RESEARCH ARTICLE

Introducing Steric Bulk into Silylboranes: Enhanced Bench Stability and Novel Chemical Reactivity

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Abstract: Silylboranes are versatile intermediates in organic synthesis, and a wide range of structural variants of silylboranes have already been synthesized. However, the stability of silylboranes varies significantly, and their decomposition mechanism remains to be fully understood. Moreover, some silylborane motifs have not yet been applied as synthetic reagents due to their instability. To address this issue, we first investigated the decomposition mechanism of silylboranes in air and moisture using experimental and theoretical methods. We discovered that oxygenation by atmospheric oxygen is the major decomposition pathway, resulting in the formation of a borylsilylether, and that the introduction of a bulky silyl group suppresses this decomposition. Based on these results, we synthesized triisopropylsilyldimesitylborane (*i*-Pr_3Si–$BMes_2$), which exhibits high bench stability. Moreover, *i*-Pr_3Si–$BMes_2$ reacts with carbon monoxide (CO), which is the first example for a reaction between a silylborane and CO. Further computational studies revealed that electronic effects, including hyperconjugation between the Si–B σ-bond and C–O π*-bond, are crucial for CO activation. Furthermore, we prepared a bench-stable bissilylaminoborane by introducing triisopropylsilyl groups, providing a bissilylchloroborane upon hydrogen chloride treatment. These findings provide valuable insights into how steric and electronic effects can be used to optimize the balance between stability and reactivity in silylboranes.

Introduction

Although silylboranes are versatile reagents with great utility in organic synthesis, many of these reagents exhibit only modest bench stability. Nevertheless, the reactivity of silylborane reagents is diverse when activated by transition metals and bases (Figure 1a).[1] (Dimethylphenylsilyl)boronic acid pinacol ester [Me_2PhSi–B(pin)], first reported by Suginome and Ito in 1996,[2] has become a typical silylborane reagent used for a variety of organic reactions, including silylations, borylations, and silaborations.[1] In 2008, Hartwig reported the synthesis of trialkylsilylboranes via the Ir-catalyzed borylation of hydrosilane.[3a] Subsequently, our group has reported an additional, more general method for the synthesis of various silylboranes, further enabling the iterative synthesis of complex oligosilanes by the generation of nucleophilic silyl species from silylboranes with bases.[4] Moreover, silylboranes have recently been used as a silyl-radical source by using a base in combination with photoirradiation to promote a silylation reaction.[5] These advances have created significant interest in developing synthetic methods for novel silylboranes with unique reactivity.

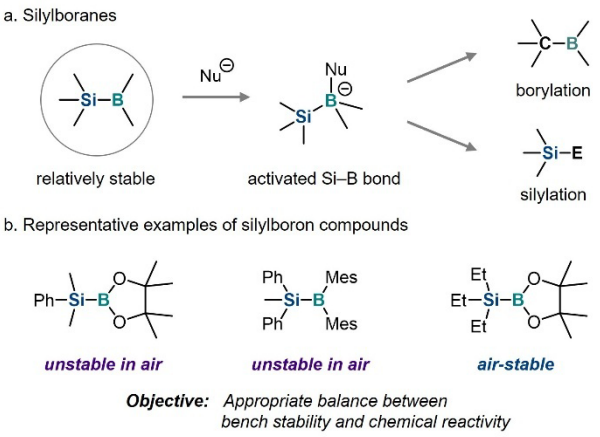


Figure 1. Examples of representative silylboranes and objective of this study.

Although the use of silylboranes as reagents is advancing rapidly, studies that examine the relationship between their structure, bench stability, and chemical reactivity remain limited. While the most representative silylborane reagent, Me_2PhSi–B(pin), is relatively stable, exposure to air gradually produces the corresponding borylsilylether, Me_2PhSi–O–B(pin), and thus Me_2PhSi–B(pin) requires careful storage and handling. Surprisingly, however, there are no studies on the degradation mechanism(s) of Me_2PhSi–B(pin), and it is not clear even whether this compound is oxidized by oxygen or hydrolyzed by atmospheric water.[6] Trialkylsilylboranes are more stable than Me_2PhSi–B(pin), and their bench stability increases with increasing steric bulk of the trialkylsilyl group, e.g., [*i*-Pr_3Si–B(pin)

