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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^3) bonds and one C(sp^2)–C(sp^3) 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 tricycle having 6/6/6 ring fusion by reacting in a related but different way involving a 6-*exo-tet* ring closure.

Introduction

We recently became interested in the reactivity of catalytically generated silicon electrophiles towards cyclopropane derivatives.[1–3] Our investigations typically comprise B(C$_6$F$_5$)$_3$/hydrosilane combinations[4] and silylium-ion-like reactants[5] emerging from hydrosilanes and the trityl salt Ph$_3$C$^+$[B(C$_6$F$_5$)$_4$]$^-$ as an initiator. VCPs as substrates specifically caught our attention because these versatile building blocks can react in diverse ways.[6] This is also true for their reactions with silicon electrophiles (Scheme 1, top).[2,3] These reactions involve the intermediacy of β-silicon-stabilized[7] cyclopropylcarbinyl cations[8] with different counteranions (gray boxes). Depending on the hydride source, the outcomes could not be more different. For aryl-substituted VCPs, the B(C$_6$F$_5$)$_3$-catalyzed hydrosilylation proceeds generally with little ring opening (top left).[2] In contrast, treatment of these VCPs with Ph$_3$C$^+$[B(C$_6$F$_5$)$_4$]$^-$ 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).[3] 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$_6$F$_5$)$_3$ catalysis is now plagued with ring opening, likely due to poorer stabilization of the carbocation intermediate (bottom left).[2] Strikingly, the silylium-ion-promoted

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$_3$C$^+$[B(C$_6$F$_5$)$_4$]$^-$ as an initiator, we began investigating the reaction of VCP **1a** and excess Et$_2$SiH$_2$ (**2a**) in
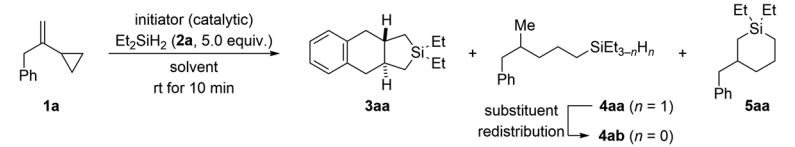

Scheme 1 Diverse outcomes from the reaction of phenyl- and benzyl-substituted VCPs and hydrosilanes (R$_3$SiH = 3°, 2°, and 1° hydrosilanes with R = alkyl and/or aryl).

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Table 1 Optimization of the trityl-cation-initiated cycloaddition[a]

Entry	Initiator (mol%)	Solvent	Yield[b] (%)		
			3aa	**4aa/4ab**	**5aa**
1	$Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%)	Benzene	51	34	9
2[c]	$Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%)	Toluene-d_8	61	26	9
3[d]	$Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%)	Benzene	41	47	8
4[e]	$Ph_3C^+[B(C_6F_5)_4]^-$ (1.0 mol%)	Benzene	28	28	<5
5	$Ph_3C^+[B(C_6F_5)_4]^-$ (5.0 mol%)	Benzene	55	30	13
6[f]	$Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%)	Benzene	52	33	11
7	$Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%)	Chlorobenzene	56	20	14
8	$Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%)	1,2-$C_6H_4Cl_2$	61	19	9
9	$Ph_3C^+[B(C_6F_5)_4]^-$ (2.0 mol%)	Toluene-d_8	65	21	13
10	$Et_3Si^+[CHB_{11}H_5Br_6]^-$ (2.0 mol%)	Toluene-d_8	50	23	25
11	$[(C_6H_6)\cdot H]^+[CHB_{11}H_5Br_6]^-$ (2.0 mol%)	Toluene-d_8	48	26	23

