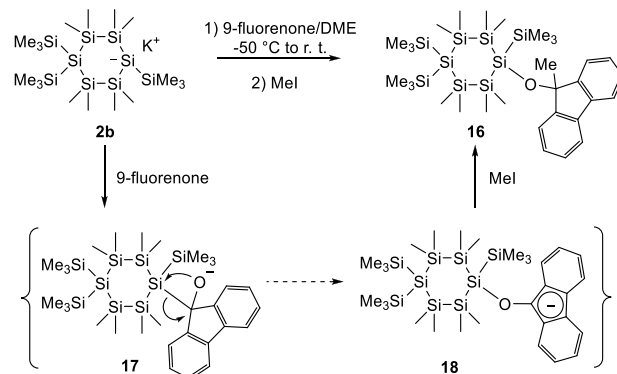
fused aromatic substituent for delocalization of the negative charge leads to significant stabilization of **18**, thus making this reaction pathway energetically more favorable.

Although **18** was too unstable to allow in situ characterization by NMR spectroscopy, it could be trapped by the addition of methyl iodide. The resulting methyl derivative **16** was isolated from the reaction mixture by column chromatography. Analytical data and spectral assignment (compare the Experimental Section) are fully consistent with the proposed structure.

Reaction of 2b with Diphenylcyclopropenone. Only a few years ago, Kira and co-workers generated the isolable 4-silatriafulvene **II** (Chart 1) by a sila-Peterson type reaction from (tBuMe$_2$)$_3$SiLi and di-tert-butylcyclopropenone.[14] Now we have discovered that the reaction of silanide **2b** with diphenylcyclopropenone affords neither the expected silene nor addition products of **2b** to the C=O moiety. Instead, the spirocyclic silacyclobutene **22** (Scheme 7) was isolated after

Scheme 7. Reaction of 2b with Diphenylcyclopropenone
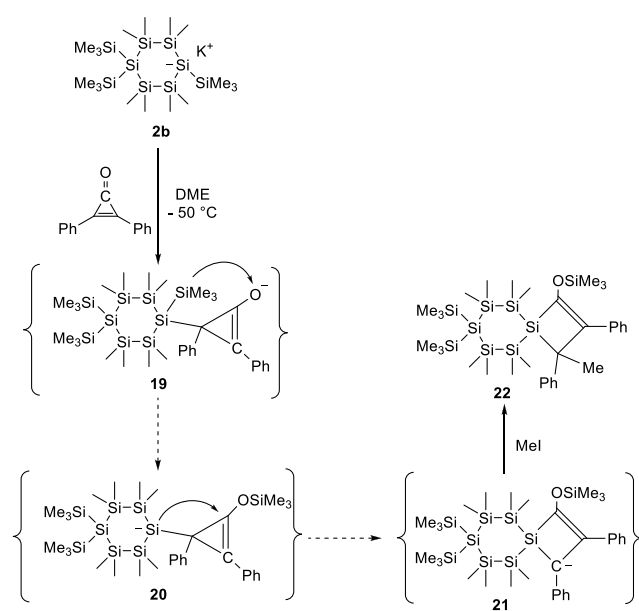
addition of methyl iodide to the reaction mixture. In ^{29}Si NMR the signal of the OSiMe$_3$ unit at $\delta(^{29}$Si) 17.83 ppm is significantly deshielded and is characteristic for an OSiMe$_3$ group at a vinylic position.[38] The resonance line at $\delta(^{29}$Si) −3.64 ppm is easily assigned to the spiro-silicon atom. The observed reaction course can be rationalized by assuming an initial conjugate 1,4-addition of the alkali-metal silanide to give the oxoanion **19**. Intermediate **19** undergoes a Si→O trimethylsilyl shift with formation of the silanide **20**, which subsequently rearranges by ring enlargement to the carbanion **21**, which reacts with MeI to give the final product **22**. This mechanism is conclusive in light of the fact that conjugate addition of organometallic reagents such as organolithiums or Grignards to α,β-unsaturated ketones is an important and well-known method of assembling structurally complex organic molecules.[39,40] An earlier report, for instance, describes the formation of the corresponding carboxylic acids as a result of the conjugate addition of phenyllithium and diphenylmethyllithium to diphenylcyclopropenone.[41]

X-ray Crystallography. Crystals suitable for single-crystal X-ray structure determination could be obtained for the

