

## Article

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# Stereocontrolled syntheses of functionalized *cis*- and *trans*siladecalins.

Eric A. Marro, Carlton P. Folster, Eric M. Press, Hoyeon Im, John T. Ferguson, Maxime A. Siegler, Rebekka S. Klausen\*

Department of Chemistry, Johns Hopkins University, 3400 N. Charles St, Baltimore, MD, 21218.

**ABSTRACT:** We report the synthesis of both diastereomers of an all-silicon analog of decalin, the ubiquitous bicyclic structural motif. The synthesis provides materials functionalized with either Si–Ph or Si–H groups, versatile entry points for further chemical diversification. The synthesis of silicon-stereogenic silanes is significantly less precedented than the synthesis of asymmetric carbon centers and strategies for control of relative stereochemistry in oligosilanes are hardly described. This study offers insights of potential generality, such as the epimerization of the *cis*-isomer to the thermodynamically downhill *trans*-isomer via a hypothesized pentavalent intermediate. Decalin is a classic example in the conformational analysis of organic ring systems and the carbocyclic diastereomers have highly divergent conformational profiles. Like the carbocycle, we observe different conformational properties in *cis*- and *trans*-siladecalins with consequences for NMR spectroscopy, optical properties, and vibrational spectroscopy. This study showcases the utility of targeted synthesis for preparing complex and functionalized polycyclic silanes.

#### Introduction

Silicon, a central material in technology and energy science, possesses a diamond lattice crystal structure that inspires interest in the properties of complex polycyclic silanes.<sup>1</sup> However, polycyclic silanes are a significant challenge for synthesis.<sup>2-6</sup> target-oriented Silicon clusters (e.g. octasilacubane<sup>7,8</sup>) are typically more oxidatively sensitive than the corresponding hydrocarbons.9 These Group 14 platonic solids have been prepared by reductive coupling of halosilane precursors, although reductive coupling limits both scale and molecular diversity: low selectivity for a target compound, with correspondingly low yields, is common and few functional groups tolerate the strongly reducing reaction conditions.

Nonetheless, polycyclic silanes exhibit unusual properties that are less well-understood than linear silanes.<sup>10,11</sup> In a recent example, Kyushin synthesized the bowl-shaped tricyclic silane **1** in 5% yield via reduction of a hexabrominated decasilane.<sup>12</sup> The molecule's bowl shape induces overlap of the Si-C  $\sigma^*$ orbitals such that the LUMO has "pseudo- $\pi^*$ " symmetry, resulting in a bathochromically shifted absorption spectrum relative to linear oligosilanes of a similar size.

Silyl anions are a class of important intermediates for the synthesis of cyclosilanes. Marschner described the synthesis of bridged cyclosilanes, such as 2 and silanorbornane 3,<sup>13,14</sup> from the coupling of potassiosilyl anions<sup>15</sup> (potassium silanides) with halosilanes. Lewis acid-mediated skeletal rearrangement of a derivative of 3 led to the landmark synthesis of siladamantane 4.<sup>16</sup> Silanide chemistry<sup>17</sup> has also made an impact in the rare preparation of functionalized polycyclic silanes. Nuckolls et al. converted 2 into thiomethyl-functionalized 6, as part of a study demonstrating conformational control of  $\sigma$ -conjugation and molecular conductance.<sup>18,19</sup>

Siladecalin is a long-standing challenge for chemical synthesis. In 1972, West reported the characterization of the

multiple products of dimethyldichlorosilane and trimethylchlorosilane reductive coupling.<sup>20</sup> The major products were a polysilane (78%) and dodecamethylcyclohexasilane (Si<sub>6</sub>Me<sub>12</sub>, 10%). Six other silanes were isolated and one with the molecular formula of Si<sub>10</sub>Me<sub>18</sub> (4% yield) was suggested to be permethylsiladecalin. However, definitive assignment was not possible until Hengge later identified this product as the *trans*-siladecalin by X-ray crystallography.<sup>21</sup>

We describe the synthesis of functionalized siladecalin scaffolds via disilanide-halosilane coupling. Two advantages accrue from this approach: control of relative stereochemistry and functional group interconversion.

The preparation of silicon-stereogenic silanes has focused on monosilanes as reagents and intermediates in asymmetric organic synthesis,<sup>22–27</sup> with isolated examples of cyclohexa- or cyclopentasilanes exhibiting *cis-trans* stereoisomerism.<sup>13,28</sup> We include comprehensive details of our efforts to control relative stereochemistry at the siladecalin ring fusion. Ultimately, we identified a selective route to the *cis*-siladecalin skeleton, which could be equilibrated to the lower energy *trans*-isomer.

The selective synthesis of both diastereomers enables the description of isomer-dependent properties. The diastereomers of carbocyclic decalin have markedly different properties.<sup>29</sup> The *trans*-decalin structure does not allow for ring inversion (chair flipping) and the room temperature <sup>1</sup>H NMR spectrum shows a broad, partially resolved band composed of overlapping axial and equatorial protons.<sup>30,31</sup> In contrast, chair interconversion in *cis*-decalin is rapid, resulting in a single sharp resonance even at -121 °C.<sup>30</sup> Similar conformational dynamics in siladecalin scaffolds underly differences in optical properties described herein.

