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Homogeneous Catalysis

Catalytic Access to Diastereometrically Pure Four- and Five-Membered Silyl-Heterocycles Using Transborylation

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Abstract: Silyl-heterocycles offer a unique handle to expand and explore chemical space, reactivity, and functionality. The shortage of catalytic methods for the preparation of diverse and functionalized silyl-heterocycles however limits widespread exploration and exploitation. Herein the borane-catalyzed intramolecular 1,1-carboboration of silyl-alkynes has been developed for the synthesis of 2,3-dihydrosilolyl and silylcyclobut-2-enyl boronic esters. Successful, catalytic carboboration has been achieved on a variety of functionally diverse silyl-alkynes, using a borane catalyst and transborylation-enabled turnover. Mechanistic studies, including ^{13}C-labelling, computational studies, and single-turnover experiments, suggest a reaction pathway proceeding by 1,2-hydroboration, 1,1-carboboration, and transborylation to release the alkenyl boronic ester product and regenerate the borane catalyst.

The synthesis of silicon-containing heterocycles has been of interest to both organic and inorganic chemists for over half a century.[1] These were originally seen as synthetically challenging and a curiosity, but have since found potential applications in medicinal and materials chemistry.[2] Wider exploitation of silyl-heterocycles is however limited by the lack of preparative methods, and the scope of these methods to give structurally diverse silyl-heterocycles which are essential for wider applications.[1a,3] The use of stoichiometric organometallics dominate the synthesis of silyl-heterocycles and thus offer limited options to vary the core scaffold.[4] Transition metal catalysis has emerged as a potential method for the synthesis of silyl-heterocycles, but the need for highly pre-functionalized starting materials, including designer silanes and synthetically challenging reagents, has limited the scope of these reactions.[5] Where readily available starting materials have been used, substitution about the silyl-heterocycle ring has been limited in functionality.[6] Metal-free examples have been reported based on the catalytic generation of silylium ions for skeletal rearrangements, but are limited in scope by the highly reactive nature of these cationic species.[7]

Silicon-containing active pharmaceutical ingredients have been of particular interest to medicinal chemists due to their unique properties, which provides an alternative pathway for drug optimization.[2a] The increased bond length of a Si–C bond (ca. 1.87 Å) compared to a C–C bond (ca. 1.54 Å) as well as lower Pauling electronegativity ($\chi_c = 2.50$; $\chi_{Si} = 1.75$) can alter the shape and conformation of a drug molecule, allowing for the wider exploration of chemical space. The increased lipophilicity of organosilanes can lead to improved uptake through cell membranes (Scheme 1a).[4c,8] Because of this, silicon has been utilized in drug discovery through a "silicon switch", where carbon is substituted with silicon in biologically active compounds.[4a,b] Organosilanes have been proposed as a bioisostere to *cis*-alkenes due to the similarity in distance between the substituents (ca. 3 Å).[9] Beyond biological applications, silyl-heterocycles, such as silole, have found use in materials applications as organic light-emitting materials and dyes.[2]

The stoichiometric 1,1-carboboration of secondary alkylboranes with group-14 alkynyl reagents (e.g. $-SiR_3$, $-GeR_3$, $-SnR_3$, $-PbR_3$) was developed by Wrackmeyer.[10] The intramolecular 1,1-carboboration readily occurred on silyl-alkynes to give air- and moisture-sensitive borane-substituted silyl-heterocycles.[11] With highly Lewis acidic boranes, stoichiometric carboboration was possible on non-silylated alkynes,[12] but no examples of main-group-catalyzed 1,1-carboboration of alkynes have been reported to date and only a single metal-catalyzed example is known, which required a diazo coupling partner.[13]

Transborylation has been used to render stoichiometric organoborane reactions catalytic,[14] including for C–C bond forming reactions.[15] Gellrich's borane-catalyzed reductive dimerization of allenes is the only example where a C–C bond is formed, and the turnover reagent (pinacolborane) is maintained in the isolated product.[16] Herein, the boron-catalyzed synthesis of air- and moisture stable boronic ester-substituted 4- and 5-membered silyl-heterocycles is reported using transborylation to enable turnover (Scheme 1c).