[a] All reactions were performed with VCP **1a** (0.10 mmol) and the indicated amounts of the initiator and Et_2SiH_2 (**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 ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. [b] Yields were estimated by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard and tend to be too high because of the long relaxation time of CH_2Br_2. [c] 1.0 equiv. of norbornene used. [d] 2.0 equiv. of Et_2SiH_2 (**2a**) used. [e] 39% of VCP **1a** recovered. [f] 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-1H-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,[1] we speculated that the formation of saturated **4ab** (through initially formed **4aa**)[9,10] involves an additional alkene hydrogenation by protonation of the VCP to form a cyclo-propylcarbinyl 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[1] 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 $Ph_3C^+[B(C_6F_5)_4]^-$ 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 $Et_3Si^+[CHB_{11}H_5Br_6]^-$ (ref. 11) and the benzenium ion $[(C_6H_6)\cdot H]^+[CHB_{11}H_5Br_6]^-$ (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[13] to mainly afford **3aa** rather than **3ea**. Similarly, Et_3Si-substituted **1f** suffered complete desilylation[14] 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
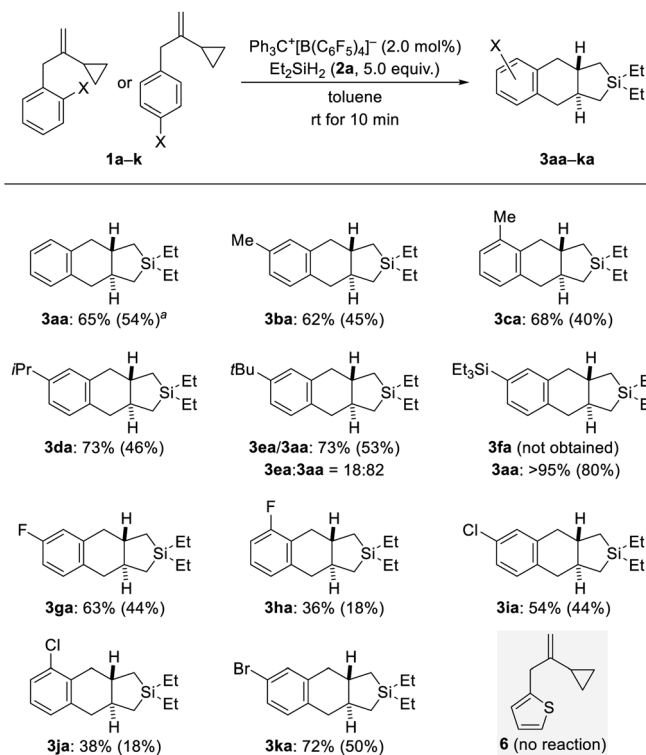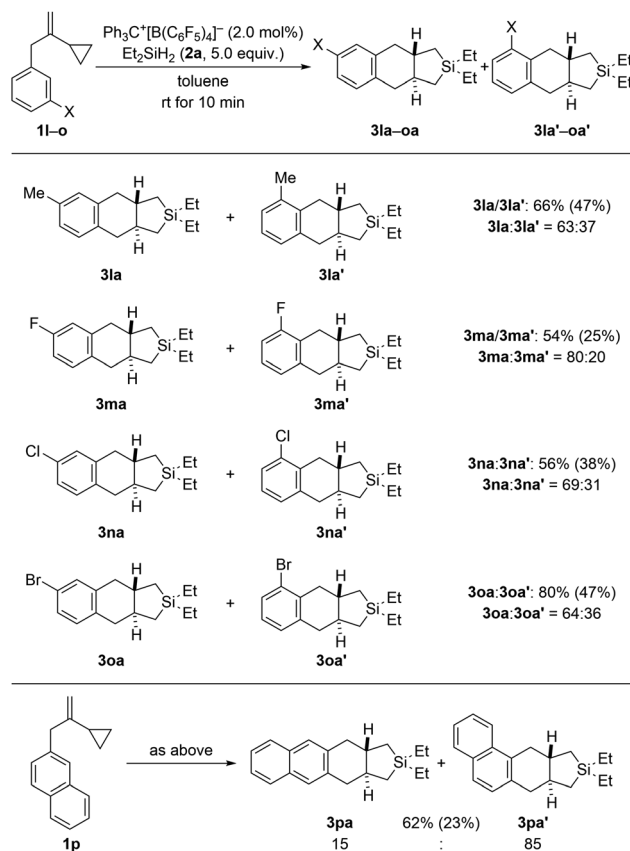
Scheme 2 Scope I: variation of the *ortho*- and *para*-substituent of the benzyl group in VCPs **1**. All reactions were performed on 0.30 mmol scale unless noted otherwise. Conversion was generally greater than 95% as estimated by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard. Yields were estimated by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard and tend to be too high because of the long relaxation time of CH_2Br_2; isolated yields in parentheses are of analytically pure material after flash chromatography on silica gel. [a]65% (48%) on a 1.2 mmol scale.