Our synthesis opens the door to the preparation of a wide variety of functionalized siladecalin skeletons. The diaryl disilanide used in this study enables site-specific functionalization. Arylsilanes are latent electrophiles: treatment with strong acid (e.g. triflic acid)<sup>32</sup> reveals a reactive silyl triflate with formation of benzene. Here, we show that a dearylation/hydrogenation sequence introduces Si–H residues into the siladecalin. The Si–H bond is a versatile functional group for further derivatization via hydrosilation and other chemistries.<sup>33–35</sup>



Figure 1. Polycyclic silanes. a) Examples of fused polycyclic methylsilanes synthesized by reductive coupling. b) Examples of bridged polycyclic methylsilanes synthesized by salt metathesis. c) Functionalized polycyclic silanes. d) Functionalized siladecalin retrosynthesis and avenues of stereochemical control.

## Results and Discussion

**1.** Synthesis. We envisioned a different approach to siladecalin synthesis via coupling of a disilanide and a bifunctional cyclosilane (Figure 1d). Siladecalin  $Si_{10}Ph_4$  could arise from coupling of 7 and previously unreported dichlorocyclohexasilane 8. Earlier work from our group identified disilanide [(18-cr-6)K]<sup>+</sup><sub>2</sub>7 as a versatile intermediate in the preparation of site-selectively functionalized silicon rings.<sup>36–39</sup> We further expected that  $Si_{10}Ph_4$  would serve as an entry point to a family of siladecalin frameworks, such as  $Si_{10}H_4$ , via acid-mediated dearylation and derivitization.<sup>32</sup>

This synthetic approach provides at least two avenues for control of the relative stereochemistry at the siladecalin ring fusion. Cyclohexasilane **8** is itself chiral – could the building block dictate the outcome of the coupling reaction? The stereochemical course of nucleophilic substitution at tetrahedral silicon atoms has long been recognized to be more complex than for alkanes and examples of both retention and inversion of configuration are known.<sup>40–42</sup> With respect to nucleophiles and electrophiles similar to the current work, substitution at a silicon-stereogenic chlorosilane with an achiral lithium silanide was reported to proceed with inversion of stereochemistry.<sup>43</sup> We also anticipated the possibility of thermodynamic equilibration of the *cis*- and *trans*-siladecalins.

Scheme 1. Synthesis of cyclohexasilane 13. i) *i*PrMgCl, THF, 0 °C  $\rightarrow$  rt, 15 h, 73% ii) 1.) TfOH (2.0 equiv.), DCM, 0 °C  $\rightarrow$  rt, 2 h / LiBr, Et<sub>2</sub>O, r.t., 98% iii) Mg (Powdered, 2.5 equiv.), THF, reflux, 2.5 h, 54%.



To examine these questions, we devised a three step synthesis of **13**, a precursor to **8** via dearylation-hydrogenation (Scheme

1).<sup>32,44</sup> Uhlig reported **13** in 1993, but synthetic procedures were not provided.<sup>45</sup> Coupling of known **9** and **10** in tetrahydrofuran yielded **11** in 73% yield. Selective terminal bis-dearylation was

accomplished with triflic acid. Magnesium reduction of the hexasilane framework yielded a mixture of *cis*- and *trans*-13.



Figure 2. NMR spectra of *cis*- and *trans*-**13**. a) <sup>1</sup>H NMR spectra 400 MHz, CDCl<sub>3</sub>) comparing (top to bottom) trans, cis, and the as isolated mixture of isomers. Only the methyl region is shown for clarity. b) <sup>29</sup>Si {<sup>1</sup>H} DEPT NMR spectra (79 MHz, CDCl<sub>3</sub>) comparing (top to bottom) *trans*, *cis*, and the as isolated mixture of isomers.



Figure 3. Displacement ellipsoid plots (50% probability level) of trans- and cis-13. Black = carbon, blue = silicon at 110(2) K. Hydrogens are omitted for clarity.

The *cis* and *trans* isomers of **13** were partially separable by column chromatography. Recrystallization of the enriched samples obtained from column chromatography led to isolation

of diastereomerically pure samples of each, allowing assignment of the crude mixture arising from reductive cyclization to a 55:45 *trans:cis* ratio of diastereomers based on integration of the <sup>1</sup>H NMR spectrum (Figure 2a).

Crystal structures of *cis*- and *trans*-13 were determined (Figure 3). A chair-like conformation of the cyclohexasilane was observed in both isomers. Typical bond lengths and angles for cyclohexasilanes were observed. In *trans*-13, both phenyl groups were found at equatorial positions, while in *cis*-13, one phenyl ring is in the equatorial position while the other is in a pseudo-axial position.