> Et_3Si–B(pin) > Me_3Si–B(pin)].[3a,c,4a] The stability of silylboranes also strongly depends on the borane substituent. The B(dan) group (dan = naphthalene-1,8-diaminato) enhances the stability of silylboranes.[7a] Although the introduction of BAr_2 groups would enrich the reactivity of such organoboron compounds, this would also make the corresponding silylboranes more unstable, for example, $MePh_2Si$–$BMes_2$ is known to be air sensitive, thus hindering efforts to explore the reactivity and physical properties of silylborane compounds.[7b-d] Furthermore, rare silylboranes bearing sterically undemanding and purely organic substituents have been synthesized through a Umpolung strategy employing a nucleophilic boron reagent, rather than the commonly used silyl nucleophile.[7e] These silylboranes facilitate catalyst-free silaboration reactions, thus expanding the synthetic utility of silylboranes under mild conditions.[7f] However, these silylboranes with BAr_2 group are typically air sensitive, thus hindering further efforts to explore the reactivity and physical properties of silylborane compounds In order to advance the use of silylboranes as reagents in organic synthesis and as organic materials, it is necessary to understand their degradation processes and to find molecular design principles that ensure bench stability while maintaining good reactivity.

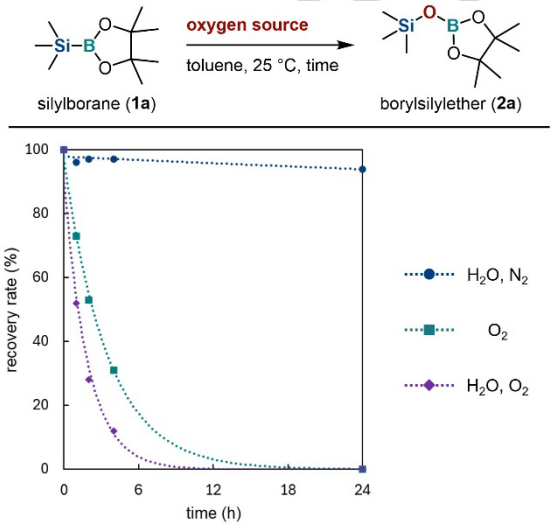
Accordingly, we began our study by investigating the mechanism of decomposition of silylboranes upon exposure to air and moisture using a combination of experimental and theoretical methods. The thus obtained results revealed that the oxygenation of the Si–B bond, followed by disproportionation with another silylborane molecule, produces a borylsilylether. Our results furthermore suggest that introducing a bulky silyl group can suppress the oxygenation of the Si–B bond. Based on these findings, we synthesized triisopropylsilyldimesitylborane (*i*-Pr_3Si–$BMes_2$) and bissilylaminoborane [$(R_3Si)_2B$–NEt_2], as first examples of bench-stable silyldimesitylboranes and bissilylaminoboranes.[8] Furthermore, we found that *i*-Pr_3Si–$BMes_2$ reacts in an unprecedented way with carbon monoxide (CO) to furnish products that result from the cleavage of the carbon-oxygen triple bond and the dearomatization of the mesityl groups, commensurate with the first example of a reaction between a silylborane and CO. In addition, the bissilylaminoborane reacts with hydrogen chloride to form bissilylchloroborane [$(R_3Si)_2B$–Cl], which can be coordinated by an *N*-heterocyclic carbene (NHC) to stabilize the B–Cl bond, rendering it air-stable. Further density-functional-theory (DFT) calculations revealed that the interaction between the σ(Si–B) orbital and the π*(C–O) orbital plays a crucial role in the high reactivity of the silylboranes toward CO. These findings highlight the importance of both steric and electronic factors in balancing the bench stability and chemical reactivity of silylboranes.

Results and Discussion

Decomposition of Silylboranes

First, we investigated the reaction mechanism involved in the degradation of silylboranes to borylsilylethers. In order to determine the oxygen source for the degradation of the silylboranes to borylsilylethers, the consumption rate of the starting silylborane was measured using Me_3Si–B(pin) (**1a**) at room temperature in the presence of either water, oxygen, or both water and oxygen (Table 1). In the presence of water without oxygen, the recovery rate of **1a** was 94%, even after 24 hours of reaction, with scarce production of borylsilylether **2a** detected, indicating that hydrolysis by water does not contribute to the degradation process. On the other hand, under an oxygen atmosphere without water, all the silylborane was consumed after 24 hours, quantitatively providing **2a**. In addition, in the presence of both water and oxygen, a slightly faster degradation rate was observed compared to the oxygen atmosphere alone, albeit that the exact role of water in this process remains unclear at present. These results indicate that the degradation of silylboranes predominantly occurs through oxidation by atmospheric oxygen.

