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## Introduction

We recently became interested in the reactivity of catalytically generated silicon electrophiles towards cyclopropane derivatives.<sup>1–3</sup> Our investigations typically comprise  $B(C_6F_5)_3$ /hydrosilane combinations<sup>4</sup> and silylium-ion-like reactants<sup>5</sup> emerging from hydrosilanes and the trityl salt  $Ph_3C^+[B(C_6F_5)_4]^-$  as an initiator. VCPs as substrates specifically caught our attention because these versatile building blocks can react in diverse ways.<sup>6</sup> This is also true for their reactions with silicon electrophiles (Scheme 1, top).<sup>2,3</sup> These reactions involve the intermediacy of  $\beta$ -silicon-stabilized<sup>7</sup> cyclopropylcarbanyl cations<sup>8</sup> with different counteranions (gray boxes). Depending on the hydride source, the outcomes could not be more different. For aryl-substituted VCPs, the  $B(C_6F_5)_3$ -catalyzed hydrosilylation proceeds generally with little ring opening (top left).<sup>2</sup> In contrast, treatment of these VCPs with  $Ph_3C^+[B(C_6F_5)_4]^-$  in the presence of various hydrosilanes affords silicon-containing six-membered rings as a result of a formal (5 + 1) cycloaddition accompanied by an aryl migration (top right).<sup>3</sup> The situation changes again when replacing the aryl substituent by a benzyl group (Scheme 1, bottom). The additional methylene group makes a huge difference. The hydrosilylation under  $B(C_6F_5)_3$  catalysis is now plagued with ring opening, likely due to poorer stabilization of the carbocation intermediate (bottom left).<sup>2</sup> Strikingly, the silylium-ion-promoted

# Intramolecular Friedel–Crafts alkylation with a silylium-ion-activated cyclopropyl group: formation of tricyclic ring systems from benzyl-substituted vinylcyclopropanes and hydrosilanes†

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A trityl-cation-initiated annulation of benzyl-substituted vinylcyclopropanes (VCPs) with hydrosilanes is reported. Two Si–C(sp<sup>3</sup>) bonds and one C(sp<sup>2</sup>)–C(sp<sup>3</sup>) bond are formed in this process where an intramolecular 6-*endo-tet* Friedel–Crafts alkylation of a silylium-ion-activated cyclopropane ring is the rate-determining key step. The reaction mechanism is proposed based on computations and is in agreement with experimental observations. The new reaction leads to an unprecedented silicon-containing 6/6/5-fused ring system. A phenethyl-substituted VCP derivative yields another unknown tricyclic ring fusion by reacting in a related but different way involving a 6-*exo-tet* ring closure.

setup gives rise to yet another product where the aryl group becomes part of the product's ring system (bottom right). We report here a new trityl-cation-initiated cycloaddition of benzyl-substituted VCPs and hydrosilanes involving an intramolecular Friedel–Crafts alkylation. Our study includes a full experimental and computational mechanistic analysis.

## Results and discussion

Using 2 mol% of  $Ph_3C^+[B(C_6F_5)_4]^-$  as an initiator, we began investigating the reaction of VCP **1a** and excess  $Et_2SiH_2$  (**2a**) in

### Phenyl-substituted VCP in the reaction with silicon electrophiles



### Benzyl-substituted VCP in the reaction with silicon electrophiles

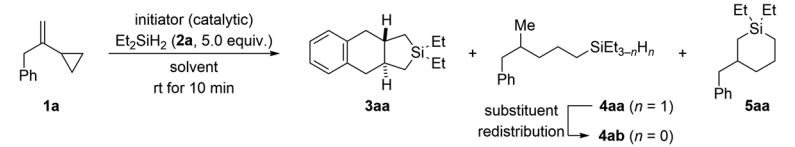


**Scheme 1** Diverse outcomes from the reaction of phenyl- and benzyl-substituted VCPs and hydrosilanes ( $R_3SiH = 3^\circ, 2^\circ,$  and  $1^\circ$  hydrosilanes with  $R =$  alkyl and/or aryl).