*trans*-13 is a chiral,  $C_2$  symmetric molecule, with three chemically inequivalent silicon atoms, and <sup>29</sup>Si {<sup>1</sup>H} DEPT NMR spectroscopy showed three resonances (Figure 2b). Five resonances were observed in the alkyl region of the <sup>1</sup>H NMR spectrum and were assigned to the five diastereotopic methyl groups. Aromatic resonances were also observed. *cis*-13 is meso achiral and rapidly interconverting chair conformers were anticipated. The expected three chemically inequivalent silicon resonances were observed by <sup>29</sup>Si DEPT NMR spectroscopy, as well as five resonances in the alkyl region of the <sup>1</sup>H NMR spectrum that were assigned to the methyl protons. Peak assignments are indicated in Figure 2 and are based on <sup>1</sup>H-<sup>29</sup>Si HMBC spectroscopy (Figures S1-2). We were not able to distinguish axial and equatorial methyl peaks on the basis of NOESY spectroscopy.

Studies towards the synthesis of **8** began with the as isolated 55:45 *trans:cis* mixture of **13** (Table 1). Treatment with triflic acid (TfOH) in dichloromethane (DCM) led to skeletal rearrangement and an inseparable mixture of structural isomers.

Skeletal rearrangement was also observed with acetyl chloridealuminum chloride (AcCl/AlCl<sub>3</sub>). Krempner et al. have observed skeletal rearrangement of a silane dendrimer in TfOH/DCM, but not in TfOH/pentane.<sup>46</sup> Upon exploring solvent effects, we observed exclusively cyclohexasilane 14 in TfOH/pentane (entry 2), but with a change in the diastereomeric ratio to 24:76 trans: cis-14. Subjecting pure trans-13 to TfOH/pentane likewise resulted in a 24:76 trans: cis mixture. In all cases, addition of triethylamine hydrochloride (Et<sub>3</sub>N•HCl) to 14 provided chlorosilane 8 with no further change in the isomeric ratio.

Table 1. Dearylation of 13: stereochemical consequences.

Me<sub>2</sub>Si

conditions

Me<sub>2</sub> Me

`Si-OTf

Si-OTf

Me

Me<sub>2</sub>

14

Me<sub>2</sub> Me

Si Me<sub>2</sub> Me

13

`Si—Ph

-Ph

Me<sub>2</sub>Si

Me<sub>2</sub>S

Starting Conditions Entry Outcome material 1 55:45 TfOH, CH<sub>2</sub>Cl<sub>2</sub> Skeletal rearrangement trans:cis 13 2 55:45 TfOH, pentane 24:76 trans: cis 14 trans:cis 13 3 trans-13 TfOH, pentane 24:76 trans:cis 14 Based on these observations, we opted to advance 13 to the siladecalin scaffold without separating isomers. The as

synthesized 55:45 trans: cis 13 was converted to 24:76 trans: cis dichlorosilane 8 in 90% yield using TfOH/pentane and Et<sub>3</sub>N•HCl (Scheme 2). Under optimized conditions (vide infra), 24:76 trans: cis 8 coupled to MgBr<sub>2</sub>•[(18-cr-6)K]<sup>+</sup><sub>2</sub>7 in THF to yield Si<sub>10</sub>Ph<sub>4</sub> in 68% yield. Si<sub>10</sub>Ph<sub>4</sub> was isolated as a 10:90 mixture of diastereomers, favoring the cis isomer. The enrichment in the diasteromeric ratio during salt metathesis merited further investigation.

Scheme 2. Synthesis of 10:90 trans: cis Si<sub>10</sub>Ph<sub>4</sub>. i) TfOH (2.2 equiv.), pentane, rt followed by Et<sub>3</sub>N•HCl, Et<sub>2</sub>O, 90%; ii) MgBr<sub>2</sub>• $[(18-cr-6)K]_{2}^{+}$ 7, Toluene, rt, 2 h, 68%. rt = room temperature.



Leaving group, silanide countercation, and solvent were investigated to determine influence of reaction conditions on diastereoselectivity (Table 2).38,47,48 Coupling of [(18-cr- $(6)K^{+}_{2}$  and 14 in toluene provided Si<sub>10</sub>Ph<sub>4</sub> in 10% yield with a 19:81 trans: cis ratio (entry 1). The assignment of diastereomers was based on X-ray crystallography (vide infra). Heating the reaction to 60 °C did not increase the yield, however, more trans-siladecalin was observed (entry 2). Magnesium bromide (MgBr<sub>2</sub>) was added to  $[(18-cr-6)K]^+_27$  to modify the countercation. The composition of this reagent has not been determined, but Marschner has shown the formation of Si<sub>2</sub>Mg species from potassium silanides and MgBr<sub>2</sub> (2 SiK + MgBr<sub>2</sub>  $\rightarrow$  $Si_2Mg + 2KBr$ ).<sup>49</sup> No reaction was observed between 14 and

MgBr<sub>2</sub>•[(18-cr-6)K] $^+_2$ 7, presumably due to the magnesium silanide's low solubility in toluene (entry 3). Attempts to investigate other solvents were thwarted by 14's poor compatibility with other solvents: upon addition of 14 to THF, an insoluble gel formed, presumably due to ring-opening polymerization of THF.

