EurJOC

European Journal of Organic Chemistry

Chemistry Europe

European Chemical Societies Publishing

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.202100768

Link to VoR: https://doi.org/10.1002/ejoc.202100768

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COMMUNICATION

Isolation of a Cyclopentasilane from Magnesium Reduction of a Linear Hexasilane

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Abstract: The reductive cyclization of two linear hexasilanes is contrasted, where a methylated precursor yielded a cyclohexasilane while the *tert*-butyl-functionalized analog unexpectedly yielded a cyclopentasilane. A comprehensive analysis using X-ray diffraction, IR, HR, HRMS, and multinuclear (^{1}H, ^{13}C and ^{29}Si) 1D and 2D NMR spectroscopy identified the 1,2-dihydrodisilane ^{t}BuPhHSi−SiHPh^{t}Bu as an additional product, which was interpreted as supportive of a mechanism involving silylene elimination. The results of this study may prove informative about substituent effects in the practice of complex organosilicon molecular synthesis.

Herein we describe the unexpected formation of a 5-membered cyclopentasilane from a 6-membered linear hexasilane precursor. The influence of steric effects on the product outcome are examined by comparison of a *tert*-butyl-functionalized linear precursor to a previously described methyl-functionalized oligosilane. This work was conducted in the context of the attempted synthesis of a tricyclic silane building block for complex polysilane synthesis.

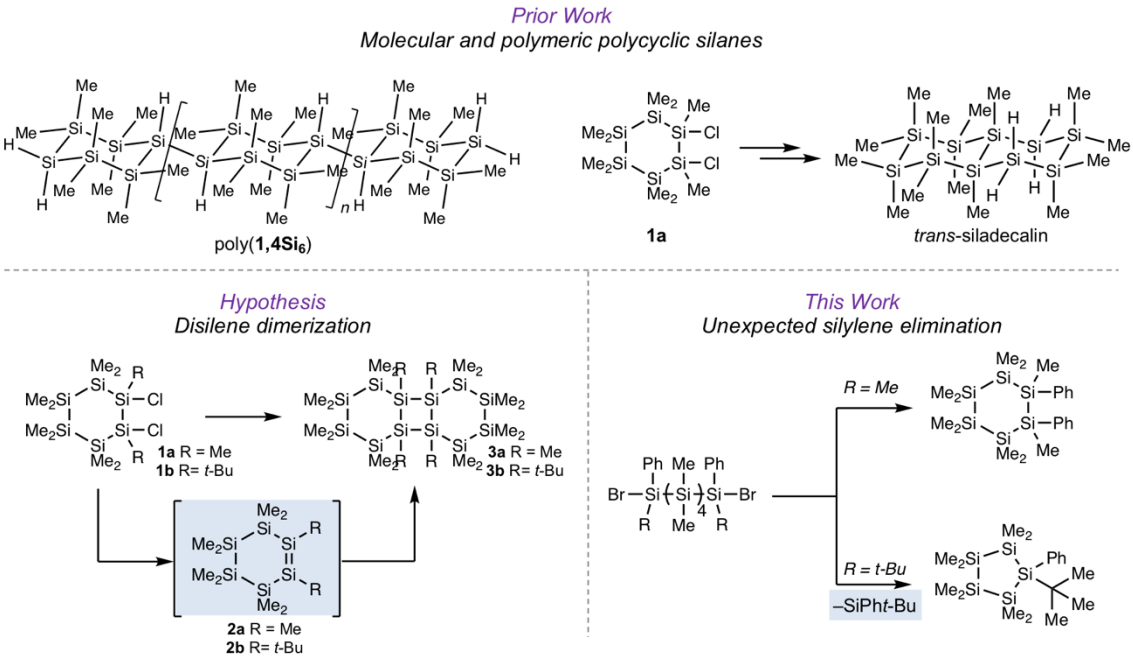
Inorganic silicon nanostructures combine biocompatibility[1] with interesting electronic and photonic properties,[2–7] which have been key to biomedical,[8–10] energy-storage,[11,12] energy production,[13] optoelectronic,[14] and semiconducting applications.[15] Towards the goal of uncovering new nanostructured materials that combine these compelling properties with the processability and tunability of organic conjugated polymers, we reported the synthesis of organosilicon polymer mimics of the crystalline silicon lattice such as polycyclosilane poly(**1,4Si$_6$**) (Scheme 1a).[16] Key to this work is the synthesis of multifunctional cyclosilanes[17,18] amenable to dehydrocoupling[19–23] or reductive polymerization.[24]