silanide **2a** and the trapping products **4a,b,d**, **7**, **8**, **12**, **14**, and **22**. The structural assignment derived from spectroscopic characterization was confirmed in all cases. Representative molecular structures are depicted in Figures 2−7 together with selected bond lengths, bond angles, and dihedral angles.[42]
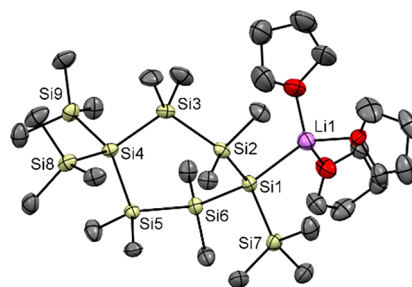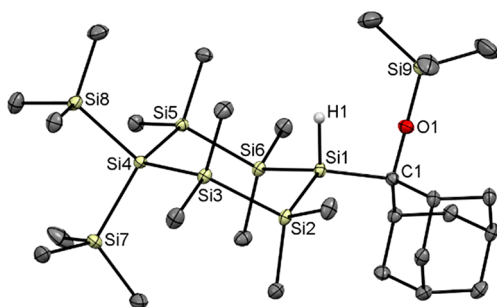
Figure 2. Molecular structure of **2a**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and bond and torsion angles (deg) with estimated standard deviations: Si−Si(mean) 2.350, Si(1)−Li(1) 2.727(5), Si−C$_{methyl}$(mean) 1.888, Si−Si−Si(mean) 109.5.
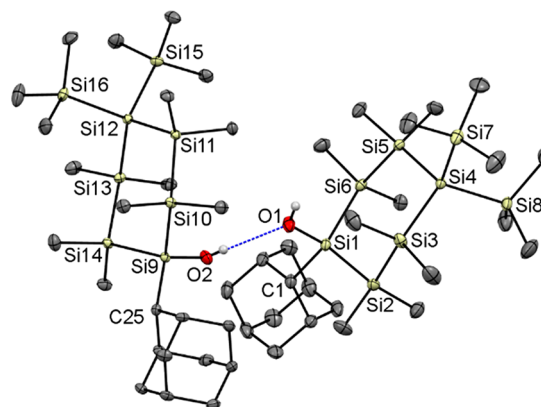
Figure 3. Molecular structure of **4b**. All hydrogen atoms are omitted for clarity except for O−H. Thermal ellipsoids are set at the 50% probability level. Two independent molecules (**4b**, **4b′**) in the asymmetric unit are linked by hydrogen bridge bonding. Selected bond lengths (Å) and bond and torsion angles (deg) with estimated standard deviations: **4b**, Si−Si (mean) 2.354, Si(9)−C(25) 1.903(2), Si(9)−O(2), 1.654(2), O(2)−O(1), 2.801(3), Si−C$_{methyl}$(mean) 1.882, Si−Si−Si(mean) 110.9; **4b′**, Si−Si (mean) 2.356, Si(1)−C(1) 1.898(3), Si(1)−O(1), 1.702(2), O(1)−O(2), 2.801(3), Si−C$_{methyl}$(mean) 1.885, Si−Si−Si(mean) 110.8.

The silanide **2a** crystallizes in the monoclinic space group $P2_1/c$ with a tetrahedral environment around the negatively charged Si atom Si1. The Si1−Li1 bond length of 2.73 Å is considerably longer than the sum of the covalent radii (Li, 1.33 Å; Si, 1.16 Å).[43] It also exceeds the Li−Si distances observed in the related molecular structures of (Me$_3$Si)$_3$SiLi·1.5DME (2.63 Å)[44] and Me$_3$SiLi·1.5TMEDA (2.70 Å)[45] possibly for steric reasons. In all structures the cyclohexasilane ring adopts puckered conformations with unexceptional Si−Si bond lengths between 2.34 and 2.40 Å. The geometry around the silicon atoms is approximately tetrahedral with average Si−Si−Si bond angles close to the respective angles found in other cyclohexasilane structures. The observed Si−O distances are close to the average Si−O bond length of 1.63 Å in compounds containing a tetracoordinate Si bound to a dicoordinate oxygen.[46] The asymmetric unit of **4b** contains two individual
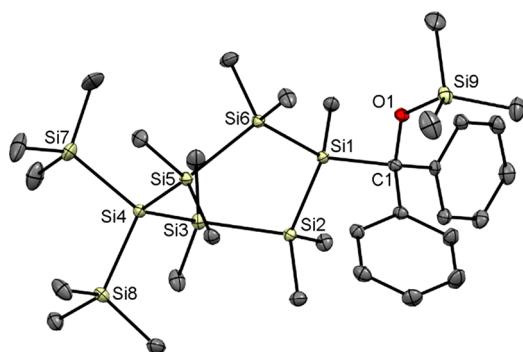
Figure 4. Molecular structure of **7**. All hydrogen atoms are omitted for clarity except for Si−H. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Si−Si(mean) 2.357, Si(1)−C(1) 1.954(1), C(1)−O(1) 1.446(1), Si(9)−O(1), 1.643(1), Si−C_{methyl}(mean) 1.882, Si−Si−Si(mean) 110.6, Si(1)−C(1)−O(1) 104.06(7), C(1)−O(1)−Si(9) 139.51(8).

Figure 5. Molecular structure of **12**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Si−Si(mean) 2.375, Si(1)−C(1) 1.968(2), C(1)−O(1) 1.451(2), Si(9)−O(1), 1.661(2), Si−C_{methyl}(mean) 1.882, Si−Si−Si(mean) 111.0, Si(1)−C(1)−O(1) 102.8(1), C(1)−O(1)−Si(9) 132.7(1).
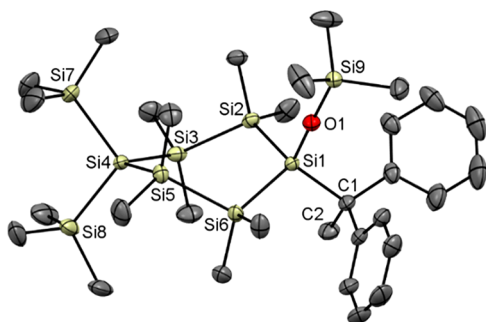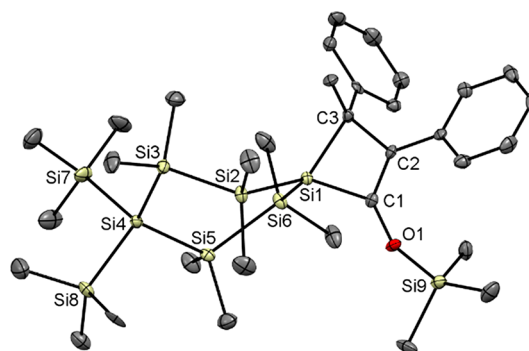

