Sila-Peterson Reaction of Cyclic Silanides

Andreas W. Kyri, Lukas Schuh, Andreas Knochel, Michael Schalli, Ana Torvisco, Roland C. Fischer, Michael Haas, and Harald Stueger*

ABSTRACT: Sila-Peterson type reactions of the 1,4,4-tris-(trimethylsilyl)-1-metallooctamethylcyclohexasilanes (Me3Si)2Si6Me8(SiMe3)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.5–12 In 1996 Apeloig et al. reported the synthesis of the persistent silene I (Chart 1) via a sila-Peterson type reaction from (RMe2Si)2SiLi 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 species15,20 1- and 2-silanaphthalene, 9-silaanthracene, 9-silaphenanthrene, and 1,2-disilabenzenene 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 VII25 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,
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 KOtBu 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. 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. $^{13}$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 $)51.7$ ppm/$\delta(13$C $)196.8$ ppm). 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, the siloxy group at the Si=C carbon of compound VII can be expected to contribute to deshielding of $^{13}$C and shielding of...
29Si signals, if resonance contributions of the types shown in Chart 3 are important.

Chart 3. Possible Resonance Structures of Brook-Type Silenes

![Chart 3](https://example.com/chart3.png)

UV/vis measurements of silene 3 showed an absorption band centered at 341 nm (Figure 1), consistent with a π→π*

![Figure 1](https://example.com/figure1.png)

transition of the Si=\(=\)C double bond. This band is considerably red shifted with respect to the corresponding acyclic silene 1 (322 nm).\(^\text{13}\) An analogous trend was observed in recent studies for the Brook-type silene (Me\(_3\)Si)\(_2\)Si=\(=\)C(O)Ad (339 nm)\(^\text{30}\) and the related cyclic compound VII (362 nm)\(^\text{31}\) and interpreted in terms of enhanced \(\sigma\)(Si=Si) conjugation within the cyclic systems.\(^\text{32}\)

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 1 (R = Me).\(^\text{4}\) 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\(_3\)N 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 methylecyclohexasilane 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.\(^\text{53}\) 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\(_4\)Cl 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 29Si 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 \(\delta\)(H) 3.89 ppm. Compound 3 thus, is formed through intermediate S, 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\(_3\)Si)\(_2\)Li with aliphatic ketones.\(^\text{34}\)

**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\(_3\)Si)\(_2\)SiLi 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).\(^\text{34}\)

![Scheme 3](https://example.com/scheme3.png)

When THF solutions of the silanide were added to acetone at −30 °C, primarily the siloxalkane 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 (\(\delta\)(Si) 8.8 ppm (OSiMe\(_3\)); \(\delta\)(H) 3.73 ppm (Si−H)) and the characteristic IR absorption band at \(\nu\)(Si−H) 2055 cm\(^{-1}\).
Reaction of 2b with Aromatic Ketones. It is well described in the literature that Peterson olefination reactions of \((\text{Me}_3\text{Si})_3\text{CLi}\) with aromatic ketones such as benzophenone readily afford the corresponding 1,1-disilylalkenes.\textsuperscript{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 \(\pi\)-system, leading to deeply colored radical anion solutions.\textsuperscript{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 adamantane 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\(\rightarrow\)O trimethylsilyl shift. 11 easily could be trapped by the addition of methyl iodide to the reaction solution at \(-50^\circ\text{C}\). 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 KOSiMe\(_3\) to the Si=\(\equiv\)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 LiOSiMe\(_3\) to the intermediate formed silene \((\text{Me}_3\text{Si})_2\text{Si}=\text{CPh}_2\).\textsuperscript{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\(\rightarrow\)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...
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 (tBuMe3)3SiLi 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 addition of methyl iodide to the reaction mixture. In 29Si NMR the signal of the OSiMe3 unit at δ(29Si) 17.83 ppm is significantly deshielded and is characteristic for an OSiMe3 group at a vinylic position.38 The resonance line at δ(29Si) −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 oxaoion 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 diphenylmethyl-lithium 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.](https://dx.doi.org/10.1021/acs.organomet.0c00106)