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Table 1 Optimization of the trityl-cation-initiated cycloaddition<sup>a</sup>


Entry	Initiator (mol%)	Solvent	Yield <sup>b</sup> (%)		
			3aa	4aa/4ab	5aa
1	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (2.0 mol%)	Benzene	51	34	9
2 <sup>c</sup>	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (2.0 mol%)	Toluene- <i>d</i> <sub>8</sub>	61	26	9
3 <sup>d</sup>	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (2.0 mol%)	Benzene	41	47	8
4 <sup>e</sup>	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (1.0 mol%)	Benzene	28	28	<5
5	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (5.0 mol%)	Benzene	55	30	13
6 <sup>f</sup>	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (2.0 mol%)	Benzene	52	33	11
7	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (2.0 mol%)	Chlorobenzene	56	20	14
8	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (2.0 mol%)	1,2-C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	61	19	9
9	Ph <sub>3</sub> C <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> (2.0 mol%)	Toluene- <i>d</i> <sub>8</sub>	65	21	13
10	Et <sub>3</sub> Si <sup>+</sup> [CHB <sub>11</sub> H <sub>5</sub> Br <sub>6</sub> ] <sup>-</sup> (2.0 mol%)	Toluene- <i>d</i> <sub>8</sub>	50	23	25
11	[(C <sub>6</sub> H <sub>6</sub> )·H] <sup>+</sup> [CHB <sub>11</sub> H <sub>5</sub> Br <sub>6</sub> ] <sup>-</sup> (2.0 mol%)	Toluene- <i>d</i> <sub>8</sub>	48	26	23

<sup>a</sup> All reactions were performed with VCP **1a** (0.10 mmol) and the indicated amounts of the initiator and Et<sub>3</sub>SiH<sub>2</sub> (**2a**) under argon atmosphere in the indicated arene solvent (0.5 mL, 0.2 M) at room temperature. Unless otherwise noted, conversion was greater than 95% for each entry as estimated by <sup>1</sup>H NMR spectroscopy using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. <sup>b</sup> Yields were estimated by <sup>1</sup>H NMR spectroscopy using CH<sub>2</sub>Br<sub>2</sub> as an internal standard and tend to be too high because of the long relaxation time of CH<sub>2</sub>Br<sub>2</sub>. <sup>c</sup> 1.0 equiv. of norbornene used. <sup>d</sup> 2.0 equiv. of Et<sub>3</sub>SiH<sub>2</sub> (**2a**) used. <sup>e</sup> 39% of VCP **1a** recovered. <sup>f</sup> Performed at 0.1 M.

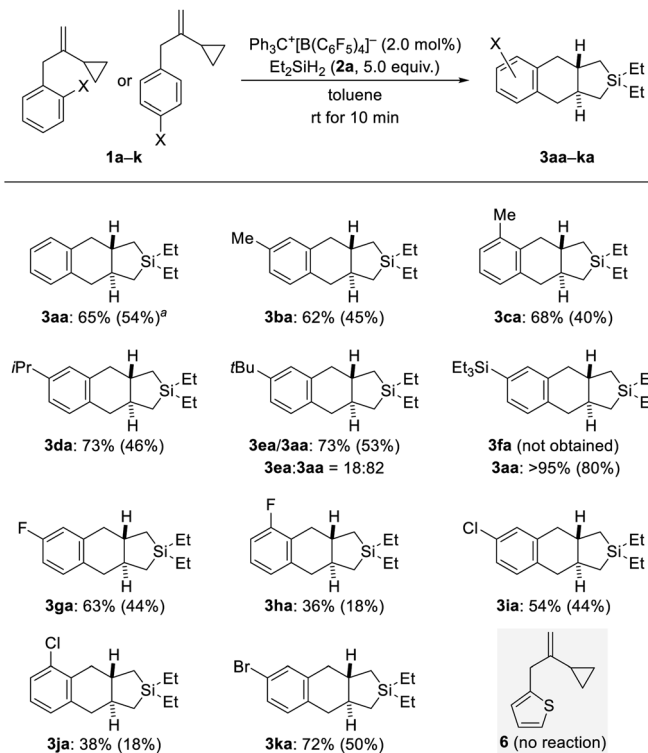
various arene solvents at ambient temperature (Table 1). In benzene as solvent, 2,2-diethyl-2,3,3a,4,9,9a-hexahydro-1*H*-naphtho[2,3-*c*]silole (**3aa**) was found as the major product along with ring-opened 4-methyl-5-phenylpentyl-substituted silane **4ab** and six-membered ring system **5aa** (entry 1). As ring-opening hydrosilylation would yield an unsaturated compound,<sup>1</sup> we speculated that the formation of saturated **4ab** (through initially formed **4aa**)<sup>9,10</sup> involves an additional alkene hydrogenation by protonation of the VCP to form a cyclopropylcarbiny cation followed by hydride transfer from the hydrosilane. The proton could be released from a Wheland intermediate in the course of an assumed Friedel–Crafts reaction. Addition of norbornene as a proton scavenger had no effect though (entry 2). In turn, the silicon-containing ring system **5aa** could be the result of the aforementioned silylium-ion-promoted hydrosilylation of cyclopropanes<sup>1</sup> coupled with an *endo* cyclization of an allylbenzene intermediate (see discussion of the mechanism).