Figure 6. Molecular structure of **14**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Si−Si(mean) 2.364, Si(1)−C(1) 1.948(2), Si(1)−O(1) 1.645(2), Si(9)−O(1), 1.635(2), Si−C_{methyl}(mean) 1.882, Si−Si−Si (mean) 110.7, C(1)−Si(1)−O(1) 108.6(1), Si(2)−Si(1)−O(1) 107.07(6), Si(6)−Si(1)−O(1) 106.71(6), Si(1)−O(1)−Si(9) 174.1(1).

molecules connected by an intermolecular hydrogen bond (Figure 3). The intermolecular O−O distance of 2.80 Å compares well to the respective values found in other hydrogen-bonded cyclohexasilanols, -diols, and -triols.[47−50]

Figure 7. Molecular structure of silacyclobutene **22**. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. The crystals contain two independent molecules with insignificantly different structural parameters in the asymmetric unit (only one molecule is shown). Selected bond lengths (Å) and bond and dihedral angles (deg) with estimated standard deviations: Si−Si(mean) 2.355, Si(1)−C(1) 1.881(5), Si(1)−C(3) 1.956(6), C(1)−C(2) 1.357(7), C(2)−C(3) 1.539(7), C(1)−O(1) 1.368(6), Si(9)−O(1), 1.662(3), Si−C_{methyl}(mean) 1.882, Si−Si−Si(mean) 110.4, Si(1)−C(1)−C(2) 94.4(3), C(1)−C(2)−C(3) 105.6(4), C(2)−C(3)−Si(1) 86.0(3), C(3)−Si(1)−C(1) 74.0(2), Si(1)−C(1)−O(1) 136.9(3), C(1)−O(1)−Si(9) 131.6(3), C(2)−C(3)−Si(1)−C(1) −1.1(3), C(3)−Si(1)−C(1)−C(2) 1.3(3), Si(1)−C(1)−C(2)−C(3) −1.7(4), C(1)−C(2)−C(3)−Si(1) 1.6(4).

Hydrogen bonding is also observed in the structures of simple silanols, silanediols, and silanetriols, leading to the formation of dimers (e.g. 2,6-$Mes_2C_6H_3Si(OH)_3$, d_{O-O} = 2.86 Å)[51] or larger aggregates (e.g. Ph_3SiOH, d_{O-O} = 2.67 Å; $^tBu_2Si(OH)_2$, d_{O-O} = 2.75 Å).[52,53] The structural properties of silanols in general strongly depend on the steric bulk of the organic substituents located at the central silicon atom and on the solvent used for crystallization.[54] Compound **22** crystallizes in the orthorhombic space group $Pca2_1$ with two independent molecules in the asymmetric unit, which comprise insignificantly different structural parameters. The cyclobutene ring is planar with an unexceptional bond length C1=C2 of 1.357(7) Å[55] and slightly elongated Si1−C3 and C2−C3 bonds.

■ CONCLUSION

In conclusion, we were able to demonstrate that the reaction of the alkali metal cyclohexasilanides **2a,b** with ketones primarily follows a sila-Peterson mechanism. The structure of the final product, however, depends on the nature of the substituents attached to the carbonyl C atom. With 2-adamantanone the moderately stable Apeloig−Ishikawa−Oehme-type exocyclic silene **3** was obtained by elimination of $MOSiMe_3$ from the silanide intermediate **6**. In the case of acetone the hydrosilane **8** was obtained instead of the silene, in line with older studies on structurally related acyclic silanides. Aromatic ketones finally exhibit enhanced propensity for the delocalization of negative charge within the aromatic π system. The initially formed intermediates **11** and **17** of the reaction of **2b** with benzophenone or 9-fluorenone thus spontaneously rearranged to the delocalized carbanionic species **13** and **18**, which could be detected by in situ NMR spectroscopy and isolated as their trapping products with MeI.