![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.](https://dx.doi.org/10.1021/acs.organomet.0c00106)

The silanide 2a crystallizes in the monoclinic space group P21/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).32 It also exceeds the Li−Si distances observed in the related molecular structures of (Me3Si)3SiLi·1.5DME (2.63 Å)44 and Me3SiLi·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 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 dicordinate oxygen.36 The asymmetric unit of 4b contains two individual
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 cyclohexasilanos, -diols, and -triols.47-50

Hydrogen bonding is also observed in the structures of simple silanols, silanediols, and silanetriols, leading to the formation of dimers (e.g., 2,6-Mes2C6H3Si(OH)3, dO–O = 2.86 Å)51 or larger aggregates (e.g., Ph2Si(OH)2, dO–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 Pca21 with two independent molecules in the asymmetric unit, which comprise significantly different structural parameters. The cyclobutene ring is planar with an unexceptional bond length C1=C2 of 1.357(7) Å and slightly elongated Si1–C3 and C2–C3 bonds.

**CONCLUSION**

In conclusion, we were able to demonstrate that the reaction of the alkali metal cyclohexasilanes 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 MSiMe3 from the silane intermediate 6. In the case of acetone the hydrolysable 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 localized 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. Commercial KOtBu (97%), MeLi (1.6 M in Et2O), Me, MeOH, Et2N, 2-adamantanone, benzophenone, acetone (99%), 9-fluorenol, and 1,2-diphenylcyclopropenone were used as purchased.

1H (299.95 MHz), 13C (75.43 MHz), and 29Si (59.59 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer either in C6D6 solution using the internal 1H-lock signal of the solvent or in toluene solution with a D2O capillary as an external lock. Chemical shift values are referenced versus TMS. Compounds 1 and 2 were synthesized according to published procedures. HRMS spectra were run on a Kratos Profile mass spectrometer equipped with a solid probe infrared. 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 Et2O) 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.

29Si{1H} NMR (THF/D2O, TMS, ppm): −184.5 (Si(SiMe3)Li), −131.4 (Si(SiMe3)2), −38.7, −32.2 (SiMe3), −8.7, −3.5 (SiMe2).

13C{1H} NMR (C6D6, TMS, ppm): 0.50 (s, 24H, SiMe3 + SiMe2), 0.54 (s, 6H, SiMe2), 0.40 (s, 6H, SiMe2), 0.44 (s, 6H, SiMe2), 0.45 (s, 6H, SiMe3), 0.38 (s, 6H, SiMe3), 0.44 (s, 6H, SiMe3), 0.61 (s, 1H, OH), 1.34−2.33 (8 lines, 15H, CHAd).

**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 KOtBu were dissolved in 20 mL of DME, and the mixture was stirred for 2 h at room temperature. 29Si NMR analysis showed the quantitative formation of the silanide of 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 silane 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 uncontrollable decomposition of 3.

29Si{1H} NMR (toluene/D2O, TMS, ppm): −131.7 (Si(SiMe3)Li), −37.8, −37.6 (SiMe3), −8.7 (SiMe3), 51.9 (Si=C).

13C{1H} NMR (toluene/D2O, TMS, ppm): −2.1 (SiMe2), −1.8 (SiMe3), 3.1 (SiMe3), 28.7, 37.7, 41.5, 42.1 (Adamantyl), 197.8 (C=Si).

1H NMR (toluene/D2O, TMS, ppm, relative intensity): 0.17 (s, 18 H, SiMe3), 0.23 (s, 12 H, SiMe3), 0.33 (s, 12 H, SiMe3); the adamantyl signals are superimposed by solvent signals.

**Trapping of 3 with MeLi/H+.** A 1.6 mL portion (1.0 mmol, 1.25 equiv) of MeLi (1.6 M in Et2O) was added to a toluene solution of silane 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 NaHCO3 was added until the mixture became colorless. After extraction of the product with 20 mL of pentane, drying of the pentane layer with Na2SO4, 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.

**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 KOtBu 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 NH4Cl solution was 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 SiO2, drying of the pentane layer with Na2SO4 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.