While coupling 8 with either  $[(18-cr-6)K]_{2}^{+}$  or CuCl<sub>2</sub>• $[(18-cr-6)K]_{2}^{+}$ cr-6)K]<sup>+</sup><sub>2</sub>7 in THF did not yield the desired product (entries 4-5), MgBr<sub>2</sub>•[(18-cr-6)K]<sup>+</sup><sub>2</sub>7 in THF provided Si<sub>10</sub>Ph<sub>4</sub> in 68% yield (entry 6). We also observed successful coupling of [(18- $(cr-6)K]_{2}^{+}7$  and 8 in toluene, providing the siladecalin in 50% yield (entry 7). Polymeric material was the major byproduct in all cases.

With the exception of the heated reaction (entry 2), all reactions yielded predominantly the *cis* diastereomer. While many details of this reaction remain to be elucidated, we suggest that a combination of the cis enrichment in 8 and 14 and an intramolecular tethering effect after formation of the first Si-Si bond contribute to the diastereoselectivity.

The ability to isolate samples enriched in the cis-siladecalin framework encouraged efforts to isolate a high purity sample of trans-Si<sub>10</sub>Ph<sub>4</sub>. We initially attempted separation techniques similar to those that had succeeded with 13; however, no separation was observed by silica gel chromatography. Chiral HPLC separation was also unsuccessful. Recrystallization of 67:33 trans: cis Si<sub>10</sub>Ph<sub>4</sub> in cold hexanes provided 88:12 *trans:cis* Si<sub>10</sub>Ph<sub>4</sub>, but further recrystallizations did not improve the trans: cis ratio.

Table 2. Investigation of Salt Metathesis Synthesis of Si<sub>10</sub>Ph<sub>4</sub>.



<sup>a</sup> SM = starting material. <sup>b</sup> dr = diastereometic ratio. <sup>c</sup> Reaction performed at 60 °C.

Thermodynamic equilibration ultimately allowed the isolation of 97:3 *trans:cis* Si<sub>10</sub>Ph<sub>4</sub>. Silanes are known to readily form pentavalent structures in the presence of anions that serve as a pathway for inversion of a tetrahedral center (Figure 4a).<sup>41,50</sup> Density functional theory (DFT) calculations suggested that *trans*-Si<sub>10</sub>Ph<sub>4</sub> is the lower energy isomer by 4.63 kcal mol<sup>-</sup> (Figure 4b). Further evidence that thermodynamic equilibration might be possible included the observation of a change in isomer ratio upon heating during exploratory studies towards  $Si_{10}Ph_4$  (Table 1, entry 1 vs 2). Hypercoordination is not expected to induce significant ring strain into the siladecalin

if the exocyclic substituents (methyl and anion) reside in the axial positions. However, a potential complication of anioninduced inversion was the known ability of organometallic reagents such as methyllithium (MeLi) and potassium tertbutoxide (KOt-Bu) to cleave Si-Si bonds. We therefore targeted the use of silanide reagents structurally related to  $Si_{10}Ph_4$  to equilibrate *cis*-Si<sub>10</sub>Ph<sub>4</sub> to *trans*-Si<sub>10</sub>Ph<sub>4</sub> and avoided nucleophiles like fluoride that might react irreversibly (Figure 4c).



Figure 4. Epimerization Studies. a) Hypothesis: anion-induced inversion via pentavalent intermediate or transition state. b) Calculated energy difference between cis-Si<sub>10</sub>Ph<sub>4</sub> and trans-Si<sub>10</sub>Ph<sub>4</sub> (B3LYP/6-31G(d)). c) Dianion 7 and monoanion 15 used for epimerization of Si<sub>10</sub>Ph<sub>4</sub>

Heating a 19:81 *trans:cis* sample of  $Si_{10}Ph_4$  in toluene alone or with neutral species such as KCl or 18-cr-6 did not change the *dr* (Table 3, Entries 1-4). However, heating a solution of  $[(18-cr-6)K]^+_27$  and  $Si_{10}Ph_4$  to 60 °C for three hours had a dramatic effect on *dr* (Table 2, entry 5). With 0.25 equivalents of  $[(18-cr-6)K]^+_27$ , a 97:3 *trans:cis* ratio was reached in ca. 3 hours. A lower anion loading (0.1 equivalents of  $[(18-cr-6)K]^+_27$ ) required 72 hours to obtain a 92:8 mixture of *trans*-Si<sub>10</sub>Ph<sub>4</sub>. In both cases, a small amount of an unidentified byproduct was seen by <sup>1</sup>H NMR spectroscopy, which does not correspond to  $[(18-cr-6)K]^+_27$ . Isolated yield with 0.1 loading of  $[(18-cr-6)K]^+_17$  is slightly lower than 0.25 equivalents. [(18 $cr-6)K]^+15$  also epimerized Si<sub>10</sub>Ph<sub>4</sub>; however, longer reaction times (4.33 h) and lower isolated yields (56%) were observed compared to  $[(18-cr-6)K]^+_27$ .