Dimethyl(phenylethynyl)(vinyl)silane **1a** was used for reaction optimization and found to rapidly react with

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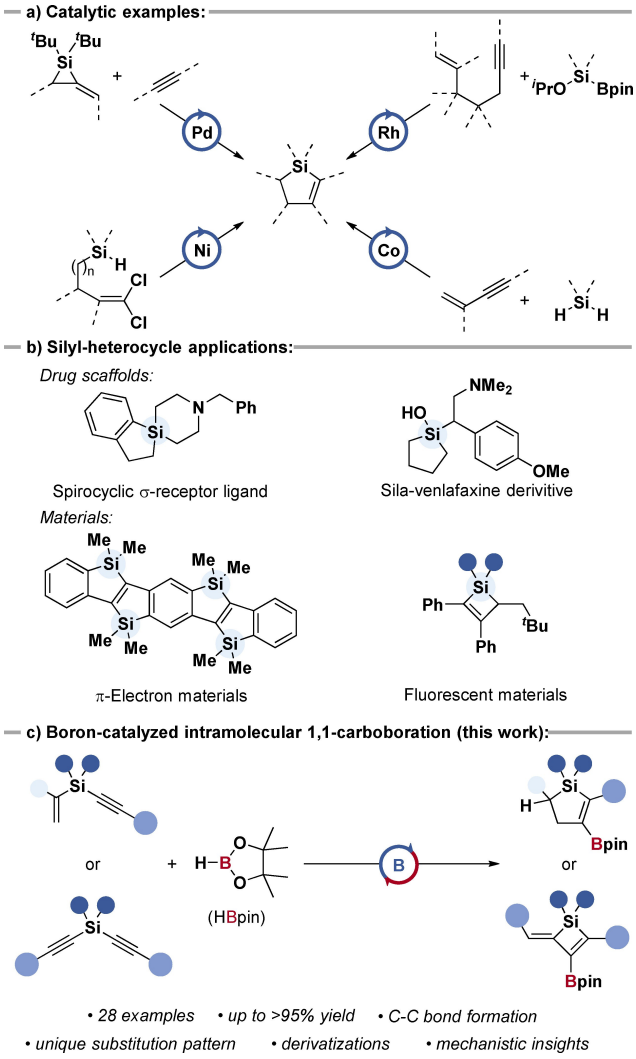
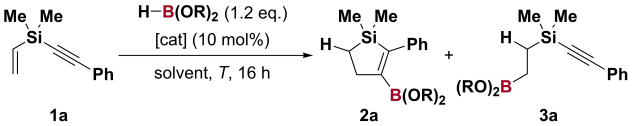


Scheme 1. a) Catalytic examples. b) Applications of silicon in drug scaffolds and materials. c) This work.

stoichiometric 9-borabicyclo[3.3.1]nonane (H-*B*-9-BBN) at room temperature to give the air- and moisture sensitive 1,1-carboboration product.[11a] As rapid 1,1-carboboration was observed, it was thought that transborylation would be rate-limiting, so a highly Lewis acidic dioxaborolane would be required to effect turnover, at a rate comparable to 1,1-carboboration.[17] Catecholborane (HBcat) was trialed, with H-*B*-9-BBN as the catalyst, however, the yield of the 2,3-dihydrosilolyl boronic ester **2a** was low. Instead of cyclization, alkene hydroboration, and then transborylation, of the alkene was observed to give an alkyl boronic ester **3a** (9 %) (Table 1, entry 1). The use of alternative boron reagents as catalysts gave only trace amounts of cyclization, predominantly giving the alkene hydroboration product **3a** (Table 1, entry 2–3). In order to slow transborylation at the intermediate trialkyl borane (the precursor to the alkyl boronic ester **3a**, see below), and thus increase the selectivity towards cyclization (to give the 2,3-dihydrosilolyl ester **2a**), the less Lewis acidic HBpin was trialed. Using HBpin, the formation of the linear alkyl boronic ester **3a** was suppressed.

Table 1: Initial catalyst screening and optimized conditions.