**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 NaHCO₃ the organic layer was dried over Na₂SO₄ 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, SiO₂, n-pentane) afforded 0.09 g (40%) of pure 8 as a colorless oil that could be recrystallized from acetone to give white crystals. Anal. Calcld for C₂₅H₃₅ClO₃Si: C, 42.33; H, 4.30; Cl, 3.94; 3.98 (SiMe₃), 10.30. Found: C, 41.98; H, 9.91. ²⁵Si{¹H} NMR (CD₂Cl₂, TMS, ppm): –131.9 (Si(SiMe₃)₂), –40.6, –36.9 (SiMe₃), –9.1, –7.8 (SiMe₃), 8.8 (OSiMe₃). ¹³C{¹H} NMR (CD₂Cl₂, TMS, ppm): –3.45, –2.3, –1.5, –0.7 (SiMe₃), 3.6, 3.9, 4.0 (SiMe₃), 33.0 (s, CMe₃), 72.9 (s, CMe₃). ¹H NMR (CD₂Cl₂, TMS, ppm, relative intensity): 0.21 (s, 9H, SiMe₃), 0.32, 0.33 (2 lines, 12H, SiMe₂), 0.39, 0.40 (2 lines, 12H, SiMe₃), 0.459, 0.465 (2 lines, 12H, SiMe₃), 1.52 (s, 6H, CH₃), 3.73 (s, 1H, Si–H). IR (neat): ν(Si–H) 2055 cm⁻¹. HRMS: calcld for [C₂₅H₃₅ClO₃Si]⁺ (M⁺), 566.2441; 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'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. The resulting crude product from acetone to give 0.11 g (40%) of colorless and crystalline 14. Subsequent column chromatography (d = 3 cm, h = 15 cm, SiO₂, 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. ²⁵Si{¹H} NMR (DME/D₂O, TMS, ppm): –131.8 (Si(SiMe₃)₂), –44.7, –36.1 (SiMe₃), –18.6 (s, OSiMe₃), –8.6, –7.8 (SiMe₃), 6.9 (OSiMe₃). ¹³C{¹H} NMR (DME/D₂O, TMS, ppm): –3.8, –2.2, –0.9 (s, SiMe₃), 2.3, 2.8, 3.8 (SiMe₃), 112.7, 125.7, 127.1, 153.6 (Ph). ¹H NMR (DME/D₂O, TMS, ppm, relative intensity): 0.49 (s, 9H, SiMe₃), 0.50 (s, 9H, SiMe₃), 0.60 (s, 14H, SiMe₃ + SiMe₆), 0.61 (s, 6H, SiMe₃), 0.65 (s, 6H, SiMe₆), 0.69 (s, 6H, SiMe₆), 6.50–7.20 (m, 10 H, Ph). HRMS: calcld for [C₁₃H₁₅OSi]⁺ (M⁺ – Ph(CH₃)a) C₂₂H₃₁OSi⁺, 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'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, SiO₂, 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. Calcld for C₉₂H₁₄Si₅: C, 52.77; H, 7.94. Found: C, 52.39; H, 8.80. ²⁵Si{¹H} NMR (CD₂Cl₂, TMS, ppm): –132.6 (Si(SiMe₃)₂), –39.3, –35.8 (SiMe₃), –24.4 (s, SiMe₃), –9.0, –7.4 (SiMe₃), 12.7 (OSiMe₃). ¹³C{¹H} NMR (CD₂Cl₂, TMS, ppm): –4.5, –3.2 (SiMe₃), –2.8 (SiMe₃), –1.0, 0.1 (s, SiMe₃), 2.9 (OSiMe₃), 4.06, 4.09 (SiMe₃), 84.2 (CPh₃), 127.1, 128.2, 129.1, 146.7 (Ph). ¹H NMR (CD₂Cl₂, TMS, ppm, relative intensity): 0.00 (s, 9H, OSiMe₃), 0.12 (s, 6H, SiMe₃), 0.24 (s, 6H, SiMe₃), 0.318 (s, 9H, SiMe₃), 0.324 (s, 9H, SiMe₃), 0.39 (2H, 2 x SiMe₃), 0.47 (s, 3H, CH₃), 7.0–7.5 (m, 10 H, Ph). HRMS: calcld for [C₉₂H₁₄OSi₅]⁺ (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 silicon oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N₂ 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. The structures were solved with use of the intrinsic phasing option in SHELXTL and refined by the full-matrix least-squares procedures in SHELXL. The space group assignments and structural solutions were evaluated with PLATON. 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 –SiMe₃ 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). The constraints EXYZ and EADP were used in modeling disorder to make the ADF 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 refined using split positions 60/40, 40/50, 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).