A diminished yield was observed at a lower loading of the dihydrosilane (2.0 instead of 5.0 equiv.; entry 3). Poor conversion was seen with less initiator; the product distribution was also affected unfavorably at 1.0 mol% catalyst loading (entry 4). More of Ph<sub>3</sub>C<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> was without effect (entry 5). Likewise, the reaction outcome did not change at lower concentration (0.1 M instead of 0.2 M; entry 6). The solvent had a minor effect on the ratio of **3aa**, **4ab**, and **5aa** (entries 7–9), and we eventually proceeded with toluene for the highest overall yield. In accordance with our mechanistic picture, both the counteranion-stabilized silylium ion Et<sub>3</sub>Si<sup>+</sup>[CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>]<sup>-</sup> (ref. 11) and the benzenium ion [(C<sub>6</sub>H<sub>6</sub>)·H]<sup>+</sup>[CHB<sub>11</sub>H<sub>5</sub>Br<sub>6</sub>]<sup>-</sup> (ref. 12) could also

be used to initiate this cycloaddition, yet with more pronounced formation of undesired cyclic **5aa** (entries 10 and 11).

With the optimized protocol in hand (Table 1, entry 9), we probed the substrate scope (Schemes 2–4). Electronic and steric effects of the substituent on the aryl group were examined with VCPs **1a–k** (*ortho* and *para*, Scheme 2) and **1l–o** (*meta*, Scheme 3). Parent VCP **1a** afforded the cycloadduct **3aa** in 54% isolated yield. Yields were moderate for VCPs with aryl rings bearing an electron-donating methyl or isopropyl group; the position of the substituent made no difference (**1b–d** → **3ba–da**). VCP **1e** decorated with a *tert*-butyl group did participate equally well but underwent predominant *de-tert*-butylation<sup>13</sup> to mainly afford **3aa** rather than **3ea**. Similarly, Et<sub>3</sub>Si-substituted **1f** suffered complete desilylation<sup>14</sup> with none of **3fa** being formed. Interestingly, the isolated yield of 80% for **3aa** was significantly higher than that obtained for the parent system (54% for **1a** → **3aa**). We explain this with loss of a silylium ion instead of a proton, thus eliminating the aforementioned formation of the saturated byproducts **4aa** and **4ab**. This finding not only provides a solution of how to bypass unwanted alkene protonation but is also evidence for the intermediacy of Wheland complexes and as such a Friedel–Crafts-type mechanism. Halogen atoms were tolerated in this reaction but there was a clear difference between *ortho*- and *para*-substituted VCP derivatives (**1g–k** → **3ga–ka**). Yields were moderate for the *para*- and low for the *ortho*-halogenated substrates (the preparation of the *ortho*-bromine-substituted VCP was unsuccessful). Both electronic and steric effects could be responsible for that. Besides, we also subjected VCP **6** with a thien-2-yl instead of the phenyl group to the procedure but did