The rational design and synthesis of new building blocks could further expand the structural and functional diversity of polycyclosilanes and other nanostructured silanes. We previously reported the stereocontrolled synthesis of *cis*- and *trans*-siladecalins where a key intermediate was 1,2-dichlorocyclosilane **1a** (Scheme 1a).[25] To further explore the potential applications of **1a**, we envisaged reductive dimerization via a postulated intermediate disilene **2a** to yield **3a**, a strained permethylated silicon analogue of dodecahydrobiphenylene (Scheme 1b). Embedding silicon in a four-membered ring results in compelling properties such as enhanced Lewis acidity,[26] unusual conductance[27] and visible light emission,[28,29] as well as utility in ring-opening polymerization.[30,31] The [2+2] cyclodimerization of an endocyclic disilene has been observed as an undesired pathway during the attempted synthesis of a homocyclic silylene.[32,33]

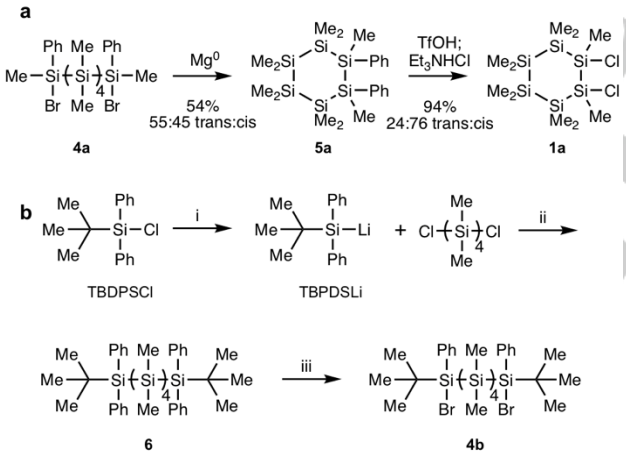
However, attempts to dimerize **1a** using several conditions and reducing agents did not cleanly afford **3a**. Product identification was complicated by the methylated structure which resulted in similar polarity, difficult chromatographic separation and complex, overlapping spectra. Despite the uncertain fate of **1a**, we hypothesized two possible outcomes: (i) decomposition of tricyclic **3a**, as strained cyclosilanes are known to rapidly ring-expand upon exposure to adventitious oxygen[34] or (ii) competitive trimerization to a larger central ring system.

A potential solution to both challenges is partial replacement of methyl groups with the more sterically demanding *tert*-butyl group. Bulky substituents afford kinetic stabilization to disilenes[35,36] and strained cyclotetrasilanes.[28] Reduction of dichlorodialkylsilanes with larger alkyl groups is also known to favor smaller rings,[37] as in the lithium reduction of $Cl_2SiMe(t\text{-}Bu)$[37] and $Cl_2Si(t\text{-}Bu)_2$[38,39] to cyclotetrasilanes. Therefore, we hypothesized that 1,2-di-*tert*-butyl-1,2-dichloro cyclohexasilane **1b** might be a reasonable precursor for the synthesis of tricyclic **3b** (Scheme 1b).