**ACKNOWLEDGMENTS**

We thank the FWF (Wien, Austria) for financial support (project number P29899-N34).

**REFERENCES**

(1) Ager, D. J. The Peterson Reaction. *Synthesis* 1984, 1984, 384–398.

(2) Ager, D. J. The Peterson Olefination Reaction. *Organic reactions*; Wiley Online Library: Hoboken, NJ, 2003; pp 1–223.

(3) Oehme, H.; Wustrack, R. Über die Reaktion des Tris(trimethylsilyl)-silyllithiums mit Aceton. *Z. Anorg. Allg. Chem.* 1987, 552, 215–220.

(4) Bravo-Zhivotovskii, D.; Braude, V.; Stanger, A.; Kapon, M.; Apeloig, Y. Novel route to carbon-silicon double bonds via a Peterson-type reaction. *Organometallics* 1992, 11, 2326–2328.

(5) Ohshita, J.; Masaoka, Y.; Ishikawa, M. Silicon-carbon unsaturated compounds. 34. The formation of bis(trimethylsilyl)-silenes from acyltris(trimethylsilyl) silanes via a Peterson-type reaction. *Organometallics* 1991, 10, 3775–3776.

(6) Brook, A. G.; Brook, M. A. The Chemistry of Silenes. In *Advances in Organometallic Chemistry: Multiply Bonded Main Group Metals and Metalloids*; Gordon, F., Stone, A., West, R., Eds., Academic Press: 1996; pp 71–158.

(7) Lee, V. Y.; Sekiguchi, A. Cyclic polyenes of heavy group 14 elements: new generation ligands for transition-metal complexes. *Chem. Soc. Rev.* 2008, 37, 1652–1665.

(8) Morkin, T. L.; Leigh, W. J. Substituent effects on the reactivity of the silicon-carbon double bond. *Acc. Chem. Res.* 2001, 34, 129–136.

(9) Müller, T.; Ziche, W.; Auner, N. Silicon-Carbon and Silicon-Nitrogen Multiply Bonded Compounds. In *The chemistry of organic silicon compounds*; Patai, S., Ed.; John Wiley & Sons, Ltd.: 1998; pp 857–1062.

(10) Ottosson, H.; Eklöf, A. M. Silenes: Connectors between classical alkenes and nonclassical heavy alkenes. *Coord. Chem. Rev.* 2008, 252, 1287–1314.

(11) Ottosson, H.; Steel, P. G. Silenes, silynes, and disilenes: novel silicon-based reagents for organic synthesis? *Chem. - Eur. J.* 2006, 12, 1576–1585.

(12) West, R. Multiple bonds to silicon: 20 years later. *Polyhedron* 2002, 21, 467–472.

(13) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Blaser, D.; Boese, R. Novel stable silenes via a sila-Peterson-type reaction. *Organometallics* 2003, 22, 5336–5337.

(14) Sekiguchi, A. Conversion of a silene to an allene. *Angew. Chem., Int. Ed.* 2002, 41, 1402–1404.

(15) Bravo-Zhivotovskii, D.; Korogodsky, G.; Apeloig, Y. Synthesis of the first long-lived bis-silene. *J. Organomet. Chem.* 2003, 686, 58–65.

(16) Touloukhonova, I. S.; Guzei, I. A.; West, R. Synthesis of a silene from 1,1-dilithiosilole and 2-adamantanone. *J. Am. Chem. Soc.* 2004, 126, 5336–5337.