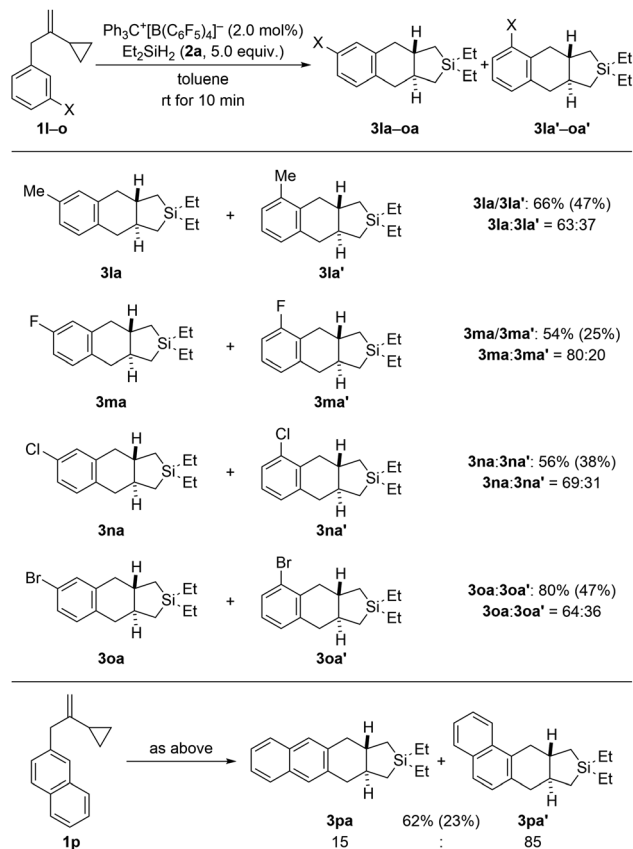




**Scheme 2** Scope I: variation of the *ortho*- and *para*-substituent of the benzyl group in VCPs **1**. All reactions were performed on 0.30 mmol scale unless noted otherwise. Conversion was generally greater than 95% as estimated by <sup>1</sup>H NMR spectroscopy using CH<sub>2</sub>Br<sub>2</sub> as an internal standard. Yields were estimated by <sup>1</sup>H NMR spectroscopy using CH<sub>2</sub>Br<sub>2</sub> as an internal standard and tend to be too high because of the long relaxation time of CH<sub>2</sub>Br<sub>2</sub>; isolated yields in parentheses are of analytically pure material after flash chromatography on silica gel. <sup>a</sup>65% (48%) on a 1.2 mmol scale.

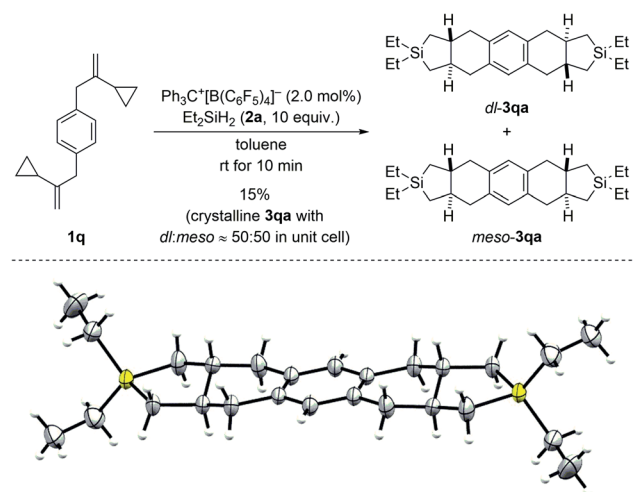
not obtain the cycloadduct; **6** was almost completely recovered (gray box, Scheme 2).

Regioisomeric mixtures of the cycloadducts were generated when starting from representative VCPs with *meta*-substituted aryl groups (**1l-o** → **3la-oa/3la'-oa'**, Scheme 3, top). Bond formation occurred preferentially in the less hindered *ortho*-position with regioisomeric ratios ranging from 63 : 37 to 80 : 20. Conversely, VCP **1p** with a naphth-2-yl group yielded the kinetically favored, more hindered cycloadduct **3pa'** with good regiocontrol (Scheme 3, bottom). The cycloaddition of a bis(vinylcyclopropane) system was also tested (**1q** → **3qa/3qa'**, Scheme 4, top); *para*-substituted **1q** would first convert into a *meta,para*-disubstituted intermediate (not shown) which, in turn, would then give rise to a mixture of the regioisomers **3qa** and **3qa'** (not shown) in the second cycloaddition event. A complex reaction mixture was experimentally found, and the separation by various chromatography methods failed. Part of the problem is that **3qa** is formed as a mixture of racemic *dl* and *meso* diastereomers in approximately 50 : 50 ratio; the same likely applies to regioisomeric **3qa'** which we were not able to isolate (not shown). Slow evaporation of a solution of that regio- and diastereomeric mixture (four compounds; assuming only *trans* and no *cis* annulation) in ethyl acetate and cyclohexane



**Scheme 3** Scope II: variation of the *meta*-substituent of the benzyl group in VCPs **1**. See caption of Scheme 2 for further details. Regioisomeric ratios determined by <sup>1</sup>H NMR spectroscopy after purification.