1a **2a** **3a**

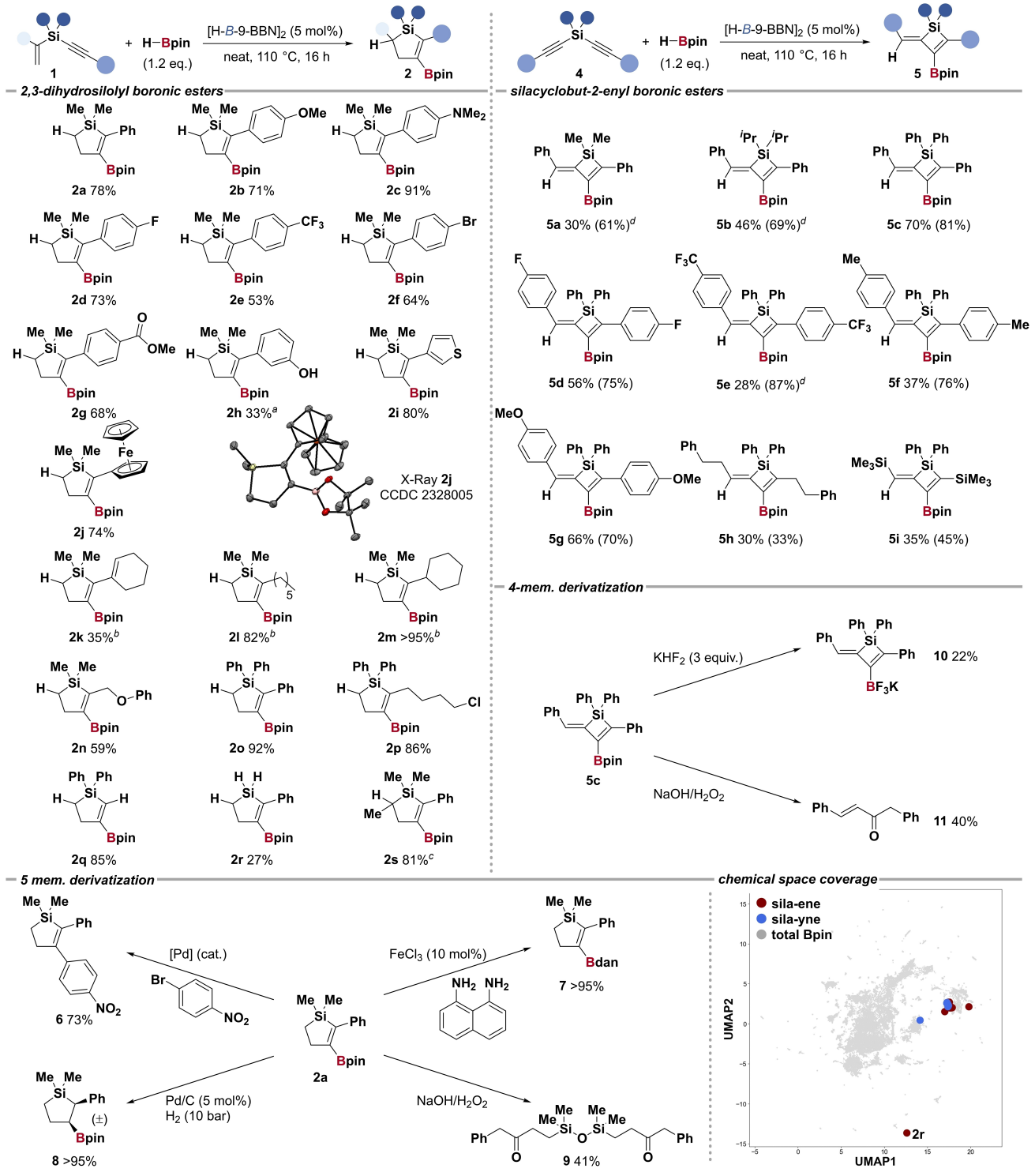
entry	[cat]	$HB(OR)_2$	solvent	*T* / °C	**2a** / %	**3a** / %
1	H-*B*-9-BBN	HBcat	THF	80	11	9
2	$H\text{-}BCy_2$	HBcat	THF	80	trace	17
3	BCl_3	HBcat	THF	80	trace	16
4	H-*B*-9-BBN	HBpin	THF	80	0	0
5	H-*B*-9-BBN	HBpin	neat	110	80	trace

Yields determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

Presumably the slower rate of transborylation using HBpin, compared to HBcat, enabled an increased amount of cyclization to proceed and thus transborylation now occurred at the cyclized alkenyl borane (Table 1, entry 4). Following optimization, catalytic 1,1-carboboration could be achieved at 110 °C without the need for a solvent and with full control of chemo- and regioselectivity (Table 1, entry 5) (see Supporting Information Table S1 for optimization).