(17) Motomatsu, D.; Ishida, S.; Ohno, K.; Iwamoto, T. Isolable 2,3-disila-1,3-butadiene from a double silyl-anion Peterson-type reaction. *J. Organomet. Chem.* 2004, 686, 37–44.

(18) Inoue, S.; Ichinohe, M.; Sekiguchi, A. Conversion of a disilene into a silene: silyl-anion-substituted silene by a sila-Peterson-type reaction from an sp3-type silyl anion. *Angew. Chem., Int. Ed.* 2007, 46, 3346–3348.

(19) Lee, V. Y.; Sekiguchi, A. Aromaticity of group 14 organometallics: experimental aspects. *Angew. Chem., Int. Ed.* 2007, 46, 6596–6620.

(20) Tokito, N. New progress in the chemistry of stable metallaoaromatic compounds of heavier group 14 elements. *Acc. Chem. Res.* 2004, 37, 86–94.

(21) Igarashi, M.; Ichinohe, M.; Sekiguchi, A. Air-stable disilacyclobutenes with a Si = C bond and its conversion to disilacyclopentenium ions: silicon-carbon hybrid 2r-electron systems. *J. Am. Chem. Soc.* 2007, 129, 12660–12661.

(22) Bejan, I.; Inoue, S.; Ichinohe, M.; Sekiguchi, A.; Scheschke, D. 1,2-Disilacyclobut-2-enes: donor-free four-membered cyclic silenes.
from reaction of disilenes with vinylbromides. Chem. - Eur. J. 2008, 14, 7119–7122.

(23) Bejan, I.; Güclü, D.; Inoue, S.; Ichinohe, M.; Sekiguchi, A.; Scheschkewitz, D. Stable cyclic silenes from reaction of disilenes with carboxylic acid chlorides. Angew. Chem., Int. Ed. 2007, 46, 3349–3352.

(24) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. The First Isolable Dialkylsilylene. J. Am. Chem. Soc. 1999, 121, 9722–9723.

(25) 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.

(26) Haas, M.; Fischer, R.; Schuh, L.; Saf, R.; Torvisco, A.; Stueger, H. Photoinduced Rearrangement of Aryl-Substituted Acyclocyclosilanes. Eur. J. Inorg. Chem. 2015, 997–1004.

(27) Haas, M.; Radebner, J.; Winkler, C.; Fischer, R.; Torvisco, A.; Stueger, H. Isolable endocyclic silenes by thermal Brook rearrangement. J. Organomet. Chem. 2017, 830, 131–140.

(28) Fischer, R.; Konopa, T.; Ully, S.; Baumgartner, J.; Marschner, C. Route Si6 revisited. J. Organomet. Chem. 2003, 685, 79–92.

(29) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Plavac, N. Carbon−silicon−9 chemical shifts and coupling constants involving tris(alkylmethyl)silyl systems. Organometallics 1982, 1, 994–998.

(30) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, M. R.; Poon, Y. C.; Chang, Y. M.; Winnie, W. N. Stable solid silenolates. J. Am. Chem. Soc. 1982, 104, 5667–5672.

(31) Stueger, H.; Haskan, B.; Haas, M.; Rausch, M.; Fischer, R.; Torvisco, A. Photoinduced Brook-Type Rearrangement of Acyclocyclosilanes. Organometallics 2014, 33, 231–239.

(32) West, J. Electron delocalization and aromatic behavior in cyclic polysilanes. Pure Appl. Chem. 1982, 54, 1041–1050.

(33) Compare ref 9, p 937, and references cited therein.

(34) Wustrack, R.; Oehme, H. The reaction of dis(trimethylsilyl)silyl with aliphatic ketones. J. Organomet. Chem. 1988, 352, 95–106.

(35) Peterson, D. J. Carbonyl olefination reaction using silyl-substituted organosilicon compounds. J. Org. Chem. 1968, 33, 780–784.