### Table 3. Anion-Induced Epimerization.



Entry	Additive	Time	Equiv.	dr (tuanavoia)
				(trans.cis)
1	None	1 h	-	19:81
2	KCl	1 h	2.0	19:81
3	18-crown-6	1 h	2.0	19:81
4	KCl, 18-crown-6	1 h	2.0	19:81
5	$[(18-cr-6)K]_{2}^{+}7$	3 h	0.25	97:3
6	$[(18-cr-6)K]_{2}^{+}7$	1 h	0.10	45:55
7	$[(18-cr-6)K]_{2}^{+}$	3 h	0.10	53:47
8	$[(18-cr-6)K]_{2}^{+}7$	24 h	0.10	69:31
9	$[(18-cr-6)K]_{2}^{+}7$	48 h	0.10	85:15
10	$[(18-cr-6)K]^+_27$	72 h	0.10	92:8
11	[(18-cr-6)K]+15	4.33 h	0.50	89:11
12	[(18-cr-6)K]+15	72 h	0.25	92:8

Through a combination of selective synthesis and postsynthetic equilibration, we discovered routes to the functionalized siladecalin  $Si_{10}Ph_4$  framework enriched in either the *cis* or the *trans* isomer. Each of these isomers could be further derivatized without significant erosion of the ring fusion relative stereochemistry (Scheme 3). Dearylation of 10:90 *trans:cis*  $Si_{10}Ph_4$  with TfOH and reduction with LAH provided 15:85 *trans:cis*  $Si_{10}Ph_4$  in 65% yield. Similar reaction conditions with 97:3 *trans:cis*  $Si_{10}Ph_4$  provided 95:5 *trans:cis*  $Si_{10}H_4$  in 68% yield.

#### Scheme 3. Synthesis of cis- and trans-Si<sub>10</sub>Ph<sub>4</sub>.



**2. Siladecalin X-Ray Crystallography.** Single crystal X-ray crystallography facilitated assignment of the *cis* and *trans* isomers of  $Si_{10}Ph_4$  and  $Si_{10}H_4$ . Crystallization of 67:33 *trans:cis*  $Si_{10}Ph_4$  in cold hexanes provided crystals enriched to 88:12 *trans:cis*  $Si_{10}Ph_4$ . Both diastereomers were found in the crystal structure. The occupancy factor matched the isomer ratio determined by <sup>1</sup>H NMR spectroscopy: the occupancy factor of the *trans*- $Si_{10}Ph_4$  isomer (major component) refines to 0.8867(13).

While DFT calculations predicted a chair-chair conformation for *trans*- $Si_{10}Ph_4$  in the gas phase (Figure 4b), in the solid state the SiPh<sub>2</sub> ring adopted a chair conformation, while the permethylated ring adopted a twist-boat conformation (Figure 5a,c). DFT calculations suggested that both the chair-chair and chair-twist conformers are energetic minima, in which the chair-chair conformer is lower in energy by 1.19 kcal mol<sup>-1</sup> (Figure S3). *cis*- $Si_{10}Ph_4$  also adopts a contorted geometry in the solid state (Figure 5b,d). The SiPh<sub>2</sub> ring adopted a chair conformation, but the permethylated ring adopted a half-chair



Figure 5. Displacement ellipsoid plots (50% probability level) of a) *trans*- and b) *cis*-Si<sub>10</sub>Ph<sub>4</sub>. Silicon frameworks of c) trans- and d) *cis*-Si<sub>10</sub>Ph<sub>4</sub> at 110(2) K. Black = carbon, blue = silicon. Hydrogens are omitted for clarity.

Crystals of *trans*- $Si_{10}H_4$  were grown by slowly cooling a hot acetonitrile solution of a 95:5 *trans:cis*  $Si_{10}H_4$ . In the solid state, *trans*- $Si_{10}H_4$  adopts a chair-chair conformation (Figure 6). X-ray diffraction quality crystals of *cis*- $Si_{10}H_4$  could not be grown.



Figure 6. Displacement ellipsoid plot (50% probability level) of *trans*- $Si_{10}H_4$  at 110(2) K. Black = carbon, blue = silicon, pink = hydrogen. Except for Si-H bonds, hydrogens are omitted for clarity. Disorder is omitted for clarity.

**3. Siladecalin Conformational Analysis.** Like carbocyclic decalin, a key difference between *cis*- and *trans*-siladecalin skeletons is that *cis* isomers can fully invert both rings simultaneously, while *trans* isomers are conformationally locked. Although the *trans* siladecalins are not able to invert both rings simultaneously, we expect that the individual rings may still contort and sample twist-boat conformers even at room temperature. This is supported by the X-ray crystallographic structures above which show both chair and twist-boat conformations in the solid state.

Prior work has shown that cyclohexasilanes are far more conformationally flexible than cyclohexanes. NMR studies of dodecamethylcyclohexasilane (Si<sub>6</sub>Me<sub>12</sub>) showed that axial and equatorial methyl resonances do not resolve until –165 °C, whereas much higher temperatures are typical for cyclohexanes (ca. –20 °C).<sup>51</sup> *Ab initio* calculations predict that the energy difference between chair and twist conformers of Si<sub>6</sub>Me<sub>12</sub>, and the barrier to twisting is smaller, than for cyclohexane.<sup>52</sup> Flock et al. provided evidence that twist-boat conformers contribute to the room temperature solid state Raman spectrum of  $Si_6Me_{12}$ .<sup>52</sup>

**4. Vibrational Spectroscopy.** Experimental ATR-FTIR spectra of neat 15:85 *trans:cis*  $Si_{10}H_4$  and 95:5 *trans:cis*  $Si_{10}H_4$  showed intriguing differences between isomers in the v(SiH) region (Figure 7). The 15:85 *trans:cis*  $Si_{10}H_4$  spectrum displayed two broad stretches at 2069 cm<sup>-1</sup> and 2085 cm<sup>-1</sup>. The 95:5 *trans:cis*  $Si_{10}H_4$  spectrum displayed three sharper resonances at 2089 cm<sup>-1</sup>, 2080 cm<sup>-1</sup>, and 2070 cm<sup>-1</sup>.