■ EXPERIMENTAL SECTION

General Considerations. All experiments were performed under a nitrogen atmosphere using standard Schlenk or glovebox

techniques. Solvents were dried using a column solvent purification system.[56] Commercial KO^{t}Bu (97%), MeLi (1.6 M in Et$_2$O), MeI, MeOH, Et$_3$N, 2-adamantanone, benzophenone, acetone (99%), 9-fluorenone, and 1,2-diphenylcyclopropenone were used as purchased. ^{1}H (299.95 MHz), ^{13}C (75.43 MHz), and ^{29}Si (59.59 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer either in C$_6$D$_6$ solution using the internal ^{2}H-lock signal of the solvent or in toluene solution with a D$_2$O capillary as an external lock. Chemical shift values are referenced versus TMS. Compounds **1** and **2b** were synthesized according to published procedures.[28] HRMS spectra were run on a Kratos Profile mass spectrometer equipped with a solid probe inlet. Infrared spectra were obtained on a Bruker Alpha-P Diamond ATR spectrometer from the solid samples. Melting points were determined in capillaries melted off on one side using a Büchi 535 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 (0.86 mmol) of the cyclohexasilane **1** was dissolved in 15 mL of dry THF. Then 0.86 mL (1.6 equiv) of MeLi (1.6 M in Et$_2$O) was added at room temperature and the mixture was stirred for 5 h. During this time the solution became clear and changed to greenish yellow. All volatiles were removed in vacuo, and 3 mL of n-pentane was added. The solution was filtered, and the product was crystallized at −30 °C. After removal of the solvent 0.1 g (13%) of colorless crystals of pure **2a** was obtained.

^{29}Si{^{1}H} NMR (THF/D$_2$O, TMS, ppm): −184.5 (*Si*(SiMe$_3$)Li), −131.4 (*Si*(SiMe$_3$)$_2$), −38.7, −32.2 (*Si*Me$_2$), −8.7, −3.5 (*Si*Me$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −0.5, 0.35, 2.7, 3.9 (SiMe$_2$), 4.4, 4.6, 7.8 (SiMe$_3$), 25.4, 68.4 (THF). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, relative intensity): 0.50 (s, 24H, SiMe$_3$ + SiMe$_2$), 0.54 (s, 6H, SiMe$_2$), 0.57 (s, 9H, SiMe$_3$), 0.66 (s, 6H, SiMe$_2$), 0.76 (s, 6H, SiMe$_2$), 1.37 (t, 12H, THF), 3.49 (t, 12H, THF).

Reaction of 2b with 2-Adamantanone. A 0.47 g portion (0.8 mmol, 1 equiv) of the cyclohexasilane **1** and 0.95 g (0.85 mmol, 1.06 equiv) of KO^{t}Bu were dissolved in 20 mL of DME, and the mixture was stirred for 2 h at room temperature. ^{29}Si NMR analysis showed the quantitative formation of the silanide **2b**. After removal of the solvent in vacuo and addition of 10 mL of toluene the resulting mixture was added dropwise to 0.13 g (0.87 mmol, 1.09 equiv) of 2-adamantanone dissolved in 5 mL of toluene at −70 °C. Upon subsequent warming to room temperature the reaction mixture turned orange. NMR analysis showed the formation of silene **3** along with only minor amounts of byproducts. Attempts to isolate pure **3** by crystallization afforded complex mixtures of unidentified decomposition products. Complete removal of the solvent in vacuo also resulted in uncontrolled decomposition of **3**.

^{29}Si{^{1}H} NMR (toluene/D$_2$O, TMS, ppm): −131.7 (*Si*(SiMe$_3$)$_2$), −37.8, −37.6 (*Si*Me$_2$), −8.7 (*Si*Me$_3$), 51.9 (*Si*=C). ^{13}C{^{1}H} NMR (toluene/D$_2$O, TMS, ppm): −2.1 (SiMe$_2$), −1.8 (SiMe$_2$), 3.1 (SiMe$_3$), 28.7, 37.7, 41.5, 42.1 (Adamantyl), 197.8 (*C*=Si). ^{1}H NMR (toluene/D$_2$O, TMS, ppm, relative intensity): 0.17 (s, 18 H, SiMe$_3$), 0.23 (s, 12 H, SiMe$_2$), 0.33 (s, 12 H, SiMe$_2$); the adamantyl signals are superimposed by solvent signals.

Trapping of 3 with MeOH/Et$_3$N. Addition of 1.0 mL of MeOH and 0.1 mL of Et$_3$N to a toluene solution of silene **3** prepared as described above resulted in the immediate decolorization of the mixture. Subsequent removal of all volatiles in vacuo and purification of the crude product by column chromatography (d = 2 cm, h = 10 cm, SiO$_2$, n-pentane, then n-pentane/toluene 10/1) followed by recrystallization from acetone at −25 °C afforded 0.25 g (52% yield) of pure **4a** as colorless crystals.

Mp: 186−187 °C. Anal. Calcd for C$_{25}$H$_{60}$OSi$_8$: C, 49.93; H, 10.06. Found: C, 49.66; H, 9.78. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −131.9 (*Si*(SiMe$_3$)$_2$), −43.3, −35.3 (*Si*Me$_2$), −8.7, −7.2 (*Si*Me$_3$), 20.2 (*Si*OMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −3.80, −3.78, −1.1, −0.7 (SiMe$_2$), 4.2, 4.3 (SiMe$_3$), 28.6, 28.9, 32.4, 35.8, 38.2, 41.05, 42.3 (adamantyl), 54.5 (OMe). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, relative intensity): 0.335 (s, 9H, SiMe$_3$), 0.344 (s, 6H, SiMe$_2$), 0.37 (s, 9H, SiMe$_3$), 0.40 (s, 6H, SiMe$_2$), 0.44 (s, 6H, SiMe$_2$), 0.45 (s, 6H, SiMe$_2$), 1.48−2.34 (8 lines, 15H, CH^{Ad}), 3.38 (s, 3H, OMe). HRMS: calcd for [C$_{25}$H$_{60}$OSi$_8$]$^{•+}$ (M$^+$), 600.2798; found, 600.2806.