With optimized catalysis conditions, attention was turned to the scope of the reaction (Table 2). Aromatic substituents on the alkyne were well tolerated, with Lewis basic, electron-donating substituents such as anisole **2b** and aniline derivatives **2c** giving excellent yields of the corresponding 2,3-dihydrosilolyl boronic ester as a single regioisomer. Halogenated aromatic substituents **2d–f** were also well tolerated, giving very good isolated yields and complete control of regioselectivity. An ester-substituted substrate **1g** gave the silyl-heterocycle **2g** chemoselectively, and in good yield, without any reduction of the ester observed under reaction conditions.[18] A phenol-substituted alkyne **1h** gave a fair yield, requiring an extra equivalent of HBpin to act as a traceless protecting group.[14c,15a,19] Other heterocycles, such as thiophene **2i** and ferrocene **2j** gave high yields, the latter being characterized by X-ray crystallography, validating the assumed substitution pattern. A 1,3-enyne **1k** underwent selective cyclization in a fair yield and good chemoselectivity for reaction at the alkyne. Where cyclization was observed to be slow, and alkene hydroboration thus competitive, the selectivity for cyclization could be controlled by slow addition of HBpin; primary **1l** and secondary **1m** alkylalkynes gave excellent yields of the corresponding silylheterocycles **2l–m** using this method. Slow addition was not required when an ether-substituted alkyl group **2n** was used. Changing the substitution on the silane to diphenyl **2o** gave excellent yields, allowing the reaction to tolerate an alkyl chloride **2p** and terminal alkyne **1q** under standard conditions. The dihydride **2r** gave a reduced yield, showing that substitution on the silane promoted the reaction. Using a 1,1-disubstitued alkene **1s** gave an excellent yield of a highly-substituted 2,3-dihydrosilolyl boronic ester **2s**. Attempts to increase the size of the ring using a 4-sila-1,5-enyne were unsuccessful, and primarily gave the alkene

Table 2: Substrate scope and derivatizations of 2,3-dihydrosilolyl boronic esters..



Reported yields are of the isolated compound. Yields in parentheses are calculated from ^{1}H NMR spectroscopy of the crude reaction mixture, using mesitylene as an internal standard. Reaction conditions: substrate (0.5 mmol), HBpin (0.6 mmol), [H-*B*-9-BBN]$_2$ (0.025 mmol), neat, 110 °C, 16 h. [a] 2.2 equivalents of HBpin. [b] slow addition of HBpin (0.03 mmol h^{-1}), 36 h. [c] 120 °C, 24 h. [d] [H-*B*-9-BBN]$_2$ (0.05 mmol) i) Aryl bromide (1 eq.), $PdCl_2(PPh_3)_2$ (5 mol%), PPh_3 (7.5 mol%), K_2CO_3 (1.5 eq.), H_2O (2 eq.), toluene, 100 °C, 16 h. ii) 1,8-Diaminonaphthalene (1.5 eq.), $FeCl_3$ (10 mol%), Imidazole (3 eq.), 4:1 MeCN:H_2O, r.t., 24 h. iii) Pd/C (5 mol%), H_2 (10 bar), MeOH, r.t., 16 h. iv) H_2O_2/NaOH, THF, 0 °C, 30 min. Thermal ellipsoids shown at 50% probability level. Hydrogen atoms omitted for clarity.

hydroboration product (see Supporting Information for failed substrates).

The stoichiometric intramolecular 1,1-carboboration of *bis*-alkynylsilanes has also been demonstrated by Wrackmeyer to give silylcyclobut-2-enyl boranes,[20] and by Tok for 2,5-dihydrosiloles.[11d] Dimethyl-di(phenylethynyl)silane **4a** reacted to give a good yield of the corresponding air- and moisture-stable, 4-membered silylcyclobut-2-enyl boronic ester **5a**, a class of compounds previously unreported in catalysis. The di*iso*propyl-substituted silane **4b** gave an improved yield of the corresponding boronic ester **5b** over the dimethyl-substituted silane **5a**, presumably due to increased stability of an intermediate silicon cation. The diphenyl-substituted silane **4c** improved the yield of the corresponding boronic ester **5c** further and led to increased stability of the product. An aryl fluoride **4d** gave an excellent yield of the corresponding boronic ester **5d** and exhibited the same tolerance as the ene-yne reaction. For the aryl trifluoromethyl substituted substrate **4e**, the catalyst loading was doubled to give an excellent yield of the corresponding boronic ester **5e**. Electron-donating groups, such as the methyl- **4f** and methoxy-substituted arenes **4g** gave good yields of the corresponding boronic esters **5f–g**. The alkyl-alkyne **4h** gave a reduced yield of the corresponding boronic ester **5h** compared to the arene-containing substrates. The *bis*-silane-substituted alkyne **4i** gave a fair yield of the corresponding boronic ester **5i**, potentially due to competing carboboration on the trimethylsilyl groups.