In our earlier siladecalin synthesis, linear hexasilane **4a** was straightforwardly reduced to cyclohexasilane **5a** using Mg powder (Scheme 2a)[25] and our prior synthesis of **4a** was readily adapted to provide the *tert*-butyl analog **4b** (Scheme 2b). *tert*-Butyl(chloro)diphenylsilane (TBDPSCl) is a common alkoxy protecting group in organic synthesis. Lithium reduction with Gilman-type conditions[40–42] readily provided the silyl anion TBDPSLi as a dark red solution in THF. TBDPSLi was not isolated, but cation exchange with isopropylmagnesium chloride[43] and salt metathesis with dichlorooctamethyltetrasilane ($Cl(SiMe_2)_4Cl$) afforded the linear hexasilane **6** in 69% yield over two steps. Selective cleavage of one phenyl ring from each terminus of the linear hexasilane was accomplished by addition of TfOH, which formed an intermediate ditriflate. Conversion to the more hydrolytically stable dibromo compound was accomplished by addition of lithium bromide, yielding the target compound **4b** (50:50 d.r.) in 88% yield over two steps.



Scheme 1. a) Prior work: structures of molecular and polymeric polycyclic silanes synthesized in the Klausen group, including the stereocontrolled synthesis of *cis*- and *trans*-siladecalins via 1,2-dichlorocycohexasilane intermediate **1a**. b) Motivating hypothesis: dimerization of an endocyclic disilene as a route to tricyclic silanes. c) This work: attempted synthesis of a *tert*-butyl functionalized cyclohexasilane yields instead a cyclopentasilane via a hypothesized silylene elimination.



Scheme 2. a) Synthesis of cyclohexasilane **1a** from linear hexasilane **4a**.[25] b) Synthesis of linear hexasilane **4b**. i) Li, THF, 24 h; ii) *i*-PrMgCl (2.1 equiv.), 30 min; then $Cl(SiMe_2)_4Cl$, 15 h, 69% (two steps); iii) TfOH (2.0 equiv.), DCM, 0 °C, 2 h; then LiBr (2.1 equiv.), Et_2O, RT, 15 h, 88% (two steps). RT = room temperature.

With linear hexasilane **4b** in hand, we investigated reductive cyclization using similar conditions as had proved successful in the synthesis of methylated **5a**[25] (powdered Mg^0 (4.0 equiv.), THF) (compare Scheme 2a and Scheme 3). Upon quenching with 2-propanol (*i*-PrOH), instead of isolating the targeted cyclohexasilane **5b** as the main product, we obtained cyclopentasilane **7** in 51% yield after column chromatography (Scheme 3). Cyclopentasilane **7** was also the major product in reductive cyclization with sodium naphthenalide (NaNp). The observation of **7** from NaNp-reduction suggests that the iodine employed to activate Mg powder was not responsible for Si–Si bond cleavage. The structure of **7** was confirmed by comparison to Masamune's prior report of ^1H and ^{29}Si NMR spectroscopic data for **7** (Table 1) in a report describing ^{29}Si–^{29}Si two-bond coupling in strained cyclosilanes.[44] Masamune did not report a synthesis of cyclopentasilane **7**.

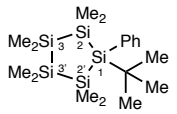
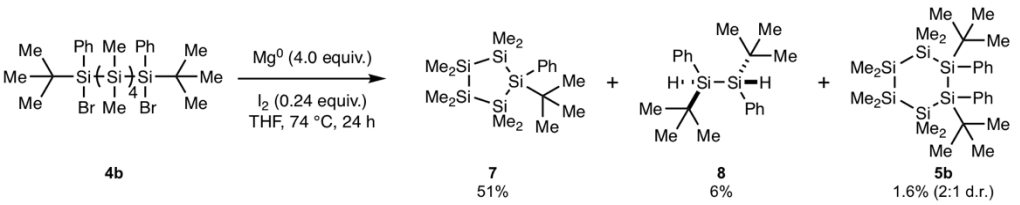


Table 1. Tabulated ^{29}Si NMR chemical shifts for compound **7**.