(1 : 1) eventually led to the co-crystallization of bis-*trans*-isomers *dl*-**3qa** and *meso*-**3qa**. The *meso* compound is depicted in Scheme 4 (bottom; see the ESI<sup>†</sup> for details).<sup>15</sup> The relative



**Scheme 4** Scope III: reaction of a bis(VCP) system (top; see caption of Scheme 2 for further details) and molecular structure of the bis-*trans*-isomer *meso*-**3qa** (bottom; thermal ellipsoids are shown at the 50% probability level).







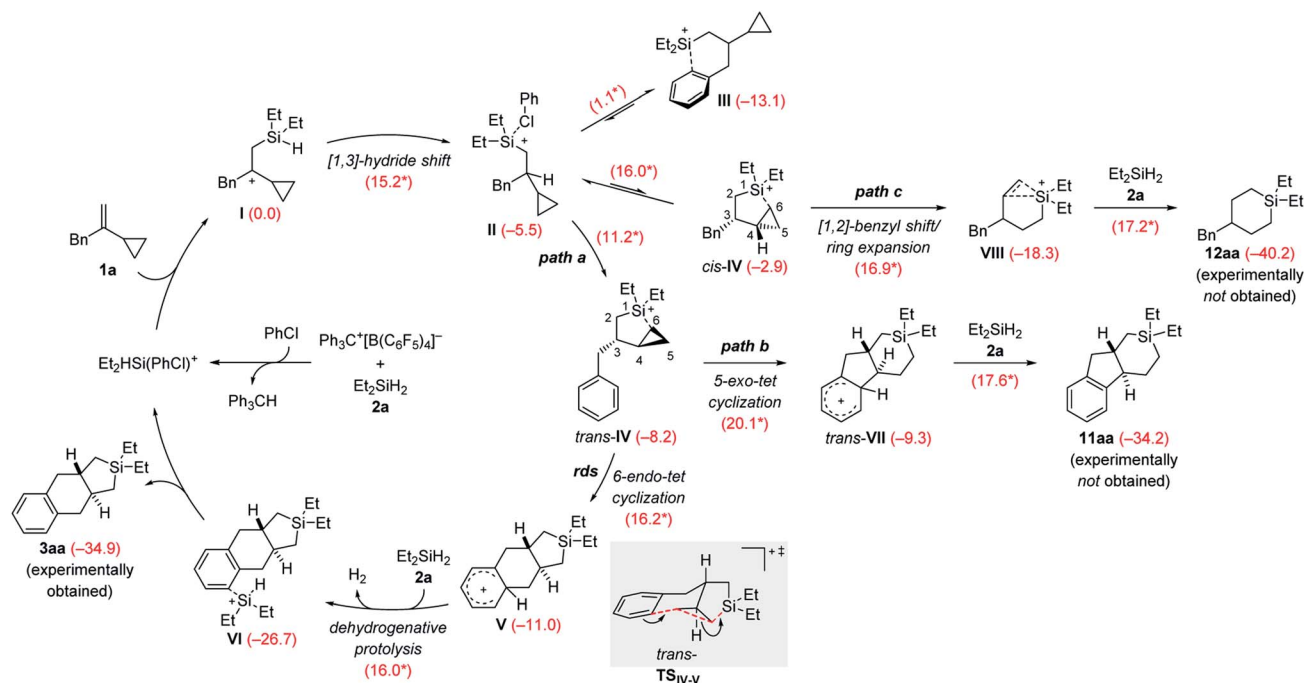
The rough mechanistic picture was refined by density functional theory (DFT) calculations at the M062X/cc-PVTZ//M062X/6-31G(d,p) level.<sup>20</sup> Computations were performed on the model reaction of VCP **1a** and Et<sub>2</sub>SiH<sub>2</sub> (**2a**) with Ph<sub>3</sub>C<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> as the initiator (Scheme 9; see the ESI for details and Fig. S85 and S86† for the free-energy profiles and the optimized structures). The solvent effect was taken into consideration using a polarizable continuum model (PCM)<sup>21</sup> for both geometry optimizations and single-point energy calculations. Chlorobenzene was chosen to avoid the complexity of possible proton exchange between Wheland intermediates and toluene. The cycloadduct **3aa** is obtained in moderate yield in chlorobenzene (Table 1, entry 7). We have previously shown that β-silicon-stabilized cyclopropylcarbanyl cation **I**, generated from the association of VCP **1a** and the hydrogen-substituted silylium ion [Et<sub>2</sub>HSi(PhCl)]<sup>+</sup>, is much more stable than other donor-stabilized silylium ions such as the corresponding chlorobenzene-, hydrosilane-, or cyclopropane-stabilized systems.<sup>3</sup> Unless otherwise noted, adduct **I** is considered the reference minimum for the estimation of the relative energy of intermediates or transition states calculated here.