To assess the novelty of these 2,3-dihydrosilolyl and silylcyclobut-2-enyl boronic esters, an assessment of the chemical space covered by existing pinacol boronic esters was carried out. Using the Reaxys® database,[21] every compound containing a pinacol boronic ester, which had been characterized by NMR spectroscopy was obtained as simplified molecular-input line-entry system (SMILES) strings. These were then sanitized to remove duplicates and compounds with incorrect SMILES, to give a total space of 51325 pinacol boronic esters. Two-dimensional descriptors were calculated using Mordred[22] and filtered (see Supporting Information Section 8) to give a total of 1420 descriptors for the Reaxys compounds and the substrates synthesized here. These descriptors were reduced to a two-dimensional space using the Uniform Manifold Approximation (UMAP),[23] which showed that the 2,3-dihydrosilolyl and silylcyclobut-2-enyl boronic esters clustered away from the majority of pinacol boronic esters, into less explored chemical space. The dihydride substrate **2r**, sat in an empty region of chemical space, representing a motif for further exploration.

Due to no previous reports of the preparation of the air- and moisture-stable silolyl boronic ester products, these were investigated for potential downstream reactivity, essential for fundamental application. A Suzuki–Miyaura coupling[24] was successfully carried out to give the 2,3-dihydrosilolyl arene **6** in good yield. Tranesterification of the Bpin group to 1,8-diaminonaphthalene (Bdan) **7**[25] proceeded in excellent yield. Reduction of the alkene also proceeded in excellent yield to give the *cis*-boryl-silolane **8**.[26] Oxidation of the silolyl boronic ester **2a** under basic conditions ($NaOH/H_2O_2$) gave an unusual ring-opened β-silyl-ketone dimer **9**. The silylcyclobut-2-enyl boronic ester **5c** was converted to the potassium trifluoroborate salt **10** in a low yield but allowed for characterization by X-ray diffraction to confirm the substitution pattern and that the (*Z*)-alkene was prepared (Figure 1). Oxidation of the silylcyclobut-2-enyl boronic ester **5c** under standard conditions ($NaOH/H_2O_2$) gave a ring-opened enone **11** in moderate yield (40%).

The mechanism of 1,1-carboboration of group 14 alkynes was proposed to occur by donation of the R_3E–C alkynyl group to the empty p-orbital of the trialkylborane, to give a zwitterionic tetracoordinate boron 'ate' species and an alkyne-coordinated cation, $[R_3E]^+$. This ion pair was proposed to undergo a 1,2-metallate rearrangement to give the 1,1-carboboration product.[10a,11a] The zwitterionic intermediates have been isolated and characterized where E = Sn and Pb,[10d,27] but there has been no such intermediate characterized where E = Si. In the case of non-activated alkyne 1,1-carboboration, a zwitterionic intermediate has been isolated and characterized between ferrocenylacetylene and $B(C_6F_5)_3$.[12c] Dimethyl(phenyl(1-^{13}C-ethynyl))-(vinyl)silane **[^{13}C]-1a** was synthesized and reacted under standard conditions to track any carbon migration (Scheme 2a), the ^{13}C-labelled product **[^{13}C]-2a** was analyzed by ^{13}C NMR spectroscopy and found to be exclusively enriched in the 3-position, *alpha* to the boron, suggesting that after hydroboration of the alkene, exchange of the alkynyl group between boron and silicon is regiospecific, supporting Wrackmeyer and co-workers' original hypothesis.[10a,11a]

Single-turnover experiments were then used to determine if transborylation occurred before or after cyclization (Scheme 2b). Exposure of [H-*B*-9-BBN]$_2$ to an excess of dimethyl(phenylethynyl)(vinyl)silane **1a** in C_6D_6 at 80 °C gave complete conversion to the *B*-9-BBN-substituted 2,3-dihydrosilole **12**, by ^{1}H and ^{11}B NMR spectroscopy within 10 minutes.[11] After removal of solvent, an equivalent of HBpin was added and the reaction was heated at 110 °C for