(36) Gröbel, B.-T.; Seebach, D. Erzeugung von und Olefinierung mit α-Si, -Se, -S und -Sn-perheterosubstituierten (Trimethylsilyl)-methylthiium-Verbindungen. Chem. Ber. 1977, 110, 852–866.

(37) Oshita, J.; Masaoka, Y.; Ishikawa, M.; Takeuchi, T. Silicon-carbon unsaturated compounds. 45. Reaction of benzoyltrimethylsilyl with aliphatic ketones. J. Organomet. Chem. 1988, 352, 95–106.

(38) Sheldrick, G. M. SHELXT - integrated space-group and crystal-structure determination. Acta Crystallogr., Sect. A: Found. Crystallogr. 2015, 71, 3–8.

(39) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Adv. 2008, 64, 112–122.

(40) Sheldrick, G. M. SHELXT - integrated space-group and crystal-structure determination. Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3–8.

(41) Stroth, C.; Sato, M.; Kato, K.; Hoshino, K. Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. 2003, 36, 7–13.

(42) Spok, A. L. Single-crystal structure validation in chemical crystallography. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148–155.

(43) Müller, P.; Herbst-Irmer, R.; Spek, A. L.; Schneider, T. R.; Sawaya, M. R. Crystal Structure Refinement; Oxford University Press: Oxford, 2006.

(44) Kafory, M.; Kapon, M.; Botoshansky, M. The structural chemistry of organosilicon compounds. In The chemistry of organic silicon compounds; Patai, S., Rappoport, Z. M., Apeloig, Y., Eds.; Wiley: Chichester, 1998; pp 181–265.

(45) Spielberger, A.; Gispalt, P.; Siegl, H.; Hengge, E.; Gruber, K. Syntheses, structures and properties of dihydroxymethylcyclosilanes and permethyloxahexasilanorbornanes. J. Organomet. Chem. 1995, 499, 241–246.

(46) Korylyuk, A. A.; Larkin, D. Y.; Chernyavskaya, N. A.; Antipin, M. Y.; Chernyavskii, A. I. Molecular structure of 1,3-dihydroxydecamethylcyclosilane. Mendeleev Commun. 2001, 11, 195–196.

(47) Stueger, H.; Fuerpass, G.; Baumgartner, J.; Mitterfellner, T.; Flock, M. Molecular structure and UV absorption spectra of OH and NH derivatives of dodecamethylcyclosilane: a combined experimental and computational study. Z. Naturforsch., B: J. Chem. Sci. 2009, 64, 1598–1606.

(48) Stueger, H.; Albarg, J.; Flock, M.; Fuerpass, G.; Mitterfellner, T. cis-cis-1, 3, 5-Trihydroxynonamethylcyclosilane: A Cyclosilane with Unusual Properties. Organometallics 2011, 30, 2531–2538.

(49) Pietschnig, R.; Belaj, F.; Tirieé, J. J. Synthesis and Intermediates in the Formation of a Terphenyl-Substituted Silanetriol: Activation through Hypervalency. Organometallics 2004, 23, 4897–4901.

(50) Bats, J. W.; Scholz, S.; Lerner, H.-W. The low-temperature phase of di-tert-butylsilanediol. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 2002, 58, No. o439.

(51) Bowes, K. F.; Hille, W.; Low, J. N. Tetrameric triphenylsilsilanol, (Ph3SiOH)4, and the adduct (Ph3SiOH)2-dimethyl sulfoxide, both at 120 K, and the adduct (Ph3SiOH)4-dioxane at 150 K: interplay of O-H and C-H π(arene) interactions. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 2002, 58, No. o409.

(52) Pietschnig, R.; Spirk, S. The chemistry of organosilanetriols. Coord. Chem. Rev. 2016, 323, 87–106.

(53) Backer, M.; Grasmann, M.; Zech, W.; Auner, N.; Wagner, C.; Herdtweck, E.; Hille, W.; Heckel, M. Silacylcubutenes - Synthesis and Reactivity. In Organosilicon chemistry II: From molecules to materials; Auner, N., Ed.; VCH: Weinheim, 1996; pp 41–47.

(54) For the rest of the structures consult the Supporting Information.