Figure 7. Experimental ATR-FTIR spectra of 95:5 *trans:cis*  $Si_{10}H_4$  (solid) and 15:85 *trans:cis*  $Si_{10}H_4$  (dashed).

Simulated IR spectra (B3LYP/6-31G(d)) were calculated to understand how configuration affects the vibrational spectra. For trans-Si<sub>10</sub>H<sub>4</sub>, we considered two conformations: the chairchair conformer seen in the crystal structure and a chair-twist conformer consistent with the crystal structure of Si<sub>10</sub>Ph<sub>4</sub> (Figure 8). Good overall agreement between theory and experiment was observed, with v(SiH) resonances predicted to fall between 2100 and 2050 cm<sup>-1</sup>. For trans-Si<sub>10</sub>H<sub>4</sub> in either conformer, the axial and equatorial Si-H bonds resonated at significantly different frequencies, with the equatorial v(SiH) approximately 20 cm<sup>-1</sup> lower frequency. These calculations suggest subtle but real differences in bond strength between axial and equatorial Si-H bonds in trans-Si<sub>10</sub>H<sub>4</sub>. Due to symmetry, both axial SiH groups have identical stretching frequencies and the same for equatorial SiH groups. Assuming that the rings in *trans*-Si<sub>10</sub>H<sub>4</sub> twist but don't fully invert, the experimental FTIR spectrum likely reflects a mixture of chair and twist isomers in which axial and equatorial SiH bonds have unique resonances. We found that all four Si-H bonds in cis- $Si_{10}H_4$  were predicted to have unique resonances due to the lower symmetry of the cis isomer. The overall greater conformational heterogeneity expected in the cis-Si<sub>10</sub>H<sub>4</sub> could explain the broad and featureless experimental IR spectrum.

Experimental ATR-FTIR spectra of diastereomeric  $Si_{10}Ph_4$  samples did not show isomer-dependent differences (Figure S4).



Figure 8. Calculated  $Si_{10}H_4$  structures and predicted v(SiH) frequencies. a) trans- $Si_{10}H_4$  (chair-chair conformer), b) trans- $Si_{10}H_4$  (chair-twist conformer), and c) cis- $Si_{10}H_4$  (chair-chair conformer). B3LYP/6-31G(d).

**5.** UV-Vis Spectroscopy. Oligosilane optical properties are strongly conformation dependent.<sup>53</sup> The HOMO-LUMO gap of linear silanes decreases as chain length increases, indicative of  $\sigma$ -conjugation.<sup>54</sup>  $\sigma$ -Conjugation is strongest in an all-*anti* conformation.<sup>55,56</sup> Deviations from the *anti* geometry contribute to short effective conjugation lengths and typical polysilanes absorb ultraviolet light  $\leq$ 350 nm<sup>57</sup> and silane dendrimers  $\leq$ 290 nm.<sup>58</sup>

The different conformational profiles of the *cis* and *trans* diastereomers suggested the possibility of stereoisomerdependent optical properties. We also expected to observe differences between aryl- and H-functionalized silanes. The absorbance spectra of aryl-substituted oligosilanes are generally bathochromically shifted compared to methylated oligosilanes due to  $\sigma,\pi$ -mixing and other effects.<sup>54,59,60</sup>

#### Table 4. Tabulated UV-vis spectral data.<sup>a</sup>

Compound	$\lambda(nm)$	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	
trans-Si10Ph4	192	235000	
	257	45600	
cis-Si <sub>10</sub> Ph <sub>4</sub>	193	194000	
trans-Si10H4	207	74300	
	240	21100	
	270	9230	
cis-Si10H4	293	*Onset of Absorption	

<sup>a</sup> Recorded in *n*-pentane at room temperature.

Absorbance spectra of all four siladecalins were obtained in *n*-pentane at room temperature (Table 4). We observed a ca. 20 nm bathochromic shift in *cis*-**Si**<sub>10</sub>**Ph**<sub>4</sub>'s onset of absorbance compared to *cis*-**Si**<sub>10</sub>**H**<sub>4</sub> (315 vs 293 nm) (Figure 9a). Time-dependent DFT calculations reproduced this trend (TD-PBE0/6-311G(d))/B3LYP/6-31G(d)) (Figure 9b). The calculated highest occupied molecular orbital of **Si**<sub>10</sub>**Ph**<sub>4</sub> showed minimal electron density on the aromatic rings. Indeed, the HOMO's of **Si**<sub>10</sub>**Ph**<sub>4</sub> and **Si**<sub>10</sub>**H**<sub>4</sub> were markedly similar and concentrated on the  $\sigma$ -framework (Figure S7). The change in onset of absorption is attributed to low-lying  $\pi^*$  orbitals centered on the aromatic rings (Figure S7 and Table S1), lending the Si<sub>10</sub>Ph<sub>4</sub> system more charge transfer character.