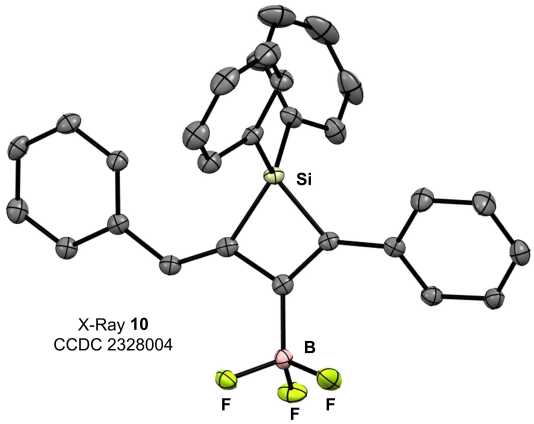
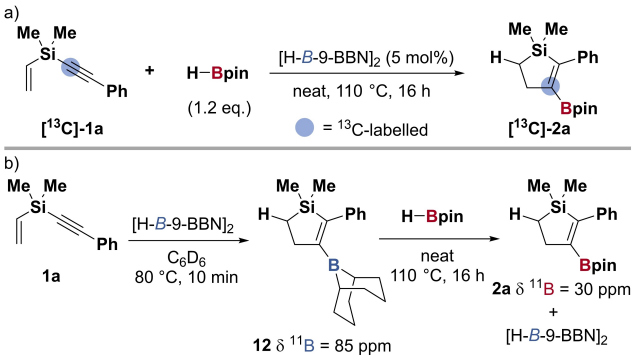


Figure 1. Crystal structure of potassium trifluoroborate salt **10**. Thermal ellipsoids shown at 50% probability level. Hydrogen and potassium atoms, and solvent omitted for clarity. Two molecules were present in the unit cell, one omitted for clarity.



Scheme 2. Mechanistic investigations: a) ^{13}C-labelling experiment; b) Single-turnover experiment.

16 hours, leading to observation of the Bpin-substituted 2,3-dihydrosilole **2a** by ^{1}H and ^{11}B NMR spectroscopy.

The mechanism was probed further using gas-phase density functional theory (DFT) calculations (M06-2X(D3)/Def2-TZVP//M06-2X(D3)/6-31G(d,p)); hydroboration of dimethyl(1-propynyl)(vinyl)silane **A** by H-*B*-9-BBN monomer proceeded with a small free energy barrier (**TS1** 12.2 kcal mol^{-1}) to give the alkylborane **B** (Figure 2). The carboboration reaction was found to proceed as predicted by Wrackmeyer,[10a] where the alkynyl silane **B** donated the alkynyl group and generated a high-lying zwitterionic intermediate **C**. This underwent cyclization with migration of the silicon with a moderate overall barrier (**TS3** 18.4 kcal mol^{-1}), consistent with the observed reactivity (< 10 minutes at 80 °C), and generated the 2,3-dihydrosilolyl borane **D**. As with previous examples,[14b,28] transborylation with HBpin was found to occur through a high-lying three-center-two-electron-bound intermediate **E** in an endergonic process, and gave a relatively small overall barrier (**TS5** 20.0 kcal mol^{-1}), inconsistent with the need for elevated reaction temperatures (110 °C). The barrier was calculated for the phenyl-substituted 2,3-dihydrosilolyl borane **D′**–**F′**, and found to be consistent with the observed experimental reactivity (**TS5′** 26.6 kcal mol^{-1}), which indicated a strong steric-dependence on the rate of transborylation.

At the same level of theory, the overall free-energy path was also calculated for dimethyl-di(1-propynyl)silane **G** (Figure 3); hydroboration from H-*B*-9-BBN monomer occurred with a small barrier (**TS6** 14.9 kcal mol^{-1}) and gave a *gem*-boryl-silylalkene **H**. The barrier was also calculated for the opposite regioselectivity, and found to be larger (**TS6′** 17.5 kcal mol^{-1}), consistent with the observed selectivity. 1,1-Carboboration to the silylcyclobut-2-enyl borane **J** proceeded through a similar path as before, but gave a much higher free energy barrier (**TS8** 27.7 kcal mol^{-1}), consistent with the conditions shown by Wrackmeyer.[20] As above, the barrier to transborylation with HBpin was found to be dependent on the steric bulk of the *β*-substituent; from the methyl-substituted silylcyclobut-2-enyl borane **J**, the barrier was low (**TS10** 19.0 kcal mol^{-1}), and elevated for the phenyl-substituted silylcyclobut-2-enyl borane (**TS9′** 24.4 kcal mol^{-1}). Independent of the substituent, the rate-