Scheme 3 Scope II: variation of the *meta*-substituent of the benzyl group in VCPs **1**. See caption of Scheme 2 for further details. Regio-isomeric ratios determined by ^{1}H NMR spectroscopy after purification.

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

(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† for details).[15] The relative
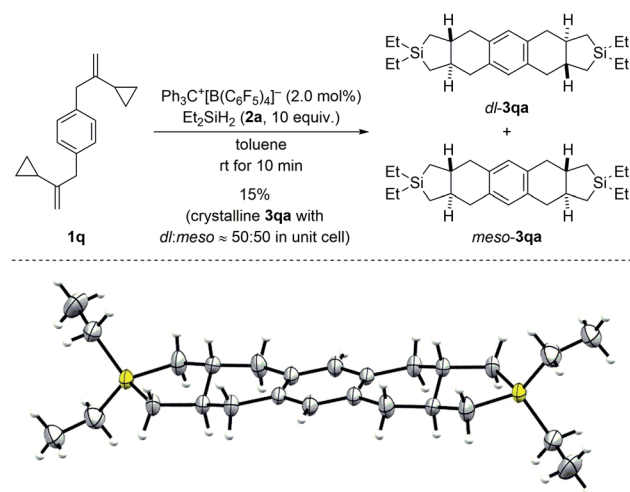
Scheme 4 Scope III: reaction of a bis(VCP) system (top; see caption of Scheme 2 for further details) and molecular structure of the bis-*trans*-isomer *meso*-**3qa** (bottom; thermal ellipsoids are shown at the 50% probability level).

configuration of all annulation products was deduced from this molecular structure and assigned as *trans*, thereby confirming the result obtained from recorded and simulated ^{1}H NMR spectra.

In our previous study (see Scheme 1, top right),[3] we had already shown that, apart from dihydrosilanes, mono-hydrosilanes can be used with similar success. The reason for this is the ability of silylium ions to cleave Si–C(sp^3) as well as Si–C(sp^2) bonds,[16,17] corresponding to an exchange of alkyl or aryl group between two silicon centers.[9] Hence, when there is no Si–H bond available (as in a quaternary silane) an alkyl or aryl group can be abstracted by another silylium ion (*cf.* the ESI† of ref. 3). We therefore tested a few tertiary hydrosilanes (**2b–d**) in the cycloaddition of model VCP **1a** (Scheme 5). As expected, Et$_3$SiH (**2b**) afforded the same product **3aa** as obtained with Et$_2$SiH$_2$ (**2a**) albeit in lower yield. Demethylation was again preferred over cleavage of an ethyl group with EtMe$_2$SiH (**2c**). Dearylation occurred when employing Me$_2$PhSiH (**2d**). These observations are in line with those made earlier.[3,16,17]

The results with the phenyl-substituted VCPs[3] and those with a benzyl substituent (see Scheme 1, bottom) underscore the structural richness that becomes accessible with this chemistry. We had already reported that the corresponding VCP with a cyclohexyl group led to a complex reaction mixture.[3] However, going from a benzyl to a phenethyl group was successful, yielding yet another unknown silicon-containing ring system (**7 → 8a**, Scheme 6). The relative configuration was deduced from the $^3J_{H,H}$ coupling (10.6 Hz) in the ^{1}H NMR spectrum of the highlighted H nuclei.