Atom	δ (this work) [a,b]	δ (ref. 35) [a,c]
Si-1	-19.00	-18.5
Si-2, Si-2'	-42.25	-41.73
Si-3, Si-3'	-43.74	-43.22

[a] Relative to $SiMe_4$. [b] 1-D ^{29}Si {^1H} DEPT (distortionless enhancement by polarization transfer) spectrum determined in benzene-d_6 (25 °C) at 79 MHz. [c] Determined in benzene-d_6 (25 °C) at 53.7 MHz.



Scheme 3. Reduction of linear hexasilane **4b** yields predominantly cyclopentasilane **7**, as well as trace quantities of disilane **8** and target cyclohexasilane **5b**.

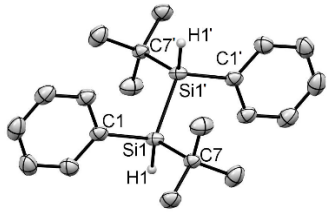


Figure 1. Displacement ellipsoid plot (50% probability level) of **8** (CCDC 2091373) at 110(2) K. H atoms and disorder are omitted for clarity. Selected bond length [Å]: Si1-Si1' 2.3483(7).

In addition to cyclopentasilane **7**, a second more polar fraction was isolated, which was observed to be a complex mixture of compounds by ^{1}H NMR spectroscopy (Figure S14). Fortuitously, after dissolution in hexanes (25 °C, 7 d), a mixture of a glassy solid and colorless crystals was observed. Single crystal X-ray crystallographic analysis suggested that the crystalline solid could be assigned to 1,2-dihydrodisilane **8** (Figure 1). The crystal structure of **8** only shows the *meso* diastereomer. The Si−Si bond distance (d_{Si-Si}) of 2.3483(7) Å was slightly shorter than the analogous d_{Si-Si} observed for the related compounds $^{i}Pr_2PhSi-SiPh^{i}Pr_2$ (2.3898(4) Å) and $^{t}BuPh_2Si-SiPh_2{}^{t}Bu$ (2.4002(6) Å).[45]

The structural assignment to 1,2-dihydrodisilane **8** was supported by extensive spectroscopic analysis. FTIR spectroscopy showed the presence of a sharp stretching frequency at $\tilde{\nu}$ = 2093 cm^{-1} consistent with a Si–H bond, but a strong, broad feature at ca. 1000 cm^{-1} consistent with a Si–OR bond was not observed (Figure S30). ^{1}H and ^{29}Si NMR spectroscopy (Figures S15 and S20) further supported the presence of a Si–H functional group, as in the observation of a one-bond correlation between ^{1}H (δ 4.55) and ^{29}Si (δ -18.03) in the ^{1}H-^{29}Si HSQC spectrum (Figure 2a). High resolution mass spectrometry (HRMS) also revealed a molecular ion consistent with **8** (calcd. M = 326.18861, found = 326.18929, Figure S27). No evidence of the other diastereomer of **8** was found, for example, the ^{29}Si NMR data in Figure 2 is consistent with only one Si–H containing compound.

HRMS also suggested the presence of trace quantities of the originally desired cyclohexasilane **5b** (calcd. M = 556.26847, found = 556.26905; calcd. for M−^{t}Bu = 499.19805, found = 499.19819, Figures S28 and S29). A series of NMR relationships made possible the identification and differentiation of cyclohexasilane **5b** and 1,2-dihydrodisilane **8** in the complex mixture isolated after column chromatography. The same δ -18.03 ^{29}Si resonance with a one-bond correlation to ^{1}H in Figure 2a (assigned to **8**) showed a three-bond ^{1}H-^{29}Si