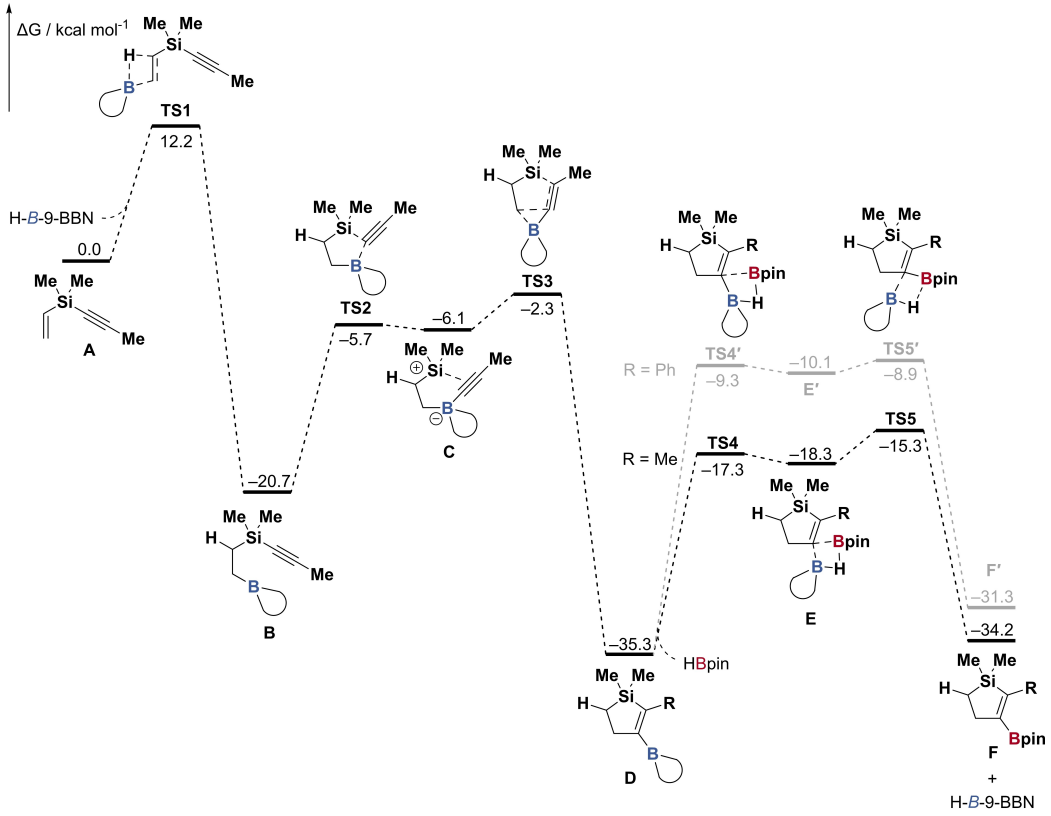


Figure 2. DFT-computed free energy values (M06-2X(D3)/Def2-TZVP//M06-2X(D3)/6-31G(d,p)) for 1,1-carboboration of alkenyl(alkynyl)silanes.