To gain insight into the reaction mechanism, we designed control experiments to distinguish between reaction pathways with the ring opening of the cyclopropyl group happening before or after manipulation of the alkene (Scheme 7). We showed before that silylium-ion-promoted ring-opening
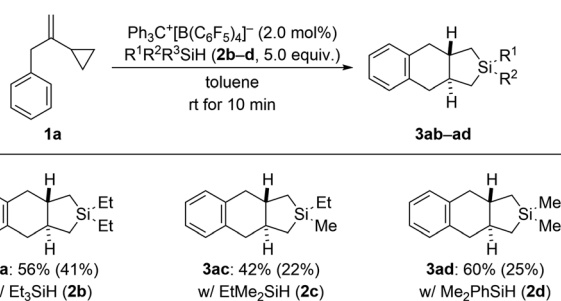
Scheme 7 Control experiments I: verification of ring opening of the cyclopropyl group in VCPs prior to engagement of the alkene unit. See caption of Scheme 2 for further details.

hydrosilylation of cyclopropanes is feasible[1] but had excluded this possibility for phenyl-substituted VCPs[3] in the (5 + 1) cycloaddition (see Scheme 1, top right). If hydrosilylation of the cyclopropyl group in VCPs **1** is the initial step, 2-substituted allylbenzene derivatives **9** are likely intermediates. When subjecting independently prepared **9ab** to the standard procedure using Et$_3$SiH (**2b**), an *endo* cyclization furnished product **5aa** in high yield (top). With **5aa** being formed as minor byproduct in the annulation reaction (*cf.* Table 1), we can state that ring opening preceding the functionalization of the alkene in the VCP is a competing pathway. In turn, potential intermediate **10aa**[2] arising from alkene hydrosilylation of VCP **1a** and Et$_2$SiH$_2$ (**2a**) transformed cleanly into the cycloadduct **3aa** upon treatment with trityl borate Ph$_3$C$^+$[B(C$_6$F$_5$)$_4$]$^-$ in the absence of external hydrosilane (bottom). Hence, the opening of the cyclopropyl ring is interlinked with the intramolecular Friedel–Crafts-type bond formation at the aryl group[18] and is downstream to the alkene hydrosilylation.

In another set of control experiments, we employed deuterium-labeled hydrosilane Et$_3$SiD (**2b-d_1**) and model VCP **1a-d_1** with an *ortho*-C–D bond (Scheme 8). When **1a** was reacted with **2b-d_1**, the deuterium label was exclusively incorporated into one of the angular positions of cycloadduct **3aa-d_1** (top). To verify whether cleavage of the *ortho*-C–H bond is involved in the rate-determining step, **1a-d_1** was subjected to the standard setup (bottom). However, H/D scrambling had occurred at all positions of the phenylene group in **3aa-d**.[19]

Scheme 5 Scope IV: variation of the hydrosilane in the cycloaddition of VCP **1a**. See caption of Scheme 2 for further details.
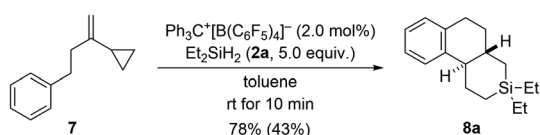
Scheme 6 Scope V: going from benzyl to phenethyl in the VCP. See caption of Scheme 2 for further details.

Scheme 8 Control experiments II: deuterium-labeling of the hydrosilane or the VCP. See caption of Scheme 2 for further details. The deuteration grades were estimated by NMR spectroscopy.

The rough mechanistic picture was refined by density functional theory (DFT) calculations at the M062X/cc-PVTZ//M062X/6-31G(d,p) level.[20] Computations were performed on the model reaction of VCP **1a** and Et_2SiH_2 (**2a**) with $Ph_3C^+[B(C_6F_5)_4]^-$ 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)[21] 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 cyclopropylcarbinyl cation **I**, generated from the association of VCP **1a** and the hydrogen-substituted silylium ion $[Et_2HSi(PhCl)]^+$, is much more stable than other donor-stabilized silylium ions such as the corresponding chlorobenzene-, hydrosilane-, or cyclopropane-stabilized systems.[3] 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^{-1}. We also calculated the potential intermolecular hydride transfer from Et_2SiH_2 (**2a**) to **I** but this pathway can be excluded because of an energetically higher transition state (19.0 *versus* 15.2 kcal mol^{-1}, 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^{-1}, 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.[18]