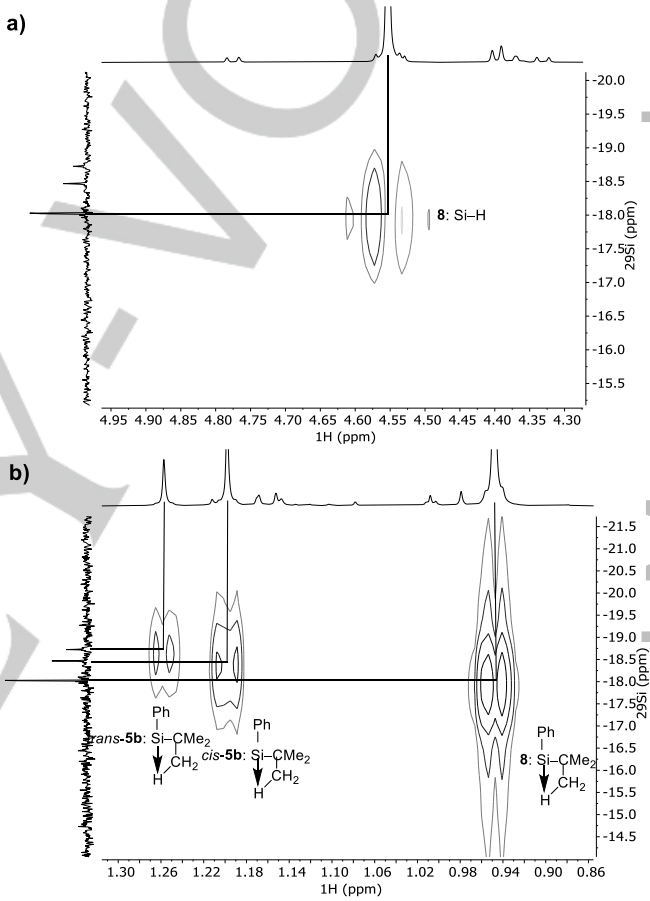


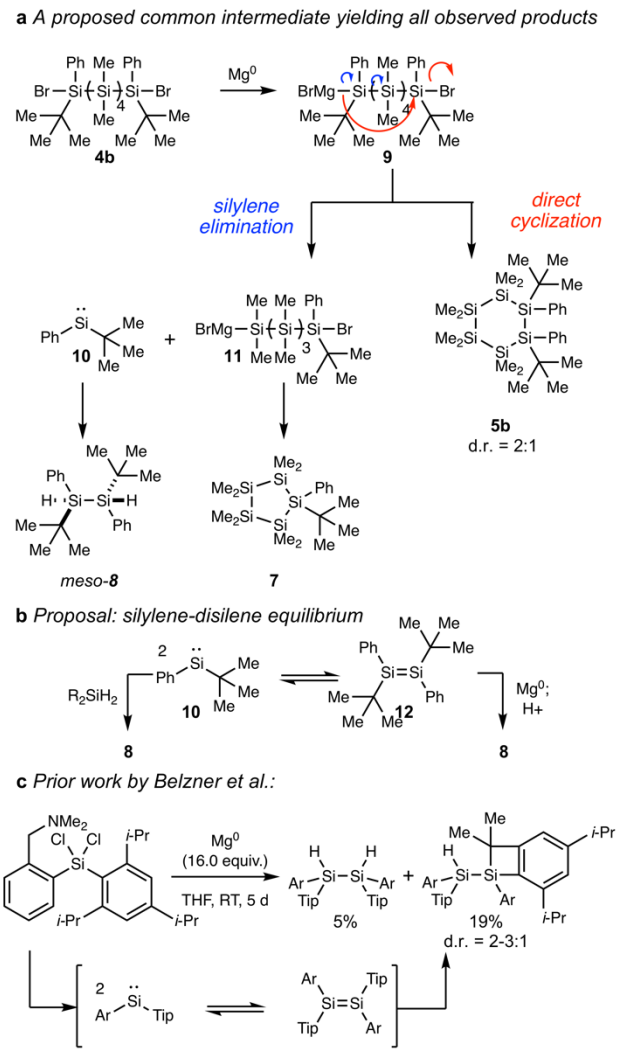
Figure 2. a) Cropped ^{1}H–^{29}Si HSQC spectrum showing one-bond ^{1}H-^{29}Si correlation assigned to disilane **8**. b) Cropped ^{1}H–^{29}Si HMBC spectrum showing three-bond ^{1}H-^{29}Si correlations assigned to **5b** and **8**.