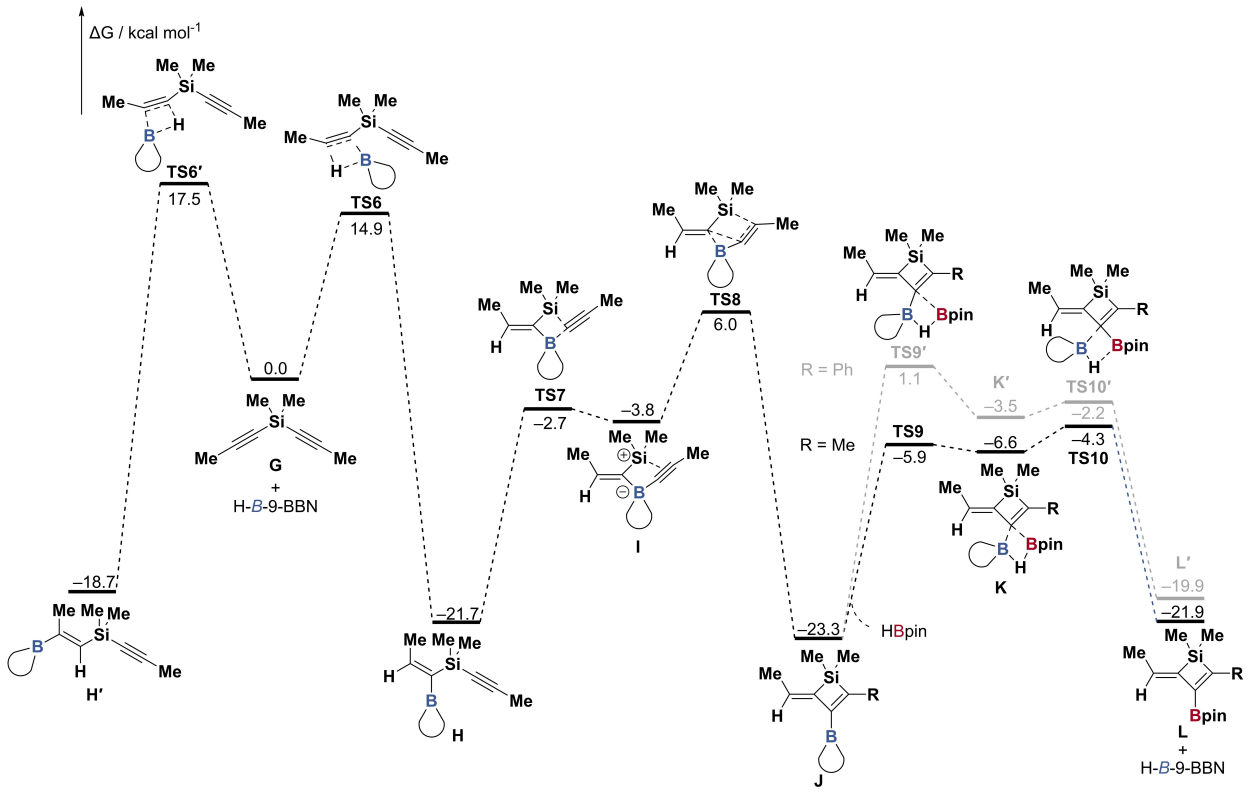


Figure 3. DFT-computed free energy values (M06-2X(D3)/Def2-TZVP//M06-2X(D3)/6-31G(d,p)) for 1,1-carboboration of *bis*-alkynylsilanes.

limiting step was calculated as carboboration, rather than transborylation, unlike the five-membered silyl-heterocycle.

The use of boron in catalysis has developed from rendering stoichiometric reactions catalytic in organoborane and attempts to mimic transition metal reactivity,[29] to having complementary and unique modes of reactivity.[30] Here, it has been demonstrated how transborylation catalysis can be used to synthesize building blocks with novel reactivity, and that occupy unexplored regions of chemical space. The findings given here also represent the first step in turning the wide array of stoichiometric 1,1-carboboration reactions into usable catalytic systems. Attempts at intermolecular carboboration and reactions with non-activated alkynes are currently being undertaken.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Main group · Catalysis · Boron · Transborylation · Silicon

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[31] Deposition Numbers 2328005 (for **2j**), 2328004 (for **10**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Communications

Homogeneous Catalysis

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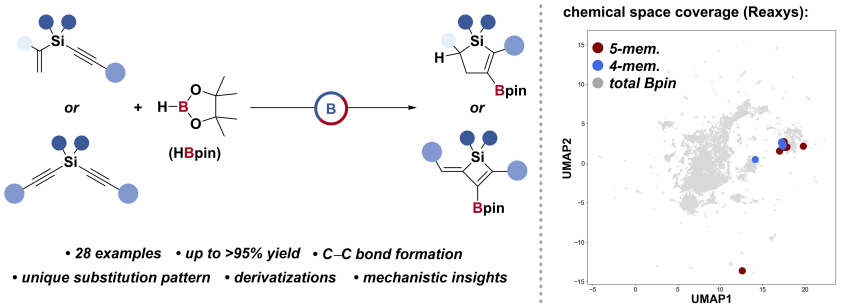
Catalytic Access to Diastereometrically Pure Four- and Five-Membered Silyl-Heterocycles Using Transborylation



Silyl-heterocycles offer a unique handle to expand and explore chemical space, reactivity, and functionality. These are limited by the lack of catalytic methods for the preparation of diverse and functionalized silyl-heterocycles. Herein the borane-catalyzed intramolecular 1,1-carboboration of silyl-alkynes has been developed for the synthesis of 2,3-dihydrosilolyl and silylcyclobut-2-enyl boronic esters.