Trapping of 3 with H$_2$O/Et$_3$N. Addition of 1 mL of H$_2$O and 0.1 mL of Et$_3$N to a toluene solution of silene **3** prepared as described above resulted in the immediate decolorization of the mixture. Subsequent removal of all volatiles in vacuo and purification of the crude product by column chromatography (d = 2 cm, h = 10 cm, SiO$_2$, n-pentane, then n-pentane/toluene 10/1) followed by recrystallization from acetone afforded 0.21 g (45% yield) of pure **4b** as colorless crystals.

Mp: 162−163 °C. Anal. Calcd for C$_{24}$H$_{58}$OSi$_8$: C, 49.07; H, 9.95. Found: C, 48.84; H, 9.69. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −131.8 (*Si*(SiMe$_3$)$_2$), −44.3, −36.5 (*Si*Me$_2$), −9.1, −7.4 (*Si*Me$_3$), 16.5 (O-*Si*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −5.3, −4.5, −1.3, −0.6 (SiMe$_2$), 4.0, 4.1 (SiMe$_3$), 28.6, 28.9, 32.6, 36.1, 38.2, 41.1, 42.6 (adamantyl). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, relative intensity): 0.30 (s, 6H, SiMe$_2$), 0.32 (s, 9H, SiMe$_3$), 0.35 (s, 6H, SiMe$_2$), 0.36 (s, 9H, SiMe$_3$), 0.38 (s, 6H, SiMe$_2$), 0.44 (s, 6H, SiMe$_2$), 0.61 (s, 1H, OH), 1.34−2.33 (8 lines, 15H, CH^{Ad}). HRMS: calcd for [C$_{24}$H$_{58}$OSi$_8$]$^{•+}$ (M$^+$), 586.2642; found, 586.2639.

Trapping of 3 with MeLi/H$^+$. A 1.6 mL portion (1.0 mmol, 1.25 equiv) of MeLi (1.6 M in Et$_2$O) was added to a toluene solution of silene **3** prepared as described above at −80 °C. Warming to room temperature resulted in the formation of an orange solution. Subsequently an aqueous solution of NaHCO$_3$ was added until the mixture became colorless. After extraction of the product with 20 mL of pentane, drying of the pentane layer with Na$_2$SO$_4$, and removal of the solvent in vacuo the crude product was recrystallized from acetone to yield 0.15 g (32%) of **4d** as a white solid.

Mp: 187−190 °C. Anal. Calcd for C$_{25}$H$_{60}$Si$_8$: C, 51.29; H, 10.33. Found: C, 51.00; H, 10.11. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −131.8 (*Si*(SiMe$_3$)$_2$), −41.2 (*Si*Me), −37.2, −36.1 (*Si*Me$_2$), −9.1, −7.05 (*Si*Me$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −4.7 (SiMe$_2$), −4.0 (SiMe), −3.8, −1.2, −0.1 (SiMe$_2$), 4.2, 4.3 (SiMe$_3$), 28.5, 28.95, 32.6, 35.7, 37.1, 38.3, 41.3 (adamantyl). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, relative intensity): 0.31 (s, 6H, SiMe$_2$), 0.33 (s, 9H, SiMe$_3$), 0.34 (s, 9 H, SMe$_3$), 0.36 (s, 6H, SiMe$_2$), 0.389 (s, 6H, SiMe$_2$), 0.392 (s, 6H, SiMe$_2$), 0.40 (s, 6H, SiMe). 1.71−2.12 (8 lines, 15H, CH^{Ad}). HRMS: calcd for [C$_{26}$H$_{60}$Si$_8$]$^{•+}$ (M$^+$), 584.2849; found, 584.2853.

Trapping of Silanide 6 at Low Temperature. A DME solution of **2b** was prepared from 0.47 g (0.8 mmol, 1 equiv) of the cyclohexasilane **1** and 0.95 g (0.85 mmol, 1.06 equiv) of KO^{t}Bu as described above. The obtained solution was cooled to −60 °C, and 132 mg (0.88 mmol, 1.1 equiv) of solid 2-adamantanone was added. After the mixture was stirred for 15 min and 5 mL of a saturated aqueous NH$_4$Cl solution added, the cooling bath was removed and the mixture was stirred for another 30 min at room temperature. Workup of the resulting colorless mixture was achieved by extraction of the product with 30 mL of pentane, filtration over SiO$_2$, drying of the pentane layer with Na$_2$SO$_4$, and removal of the solvent in vacuo. Subsequent recrystallization of the crude product from acetone afforded 0.28 g (52%) of pure **7** as white crystals.