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$_{IV–V}$** (gray box) is exergonic by −2.8 kcal mol^{-1} with an activation barrier of 16.2 kcal mol^{-1}. 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[17,22] to form the experimentally obtained product **3aa** *via* **VI** along with dihydrogen and the chlorobenzene-stabilized silylium-ion catalyst ($\Delta G^{\ddagger} = 16.0$ kcal mol^{-1}). The overall Gibbs free energy change ΔG is −34.9 kcal mol^{-1} (calculated from the Gibbs energy difference between **3aa** and **1a**/**2a**). Based on transition state *trans*-**TS$_{IV–V}$**, the predicted relative configuration of **3aa** is *trans*, and is supported by ^1H NMR spectroscopy ($^3J_{H,H} = 11.7$ Hz) and was eventually confirmed by X-ray diffraction (Scheme 4, bottom).

We considered other kinetically less favorable pathways such as a the 5-*exo-tet* cyclization (path b, cleavage of the proximal
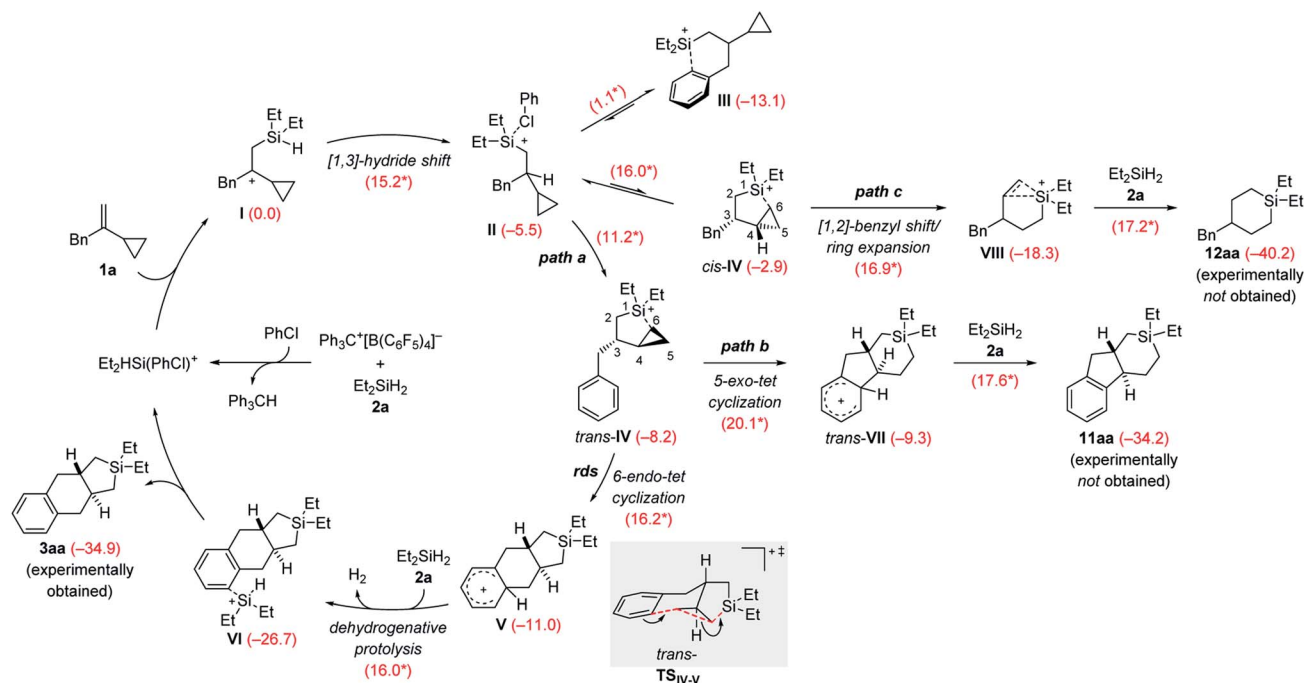
Scheme 9 Catalytic cycle of the silylium-ion-promoted cycloaddition of VCP **1a** and Et_2SiH_2 (**2a**). For each reaction step, the Gibbs free reaction energies and barriers (labeled with an asterisk) in kcal mol^{-1} were computed with the M06-2X functional (see the ESI† for details). rds = rate-determining step.
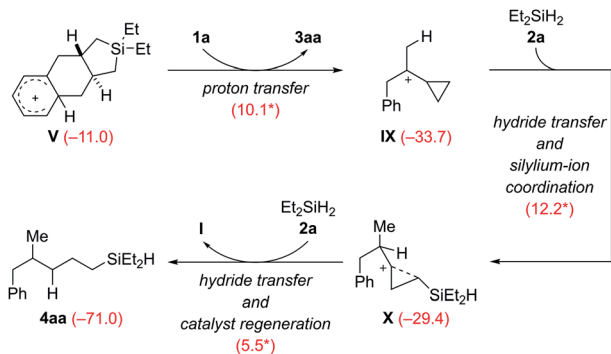
Scheme 10 Computed pathway of the formation of byproduct **4aa**, precursor of **4ab** (see discussion of Table 1).