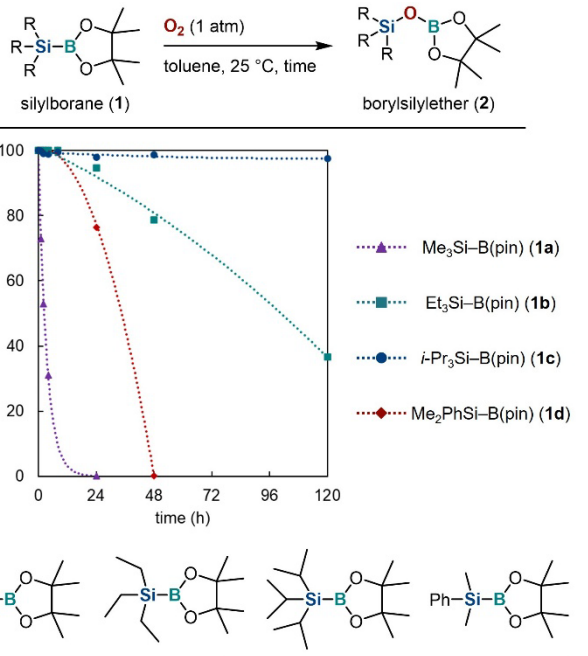
Table 1. Decomposition of silylboranes by oxygen and/or water.[a]



[a] Reactions were performed on the 0.1-mmol scale in 1 mL of toluene. The recovery rate of **1a** was determined by GC using tridecane as an internal standard.

Next, we investigated the impact of the substituents on the silicon atom on the silylborane degradation rates during the oxidation (Table 2). The commonly used silylborane Me_2PhSi–B(pin) exhibited some stability resulting in a 76% recovery after 24 hours a relatively low production of the corresponding borylsilylether (**2d**). In contrast, the sterically less hindered Me_3Si–B(pin) (**1a**) was fully oxidized within 24 hours, whereas Et_3Si–B(pin) (**1b**) was recovered in 95% after the same time period. Notably, Et_3Si–B(pin) (**1b**) significantly decomposed after 120 hours, and only 37% were recovered. On the other hand, introducing a bulky triisopropylsilyl group to the silylborane (**1c**) significantly enhanced the stability toward oxidation, resulting in a 98% recovery rate, even after 120 hours. These results experimentally demonstrate that bulky silyl groups can act as effective protecting groups against oxidation.

Table 2. Effect of silyl substituents on the oxygenation of the silylboranes.[a]



Me$_3$Si–B(pin) (**1a**) Et$_3$Si–B(pin) (**1b**) *i*-Pr$_3$Si–B(pin) (**1c**) Me$_2$PhSi–B(pin) (**1d**)

[a] Reactions were performed on the 0.1-mmol scale in 1 mL of toluene. The recovery rates of **1** were determined by GC using tridecane or trimethoxybenzene as internal standards.

To gain information on the reaction mechanism and the effect of steric hindrance on silylborane oxidation, we performed DFT calculations using the single component artificial force induced reaction (SC-AFIR) method, which is an automated reaction-path search method that enables the efficient exploration of reaction mechanisms (Figure 2a; for details, see the Supporting Information).[3b,9,10] The results of our calculations revealed that a triplet oxygen species first approaches the silylborane and cleaves the silicon-boron bond via a tetrahedral transition state (**TS1a**; activation energy: $\Delta G^{\ddagger}$ = +30.6 kcal/mol). Subsequently, the triplet state of the radical was converted to the singlet state at the same moment when the radical recombination of **int 1** occurs through the minimum energy seam crossing point (MESX), forming a silylborane peroxide (**int 2**).[11] The very low activation energy of the MESX means that this step essentially proceeds in a barrierless manner. In this step, the radical-chain reaction also proceeds to provide **int 2** and the Me$_3$Si radical from **int 1**, **1a**, and O_2 (for details, see the Supporting Information). The resulting silylborane peroxide reacts with another silylborane **1a** via oxygen transfer to yield the borylsilylether (**int 2** → **TS2a**; $\Delta G^{\ddagger}$ = +21.3 kcal/mol). Since the rate-limiting step of this reaction is the cleavage of the silicon-boron bond (**TS1**) in the initial stage of the reaction, we compared the activation energies for silylborane molecules with Me$_3$Si and *i*-Pr$_3$Si groups (Figure 2b). The activation energy for **TS1c** ($\Delta G^{\ddagger}$ = +36.6 kcal/mol) is significantly higher than that for **TS1a** ($\Delta G^{\ddagger}$ = +30.6 kcal/mol), and the Si–B bond in **TS1c** (2.25 Å) is longer than that in **TS1a** (2.16 Å) due to increased steric demand. In addition, the O^1–B distance in **TS1c** is shorter than that in **TS1a**, indicating that **TS1c** represents a later transition state, while **TS1a** corresponds to an earlier transition state. Given that the cleavage of the Si–B bond is an endergonic process, the later transition state (**TS1c**) is associated with a higher energy. These results suggest that bulky silyl groups, such as the *i*-Pr$_3$Si group, can suppress the approach of the oxygen molecule to the vacant p-orbital of boron, thus inhibiting oxidation via kinetic stabilization.