correlation (0.95, -18.03, Figure 2b) that allowed assignment of the δ 0.95 resonance to the C*Me*$_3$ group of **8**. The δ 1.20 and 1.26 ^{1}H resonances could be assigned to the C*Me*$_3$ resonances of the *cis* and *trans* diastereomers of **5b** based on similar three-bond correlations to δ -18.47 and -18.72 ^{29}Si resonances, respectively (Figure 2b). Additional NMR experiments allowed complete assignment of Si-Me resonances to the *cis* and *trans* stereoisomers of **5b** (Figures S17, S18, S23, S24).

We suggest that all four identified products, cyclopentasilane **7,** disilane **8**, and *cis* and *trans* cyclohexasilane **5b**, could arise from a common mechanism (Scheme 4a). Magnesium insertion into one Si–Br bond of **4b**

is proposed to give intermediate silanide **9**. Silanide **9** could directly cyclize to give cyclohexasilane **5b**. The known rapid stereochemical inversion of silanides[46,47] may rationalize the low diastereoselectivity in this cyclization and the cyclization of methylated **4a** (55:45 *trans:cis*).[25]

Slower rates of cyclization might be observed with **4b** relative to **4a** due to replacement of Si-Me for the bulkier Si-*t*Bu group. As a result, silylene elimination (**9**→**10**+**11**) could become competitive with direct cyclization (**9**→**5b**). Silylene elimination would provide the less hindered silanide **11** which could directly cyclize to yield cyclopentasilane **7**. We also note the alternative possibility of nucleophilic attack on an internal Si–Si bond[48–50] to directly afford cyclopentasilane **7** and a silylenoid equivalent of **10** (Ph*t*-BuSi(MgBr)Br, Figure S31).



Scheme 4. a) A silanide intermediate could account for the four isolated products *cis*-**5b**, *trans*-**5b**, cyclosilane **7** and disilane **8** via direct cyclization or competitive silylene elimination. b) A silylene-disilene equilibrium followed by two-electron reduction and protonation could account for disilane 8. c) Prior work: reduction of a dichlorodiorganosilane yields unusual disilene derivatives.[51]

We expect that 1,2-dihydrodisilane **8** arises from silylene **10** (Ph(*t*-Bu)Si) or silylenoid equivalent (Ph(*t*Bu)Si(Br)MgBr)) via one of several possible mechanisms. A 2-propanol quench was used herein and diorganosilylenes typically undergo high-yielding O–H insertion products upon alcoholysis, which would suggest *tert*-butyl(isopropoxy)(phenyl)silane as a major product. For example, West reported yields between 74-90% for the ethanol trapping reaction of the closely structurally related *tert*-butylmesitylsilylene in a variety of solvents (Mes(*t*-Bu)Si + HOEt → Mes(*t*-Bu)SiH(OEt)).[52] However, *tert*-butyl(isopropoxy)(phenyl)silane was not detected by HRMS. Another common reaction of silylenes is intramolecular C-insertion[53] and a 1,3-CH insertion reaction with the tert-butyl group would afford a silirane. Although the silirane was not detected, this does not preclude its formation, as siliranes thermally decompose.[54–56] Finally, we note the possibility that 1,2-dihydrodisilane **8** could arise from an Si–H bond insertion reaction, such as $R_2Si + R_2SiH_2 \rightarrow R_2HSi\text{-}SiHR_2$. Silane traps have frequently been used to study silylene intermediates.[55,57] However, such a reaction would be expected to produce a diastereomeric mixture. A source of Ph(t-Bu)SiH_2 is not immediately obvious. The difference in isolated yield between **7** and **8** (51% vs. 6%) may reflect that multiple reaction pathways exist (e.g. the reactive intermediate giving rise to **8** also decomposes to volatile, unidentified products).