Significant differences were also observed between diastereomeric siladecalins. Both *cis*- and *trans*- $\mathbf{Si}_{10}\mathbf{H}_4$  absorb in the deep to mid ultraviolet (UV) region, up to ca. 300 nm (Figure 9c). The absorbance spectrum of *trans*- $\mathbf{Si}_{10}\mathbf{H}_4$  had three distinct transitions at 207 nm, 240 nm, and 270 nm. These features are similar to the absorbance spectrum of *trans*-siladecalin reported by West.<sup>20</sup> The absorbance spectrum of 15:85 *trans*: *cis*  $\mathbf{Si}_{10}\mathbf{H}_4$  was broad and largely featureless.

Simulated absorbance spectra were calculated (TD-PBE0/6-311G(d)//B3LYP/6-31G(d)). The onset of absorbance of pure *cis*-Si<sub>10</sub>H<sub>4</sub> was predicted to be 15 nm blue-shifted compared to *trans*-Si<sub>10</sub> $H_4$  (Figure 9d, dashed vs. solid black lines line). That we did not observe this experimentally may reflect the minor component of *trans*-Si<sub>10</sub>H<sub>4</sub> present in the synthetic sample. We found that both a HOMO to LUMO transition and HOMO-1 to LUMO+1 transition contribute to the broad chair/chair trans-Si<sub>10</sub>H<sub>4</sub> simulated spectrum (Table 5 and Figure 10). Curious to understand the origin of the three features in the experimental spectrum, we also calculated a simulated absorbance spectrum of *trans*- $Si_{10}H_4$  in a chair-twist conformation (Figure 9d, gray) and found an absorption spectrum with a  $\lambda_{max}$  of 223 nm corresponding to the HOMO-1 to LUMO+1 transition and a shoulder at 260 nm corresponding to the HOMO to LUMO transition (Table 5).

We conclude that the three features in 95:5 *trans*-Si<sub>10</sub>H<sub>4</sub> spectrum could correspond to the presence of both chair and twist ring conformers in the synthetic sample. Flock et al. found evidence of dodecamethylcyclohexasilane twist-boat conformers at room temperature by solid-state Raman spectroscopy.<sup>52</sup> Likewise, the broadness of the spectrum of majority *cis*-Si<sub>10</sub>H<sub>4</sub> could be a consequence of chair-flipping at room temperature. We finally note that the time-dependent DFT method used in this study was selected for its prior success in predicting optical properties of linear silanes<sup>61</sup>, but a different method may be optimal for cyclosilanes.

## Table 5. Details of Simulated Absorbance Spectra. TD-PBE0/6-311G(d)//B3LYP/6-31G(d).

Structure	$\lambda$ (nm)	Transition	% Contribution	Oscillator Strength
trans-Si10H4 (Chair/Chair)	233.19	HOMO-1 $\rightarrow$ LUMO+1	77%	0.1821
	257.00	HOMO → LUMO	96%	0.1496
trans-Si <sub>10</sub> H <sub>4</sub> (Chair/Twist)	228.32	HOMO-1→ LUMO+1	75%	0.0720
	260.21	HOMO → LUMO	96%	0.0813
cis-Si <sub>10</sub> H <sub>4</sub>	221.29	HOMO-4 → LUMO	66%	0.0432
	231.24	HOMO $\rightarrow$ LUMO+1	67%	0.0368



Figure 9. Experimental and simulated absorbance spectra. Comparison of Ph- and H-functionalized siladecalins. (a) Absorbance spectra of 15:85 *trans:cis*  $Si_{10}H_4$  (solid) and 10:90 *trans:cis*  $Si_{10}Ph_4$  (dashed) in *n*-pentane. [compound] = 5 x 10<sup>-6</sup> M. (b) Calculated absorbance spectra of *cis*- $Si_{10}Ph_4$  (dashed), *cis*- $Si_{10}H_4$  (solid). TD-PBE0/6-311G(d)//B3LYP/6-31G(d). Comparison of cis- and trans- $Si_{10}H_4$ . (c) Absorbance spectra of 95:5 *trans:cis*  $Si_{10}H_4$  (solid) and 15:85 *trans:cis*  $Si_{10}H_4$  (dashed) in *n*-pentane. *n*-Pentane spectral cutoff is 190 nm. [compound] = 5 x 10<sup>-6</sup> M. (d) Calculated absorbance spectra of *cis*- $Si_{10}H_4$  (dashed), *chair/chair trans*- $Si_{10}H_4$  (solid black), and *chair/twist-boat trans*- $Si_{10}H_4$  (solid gray). TD-PBE0/6-311G(d)//B3LYP/6-31G(d).



Figure 10. Calculated HOMO, HOMO-1, LUMO and LUMO+1 of *trans*- $Si_{10}H_4$ . TD-PBE0/6-311G(d)//B3LYP/6-31G(d). Molecular orbitals are visualized with an isodensity value of 0.04.