Mp: 197−200 °C. Anal. Calcd for C$_{27}$H$_{66}$OSi$_9$: C, 49.17; H, 10.09. Found: C, 48.85; H, 9.84. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −131.8 (*Si*(SiMe$_3$)$_2$), −35.9, −34.1 (*Si*Me$_2$), −9.7, −6.4 (*Si*Me$_3$), 7.1 (O*Si*Me$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, TMS, ppm): −2.8, −2.6, −1.65, 0.1 (SiMe$_2$), 3.7, 4.15, 4.3 (SiMe$_3$), 27.6, 27.8, 32.5, 36.7, 38.5, 39.5 (adamantyl), 84.7 (*C*-OSiMe$_3$). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, relative intensity): 0.32 (s, 9H, SiMe$_3$), 0.35 (s, 9H, 2 × SiMe$_3$), 0.39 (s, 6H, SiMe$_2$), 0.44 (s, 6H, SiMe$_2$), 0.47 (s, 6H, SiMe$_2$), 0.52 (s, 6H, SiMe$_2$), 1.44−2.50 (10 lines, 14H, CH^{Ad}), 3.89 (s, 1H, Si−H). IR (neat): ν(Si−H) 2074 cm^{-1}. HRMS: calcd for [C$_{27}$H$_{66}$OSi$_9$]$^{•+}$ (M$^+$), 658.3037; found, 658.3042.

Reaction of 2b with Acetone. A toluene solution of **2b** was prepared from 0.25 g (0.4 mmol, 1 equiv) of **1** and 0.05 g (0.42 mmol, 1.05 equiv) of KOtBu as described above. The obtained solution was cooled to −80 °C, and 0.1 mL (1.3 mmol, 3.25 equiv) of acetone was added dropwise. The color vanished immediately. After the mixture was stirred for 30 min, the cooling bath was removed and the mixture was stirred for another 60 min at room temperature. After aqueous

workup with a saturated solution of $NaHCO_3$ the organic layer was dried over Na_2SO_4 and the volatile components were removed in vacuo. NMR analysis showed the predominant formation of compound **8**. Subsequent column chromatography ($d = 3$ cm, $h = 15$ cm, SiO_2, n-pentane) afforded 0.09 g (40%) of pure **8** as a colorless oil that could be recrystallized from acetone to give white crystals.

Mp: 55−58 °C. Anal. Calcd for $C_{20}H_{58}OSi_9$: C, 42.33; H, 10.30. Found: C, 41.98; H, 9.91. $^{29}Si\{^1H\}$ NMR (C_6D_6, TMS, ppm): −131.9 ($Si(SiMe_3)_2$), −40.6, −36.9 ($SiMe_2$), −9.1, −7.8 ($SiMe_3$), 8.8 ($OSiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, ppm): −3.45, −2.3, −1.5, −0.7 ($SiMe_2$), 3.6, 3.9, 4.0 ($SiMe_3$), 33.0 (s, CMe_2), 72.9 (s, CMe_2). ^1H NMR (C_6D_6, TMS, ppm, relative intensity): 0.21 (s, 9H, $OSiMe_3$), 0.326, 0.333 (2 lines, 18H, $SiMe_3$), 0.39, 0.40 (2 lines, 12H, $SiMe_2$), 0.459, 0.465 (2 lines, 12H, $SiMe_2$), 1.52 (s, 6H, CH_3), 3.73 (s, 1H, Si−H). IR (neat): ν(Si−H) 2055 $cm^{−1}$. HRMS: calcd for $[C_{20}H_{58}OSi_9]^{•+}$ (M$^+$), 566.2411; found, 566.2406.

Reaction of 2b with Benzophenone. A DME solution of **2b** was prepared from 0.25 g (0.4 mmol, 1 equiv) of **1** and 0.05 g (0.42 mmol, 1.05 equiv) of KO^{t}Bu as described above. The obtained solution was cooled to −80 °C, and a solution of 0.08 g of benzophenone (0.44 mmol, 1.1 equiv) in 3.5 mL of DME was added dropwise. The cooling bath was removed, and the mixture was stirred for another 60 min at room temperature. NMR analysis of the solution showed the predominant formation of the carbanion **13**. Subsequently 0.05 mL (0.8 mmol, 2 equiv) of MeI was added, leading to vanishing of the red color. The mixture was stirred for 15 min at room temperature, and all volatiles were removed in vacuo. Workup was accomplished by filtration of a pentane solution of the crude product over SiO_2, column chromatography ($d = 3$ cm, $h = 15$ cm, SiO_2, n-pentane) and crystallization of the resulting oily residue by slow evaporation of the solvent to yield 0.15 g (53%) of colorless and crystalline **14**.

Data for **13** are as follows. $^{29}Si\{^1H\}$ NMR (DME/D$_2$O, TMS, ppm): −131.8 ($Si(SiMe_3)_2$), −44.7, −36.1 ($SiMe_2$), −18.6 (s, $SiOSiMe_3$), −8.6, −7.8 ($SiMe_3$), 6.9 ($OSiMe_3$). $^{13}C\{^1H\}$ NMR (DME/D$_2$O, TMS, ppm): −3.8, −2.2, −0.9, −0.3 (s, $SiMe_2$), 2.3, 2.8, 3.8 ($SiMe_3$), 112.7, 125.7, 127.1, 153.6 (Ph). ^1H NMR (DME/D$_2$O, TMS, ppm, relative intensity): 0.49 (s, 9H, $SiMe_3$), 0.50 (s, 9H, $SiMe_3$), 0.60 (s, 14H, $SiMe_3 + SiMe_2$), 0.61 (s, 6H, $SiMe_2$), 0.65 (s, 6H, $SiMe_2$), 0.69 (s, 6H, $SiMe_2$), 6.50−7.20 (m, 10 H, Ph).