We considered that an equilibrium between silylene **10** and disilene **12** might instead be the origin of disilane **8** (Scheme 4b). Silylene dimerization to the corresponding disilene is well-known[52] and we have identified two different reports of 1,2-dihydrodisilanes arising from disilenes. In seminal work on tetramesityldisilene ($Mes_2Si{=}SiMes_2$), West and Michl reported that photochemical activation (λ = 254 nm) converted tetramesityldisilene to the 1,2-dihydrodisilane.[58] The authors speculated radical character to the excited state would result in C-H abstraction. Matsumoto and Nagai reported that tetra(*iso*-propyl)disilene ($(i\text{-}Pr)_2Si{=}Si(i\text{-}Pr)_2$) (generated via photolysis of an anthracene-bridged masked disilene) yielded a 1,2-dihydrodisilane (5% yield) via postulated C–H abstraction from solvent.[59]

While both reactions above were photochemical, our work was performed without high-energy irradiation. A more closely related example is a study by Belzner et al. in which Mg^0 reduction of a dichlorodiarylsilane yielded a silacyclobutane (19%) and a 1,2-dihydrodisilane (5%, diastereomer not specified) via a putative silylene-disilene equilibrium (Scheme 4c).[51] That different starting materials under similar reaction conditions yielded similar products is indicative of a common reactive intermediate. We note the use of excess Mg^0 in both reactions and suggest that the two-electron reducing agent might provide an intermediate dianion that affords a 1,2-dihydrodisilane upon protic workup (Scheme 4b). Sekiguchi reported one-electron reduction of a disilene with *tert*-butyllithium to a disilane radical anion.[60] In neither our work nor Belzner's was the typical disilene alcoholysis product ($R_2(H)Si\text{-}Si(OR)R_2$) detected which may indicate a low concentration of the disilene under the reaction conditions.

In summary, we report that the reduction of the linear hexasilane **4b** with Mg^0 resulted in the unexpected formation of the ring contraction product cyclopentasilane **7** and 1,2-dihydrodisilane **8**, as well as trace quantities of the desired cyclohexasilane **5b** as a mixture of diastereomers. The product distribution was characterized by single crystal X-ray crystallography, high resolution mass spectrometry, and ^1H

and ^{29}Si NMR spectroscopy. Ring contraction was hypothesized to arise from steric effects that reduced the rate of cyclization relative to silylene elimination. Two mechanisms by which 1,2-dihydrodisilane **8** could be formed were discussed, either directly from silylene **10** or via reduction of intermediate disilene **12**. Halosilane reduction is an exceptionally widely used reaction for both polysilane[61] and complex molecular silane synthesis[62] and single atom eliminations during reduction have been previously described,[63,64] yet the mechanism or mechanisms by which such reactions have not been elucidated. We anticipate that the differing results reported herein concerning the reduction of methylated **4a** and *tert*-butyl functionalized **4b** will also be informative about substituent effects in oligosilane chemistry.

Experimental Section

The supporting information contains synthetic procedures, characterization data, and x-ray crystallographic data.

CCDC 2091373 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgements

E. B.-M. is thankful to Universidad de Costa Rica for a permission granted to perform a postdoctoral stay in the Klausen group. This research was primarily supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, under Award No. DE-SC0020681 (building block synthesis, structural characterization).

Keywords: Magnesium • Reactive intermediates • Silanes • Silylenes • Substituent effects

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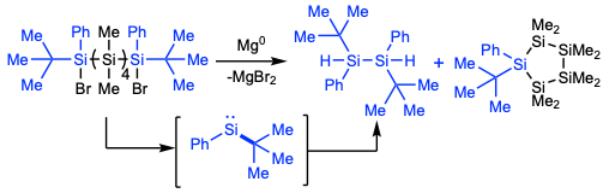

The Mg^0 promoted reduction of a sterically hindered 1,6-dibromohexasilane yielded a cyclopentasilane as the main product. The disilane *t*-BuPhHSi−SiHPh*t*-Bu was identified as a minor product, which suggests a possible mechanism involving elimination of a transient silylene SiPh*t*-Bu.

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