C4–C6 bond leading to **11aa**) or [1,2]-benzyl shift/ring expansion (path c, leading to **12aa**). Neither **11aa** nor **12aa** were observed experimentally. The route to **12aa** corresponds to the previously reported (5 + 1) cycloaddition of phenyl-substituted VCPs[3] (see Fig. S87–S90 in the ESI†). However, the annulation of a phenethyl-substituted VCP **7** to afford the 6/6/6-fused ring system **8a** can be explained by a related 6-exo-tet cyclization corresponding to path b (see Schemes 6 and S12 in the ESI† for the computed pathway).

The Wheland intermediate **V** is the proton source in this reaction that can also be the starting point of side reactions. Instead of the above dehydrogenative protolysis of the hydrosilane over a barrier of 16.0 kcal mol^{-1} (**V** → **VI**, Scheme 9), this Brønsted acid can also transfer a proton to the C=C double bond of VCP **1a**, releasing the product **3aa** and the cyclopropylcarbinyl cation[8] **IX** (Scheme 10). The barrier of this protonation step is only 10.1 kcal mol^{-1} and is as such kinetically competitive. Subsequent hydride transfer from Et$_2$SiH$_2$ (**2a**) to **IX** gives a γ-silicon-stabilized carbenium ion **X**. This undergoes hydride abstraction from another molecule of **2a** to yield open-chain product **4aa**; the silylium ion released at the same time forms the β-silicon-stabilized cyclopropylcarbinyl cation **I** with VCP **1a**. This ring-opening hydrosilylation of a cyclopropane promoted by a silylium ion is a known reaction and was recently studied by us in detail.[1] With the low barriers involved, the formation of **4aa** and eventually **4ab** after rapid substituent redistribution[9,10] cannot be avoided.

Conclusion

The present work showcases that reactions of VCPs with different electrophilic silicon reagents do lead to drastically different outcomes (*cf.* Scheme 1). The substituent on the VCP and the choice of the silicon electrophile together with the counteranion of the β-silicon-stabilized cyclopropyl carbocation intermediates decide their fate. With silylium-ion-like reagents, benzyl- and phenethyl-substituted VCPs lead to silicon-containing 6/6/5- and 6/6/6-fused ring systems, respectively, both of which previously unknown motifs. The corresponding phenyl-substituted VCPs engage in a (5 + 1) cycloaddition under otherwise identical reaction conditions.[3] The annulation

sequence is initiated by the trityl cation and then maintained by self-regeneration of the silylium-ion reagent.[5a] Two Si–C(sp^3) bonds and one C(sp^2)–C(sp^3) bond are formed with an intramolecular Friedel–Crafts alkylation of a silylium-ion-activated cyclopropane ring as the key step (6-endo-tet for 6/6/5 system starting from benzyl-substituted VCP and 6-exo-tet for 6/6/6 system starting from phenethyl-substituted VCP). Given the high number of possible reaction pathways, the chemoselectivity and preference for one product with any of the substrates is remarkable.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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