Data for **13** are as follows. Mp: 169−172 °C. Anal. Calcd for $C_{31}H_{64}OSi_9$: C, 52.77; H, 9.14. Found: C, 52.43; H, 8.96. $^{29}Si\{^1H\}$ NMR (C_6D_6, TMS, ppm): −132.7 ($Si(SiMe_3)_2$), −42.6, −36.7 ($SiMe_2$), −8.5, −8.3 ($SiMe_3$), 4.0 ($SiOSiMe_3$), 6.4 ($OSiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, ppm): −4.0, −2.8, −0.7, −0.2 ($SiMe_2$), 3.4, 3.94, 3.98 ($SiMe_3$), 25.2 (CH_3), 44.9 (CPh_2), 125.9, 128.4, 129.4, 149.8 (Ph). ^1H NMR (C_6D_6, TMS, ppm, relative intensity): 0.08 (s, 6H, $SiMe_2$), 0.21 (s, 6H, $SiMe_2$), 0.22 (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$), 0.34 (s, 9H, $SiMe_3$), 0.35 (s, 6H, $SiMe_2$), 0.42 (s, 6H, $SiMe_2$), 1.73 (s, 3H, CH_3), 7.0−7.3 (m, 10 H, Ph). HRMS: calcd for $[C_{17}H_{51}OSi_9]^{•+}$ (M$^+$ − Ph$_2$CCH$_3$), 523.1863; found, 523.1871.

Trapping of Silanide 11 at Low Temperature. A DME solution of **2b** was prepared from 0.23 g (0.4 mmol, 1.0 equiv) of **1** and 0.05 g (0.42 mmol, 1.05 equiv) of KO^{t}Bu as described above. The obtained solution was cooled to −80 °C, and a solution of 0.08 g of benzophenone (0.44 mmol) in 5 mL of DME was added dropwise. Subsequently 0.06 mL of MeI was added, leading to vanishing of the red color. The cooling bath was removed, and the mixture was stirred for another 30 min at room temperature. After removal of the volatiles in vacuo workup was accomplished by column chromatography ($d = 3$ cm, $h = 15$ cm, SiO_2, n-pentane) and recrystallization of the resulting crude product from acetone to give 0.11 g (40%) of colorless and crystalline **12**.

Mp: 149−152 °C. Anal. Calcd for $C_{31}H_{64}OSi_9$: C, 52.77; H, 9.14. Found: C, 52.39; H, 8.80. $^{29}Si\{^1H\}$ NMR (C_6D_6, TMS, ppm): −132.6 ($Si(SiMe_3)_2$), −39.3, −35.8 ($SiMe_2$), −24.4 (s, $SiMe$) −9.0, −7.4 ($SiMe_3$), 12.7 ($OSiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, ppm): −4.5, −3.2 ($SiMe_2$), −2.8 ($SiMe$), −1.0, 0.1 ($SiMe_2$), 2.9 ($OSiMe_3$), 4.06, 4.09 ($SiMe_3$), 84.2 (CPh_2), 127.1, 128.2, 129.1, 146.7 (Ph). ^1H

NMR (C_6D_6, TMS, ppm, relative intensity): 0.00 (s, 9H, $OSiMe_3$), 0.12 (s, 6H, $SiMe_2$), 0.24 (s, 6H, $SiMe_2$), 0.318 (s, 9H, $SiMe_3$), 0.324 (s, 9H, $SiMe_3$), 0.39 (s, 12H, 2 × $SiMe_2$), 0.47 (s, 3H, CH_3), 7.0−7.5 (m, 10 H, Ph). HRMS: calcd for $[C_{31}H_{64}OSi_9]^{•+}$ (M$^+$), 704.2881; found, 704.2883.

Reaction of 2b with 9-Fluorenone. A DME solution of **2b** was prepared from 0.23 g (0.4 mmol, 1.0 equiv) of **1** and 0.05 g (0.42 mmol, 1.05 equiv) of KO^{t}Bu as described above. The obtained solution was cooled to −60 °C, and 0.08 g of solid 9-fluorenone (0.44 mmol, 1.1 equiv) was added. Subsequent addition of 0.05 mL of MeI resulted in a color change to orange. The cooling bath was removed, and the mixture was stirred for another 30 min at room temperature. After removal of the volatiles in vacuo workup was accomplished by filtration of a pentane solution of the crude product over SiO_2 followed by column chromatography ($d = 3$ cm, $h = 15$ cm, SiO_2, n-pentane). Crystallization of the resulting colorless oil from acetone afforded 0.07 g (25%) of pure **16**.