The β-silylcarbenium ion **I** then undergoes an intramolecular [1,3]-hydride shift from the silicon atom to the benzylic carbon atom to arrive at the chlorobenzene-stabilized silylium ion **II** over a barrier of 15.2 kcal mol<sup>-1</sup>. We also calculated the potential intermolecular hydride transfer from Et<sub>2</sub>SiH<sub>2</sub> (**2a**) to **I** but this pathway can be excluded because of an energetically higher transition state (19.0 *versus* 15.2 kcal mol<sup>-1</sup>, Fig. S84 in the ESI†). Subsequent reorganization can lead to several intramolecularly donor-stabilized silylium ions **III**

(arene stabilization; see ref. 16*b* for a crystallographically characterized derivative) and *cis*-**IV**/*trans*-**IV** (cyclopropane stabilization with *cis*- or *trans*-configuration). In the case of benzyl-substituted VCPs, **III** is much more stable than either of the two cyclopropane-stabilized silylium ions **IV**. Conversion of **III** into *cis*-**IV** or *trans*-**IV** requires an activation barrier of 16.0 and 11.2 kcal mol<sup>-1</sup>, respectively. The *trans*-isomer is kinetically and thermodynamically more accessible than the *cis*-isomer. It is therefore *trans*-**IV** which engages in a subsequent intramolecular Friedel-Crafts alkylation reaction of a silylium-ion-activated cyclopropane ring.<sup>18</sup>

A 6-*endo-tet* ring closure by nucleophilic attack of the phenyl group at C5 with concomitant cleavage of the distal C5-C6 bond and formation of a bond between C6 and the silicon atom leads to tricyclic Wheland intermediate **V** (path a). This process through transition state *trans*-**TS**<sub>IV-V</sub> (gray box) is exergonic by -2.8 kcal mol<sup>-1</sup> with an activation barrier of 16.2 kcal mol<sup>-1</sup>. It is also the rate-determining step, consistent with the rapid reaction rate at room temperature. The Brønsted acid **V** reacts with hydrosilane **2a** by dehydrogenative protolysis<sup>17,22</sup> to form the experimentally obtained product **3aa** via **VI** along with dihydrogen and the chlorobenzene-stabilized silylium-ion catalyst (Δ*G*<sup>‡</sup> = 16.0 kcal mol<sup>-1</sup>). The overall Gibbs free energy change Δ*G* is -34.9 kcal mol<sup>-1</sup> (calculated from the Gibbs energy difference between **3aa** and **1a/2a**). Based on transition state *trans*-**TS**<sub>IV-V</sub>, the predicted relative configuration of **3aa** is *trans*, and is supported by <sup>1</sup>H NMR spectroscopy (<sup>3</sup>*J*<sub>H,H</sub> = 11.7 Hz) and was eventually confirmed by X-ray diffraction (Scheme 4, bottom).

We considered other kinetically less favorable pathways such as the 5-*exo-tet* cyclization (path b, cleavage of the proximal



**Scheme 9** Catalytic cycle of the silylium-ion-promoted cycloaddition of VCP **1a** and Et<sub>2</sub>SiH<sub>2</sub> (**2a**). For each reaction step, the Gibbs free reaction energies and barriers (labeled with an asterisk) in kcal mol<sup>-1</sup> were computed with the M06-2X functional (see the ESI† for details). rds = rate-determining step.





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