**6. NMR Spectroscopy.** Polycyclic systems can exhibit unusual NMR spectra. *cis*-Decalin undergoes rapid ring-flipping, resulting in coalescence of the signals corresponding to axial and equatorial substituents. However, *trans*-decalin does not ring flip and its <sup>1</sup>H NMR spectrum shows closely overlapping peaks assigned to inequivalent axial and equatorial protons. <sup>30,31</sup>

All *cis*- and *trans*-siladecalins isolated herein have sharp signals in their <sup>1</sup>H NMR spectra. Cropped <sup>1</sup>H NMR spectra of *cis*- and *trans*- $Si_{10}H_4$  are shown in Figure 11, focusing on the SiH region of the spectrum. Some remarkable differences are observed. The *cis*- $Si_{10}H_4$  has a single sharp peak (Figure 11, pink). We attribute this to rapid chair-flipping and coalescence of axial and equatorial SiH groups.

In contrast, the *trans*- $\mathbf{Si}_{10}\mathbf{H}_4$  has two distinct resonances: a doublet ( $\delta$  3.42, J = 2.1 Hz) and a multiplet ( $\delta$  3.35) (Figure 11, blue). Both peaks integrate to 2H and are thought to correspond

to axial and equatorial SiH's. NOESY spectroscopy was inconclusive in assigning each peak to the axial or the equatorial position.

The splitting patterns provided additional insight facilitating assignment. Long-range ( $>^3$ J) <sup>1</sup>H-<sup>1</sup>H coupling in saturated systems is typically weak, with the exception of rigid cyclic systems that achieve particularly favorable geometric alignments.<sup>62–64</sup> W-coupling refers to a coplanar, *anti*-alignment of H-C-C-C-H bonds that results in detectable long-range coupling and has been identified in 1,3-functionalized cyclohexanes and in bicyclo[1.1.1]pentane scaffolds (Figure 12).<sup>65,66</sup> Of particular resonance with the present study, Spencer et al. reported W-coupling as a diagnostic tool in the identification of *cis*- and *trans*-decalins bearing angular methyl groups: the freely rotating methyl group in *trans*-10-methyldecalin has multiple W-coupled pathways with axial protons, while *cis*-10-methyldecalin does not.<sup>67</sup> This results in

significant line broadening of the angular methyl resonance in the *trans* isomer compared to the *cis*.



Figure 11. Cropped <sup>1</sup>H NMR spectra (400 MHz,  $C_6D_6$ ) of 95:5 *trans:cis* Si<sub>10</sub>H<sub>4</sub>(top) and 15:85 *trans:cis* Si<sub>10</sub>H<sub>4</sub>(bottom). Only Si-H region shown for clarity.



Only H<sup>a</sup> is geometrically aligned for W-coupling

Figure 12. a) Examples of W-coupling in carbocyclic systems. b) Conformational analysis of W-coupling in *trans*-**Si**<sub>10</sub>**H**<sub>4</sub>. For clarity, groups not implicated in W-coupling are omitted. <sup>4</sup>J = fourbond <sup>1</sup>H-<sup>1</sup>H coupling constant;  $W_{h/2}$  = line width at half-height of angular methyl groups. For comparison, TMS  $W_{h/2}$  = 0.33 Hz. Values from references <sup>65–67</sup>.

In *trans*-**Si**<sub>10</sub>**H**<sub>4</sub>, only the axial proton is poised to undergo Wcoupling with neighboring methyl groups (H-Si-Si-C-H, Figure 12). We therefore assigned the  $\delta$  3.35 multiplet to the axial Si-H. The  $\delta$  3.42 resonance was assigned to the equatorial proton and we suggest that the splitting pattern is dominated by geminal (<sup>2</sup>J) coupling to the axial Si-H.

## Conclusions

Herein we describe stereocontrolled syntheses of several members of a family of *cis*- and *trans*-siladecalins. We access functionalized materials that may serve as useful building blocks to higher order materials.<sup>36,38,68,69</sup> The identity of the countercation in the key salt metathesis step effects diastereoselectivity, favoring the *cis* isomer. Equilibration to the thermodynamically lower energy trans isomer with an anionic additive was described. Structural assignments are supported by X-ray crystallography.

Divergent conformational properties are expected for *cis* and *trans* siladecalin scaffolds, which are supported by NMR spectroscopy. Relative stereochemistry influences conformational properties, resulting in a strong effect on optical properties. The highly flexible *cis*-siladecalins have broad, featureless absorption spectra. The less dynamic *trans*-siladecalin frameworks have multiple sharp features, which are proposed to reflect contributions from chair/chair, chair/twist, and twist/twist conformers.

Stereocontrolled synthesis is a powerful tool for the preparation of well-defined materials with novel properties. We expect the synthetic approach outlined herein to facilitate the synthesis of more examples of cyclosilanes bearing multiple chiral silicon centers.

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures, tabulated characterization data, copies of <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra, supplemental figures, details of experimental procedures, details of computational chemistry (PDF)

X-ray crystallographic data for 13,  $Si_{10}Ph_4$ , and  $Si_{10}H_4$  (CIF)

Original <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of new compounds (FID)

## **AUTHOR INFORMATION**

## **Corresponding Author**

\* klausen@jhu.edu

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