Mp: 170−173 °C. Anal. Calcd for $C_{31}H_{62}OSi_9$: C, 52.92; H, 8.88. Found: C, 52.63; H, 8.56. $^{29}Si\{^1H\}$ NMR (C_6D_6, TMS, ppm): −131.6 ($Si(SiMe_3)_2$), −41.1, −35.5 ($SiMe_2$), −13.8 ($OSiMe_3$), −8.8, −7.2, 2.1 ($SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, ppm): −3.0, −2.55, −0.8, 0.15 (-$SiMe_2$), 1.2, 4.2, 4.4 (-$SiMe_3$), 30.1 (C-CH$_3$), 82.6 (C-CH$_3$), 120.4, 124.65, 128.2, 129.3, 139.6, 150.4 (aryl). ^1H NMR (C_6D_6, TMS, ppm, relative intensity): −0.26 (s, 9H, $SiMe_3$), 0.29 (s, 6H, $SiMe_2$), 0.35 (s, 9H, $SiMe_3$), 0.42 (s, 9H, $SiMe_3$), 0.43 (s, 6H, $SiMe_2$), 0.50 (s, 6H, $SiMe_2$), 0.65 (s, 6H, $SiMe_2$), 1.63 (s, 3H, CH_3), 7.1−7.7 (m, 8H, aryl). HRMS: calcd for $[C_{24}H_{58}OSi_8]^{•+}$ (M$^+$ − fluorenyl − CH$_3$), 523.1863; found, 523.1868.

Reaction of 2b with 1,2-Diphenylcyclopropenone. A DME solution of **2b** was prepared from 0.35 g (0.60 mmol, 1.0 equiv) of **1** and 0.07 g (0.63 mmol, 1.05 equiv) of KO^{t}Bu as described above. The obtained solution was cooled to −50 °C, and 0.13 g of solid 1,2-diphenylcyclopropenone (0.63 mmol, 1.05 equiv) was added. After the mixture was stirred for 15 min, 0.1 mL of MeI was added. The cooling bath was then removed, and the mixture was stirred overnight at room temperature, resulting in a color change from red to yellow. After removal of the volatiles in vacuo workup was accomplished by filtration of a pentane solution of the crude product over SiO_2 followed by crystallization of the resulting colorless oil from acetone at −70 °C to give 0.18 g (42%) of pure **22**.

Mp: 181−184 °C. Anal. Calcd for $C_{33}H_{64}OSi_9$: C, 54.32; H, 8.84. Found: C, 53.99; H, 8.71. $^{29}Si\{^1H\}$ NMR (C_6D_6, TMS, ppm): −132.0 ($Si(SiMe_3)_2$), −39.2, −36.65, −36.0, −35.95 ($SiMe_2$), −9.1, −7.4 ($SiMe_3$), −3.6 (Si^{spiro}), 17.8 ($OSiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, ppm): −5.1, −3.5, −3.3, −3.1, −1.4, −1.2, −0.7, −0.3 ($SiMe_2$), 1.15 ($OSiMe_3$), 4.0, 4.1 ($SiMe_3$), 22.8 (CH_3), 38.6 (s, C-CH$_3$), 124.7, 126.5, 126.9, 128.4, 128.8, 129.0, 135.2, 140.4(Ph), 150.4, 155.6 (C≡ C). ^1H NMR (C_6D_6, TMS, ppm, relative intensity): −0.21 (s, 3H, $SiMe_2$), 0.19 (s, 3H, $SiMe_2$), 0.25 (s, 9H, $SiMe_3$), 0.27 (s, 3H, $SiMe_2$), 0.30 (s, 9H, $SiMe_3$), 0.33 (s, 9H, $SiMe_3$), 0.40 (s, 3H, $SiMe_2$), 0.44 (s, 3H, $SiMe_2$), 0.50 (s, 3H, $SiMe_2$), 0.51 (s, 3H, $SiMe_2$), 0.56 (s, 3H, $SiMe_2$), 1.93 (s, 3H, CH_3), 7.1−7.7 (m, 10H, Ph). HRMS: calcd for $[C_{33}H_{64}OSi_9]^{•+}$ (M$^+$), 728.2881; found, 728.2890.

X-ray Crystallography. All crystals suitable for single-crystal X-ray diffractometry were removed from a vial or a Schlenk and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryostream. XRD data collection was performed on a Bruker APEX II diffractometer with use of an Incoatec microfocus sealed tube of Mo Kα radiation (λ= 0.71073 Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS.[57,58] The structures were solved with use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL.[59−61] The space group assignments and structural solutions were evaluated using PLATON.[62,63] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles. In compound **7**, the rigid-bond restraint DELU was used in modeling the methyl groups in a −SiMe$_3$ moiety to make the ADP values of the

atoms more reasonable. Disorder was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments (PART).[64] The constraints EXYZ and EADP were used in modeling disorder to make the ADP values of the disordered atoms more reasonable. Disorder of all three THF molecules in compound **2a** attached to the lithium atom was observed and were was refined using split positions 69/31, 61/39, and 71/29, respectively. Disorder of −SiMe₃ moieties in compound **4d** was refined using split positions 60/40, 50/50, and 60/40, respectively. Compound **12** was refined as a two-component inversion twin (BASF 0.53). Compound **22** was refined as a two-component inversion twin (BASF 0.53).

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00106. .

> ¹H, ¹³C, and ²⁹Si NMR spectra of all new compounds and molecular structures of **4a,d** and **8** (PDF)

Accession Codes

CCDC 1981676−1981684 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.

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Notes

The authors declare no competing financial interest.

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