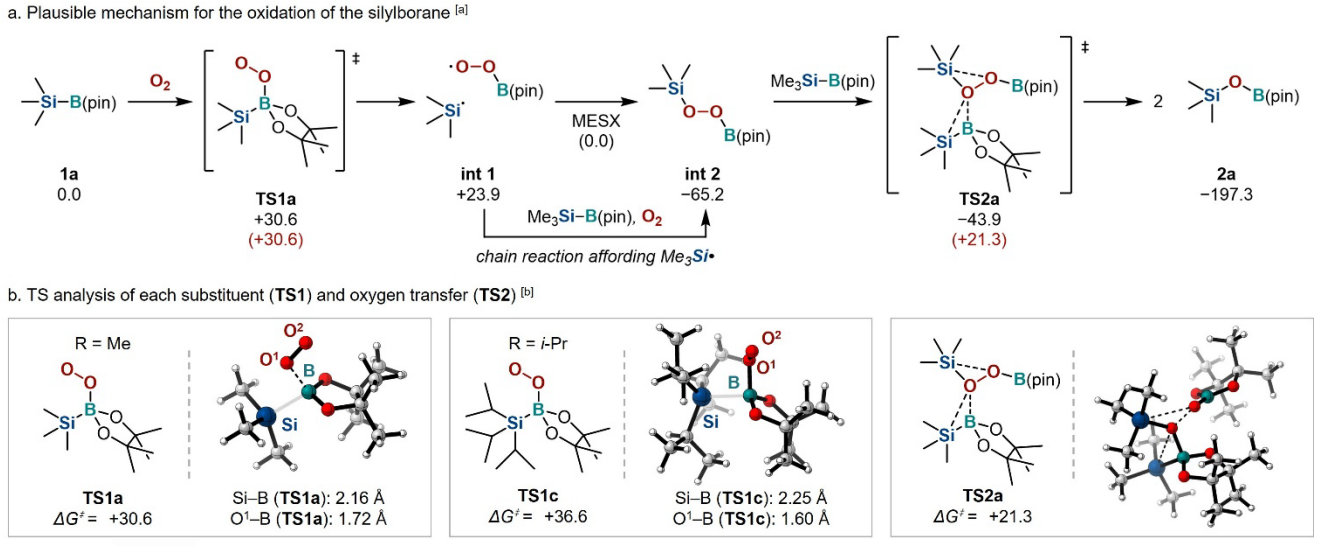


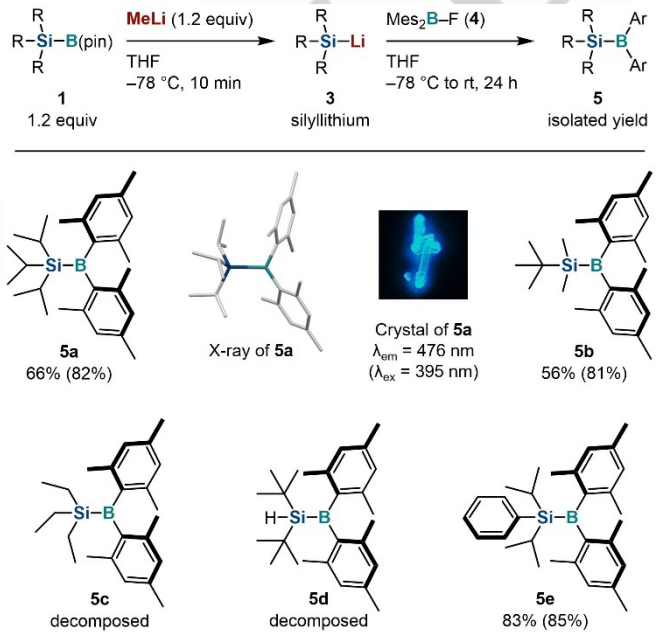
Figure 2. Results of the DFT calculations for the analysis of the silylborane oxidation mechanism. The $\Delta G^{\ddagger}$ values refer to the relative free energy with respect to the sum of **1a** and triplet oxygen, while the values shown in parentheses refer to the effective free-energy barrier associated with that step (in kcal/mol). [a] Calculation methods: SC-AFIR search (UPM6), structure refinement and single-point calculations (UB3LYP-D3BJ/6-311G(d,p)/SMD(toluene)//UB3LYP-D3BJ/6-311G(d,p)/SMD(toluene)). [b] Calculation method: UB3LYP-D3BJ/6-311G(d,p)/SMD(toluene)//UB3LYP-D3BJ/6-311G(d,p)/SMD(toluene).

Synthesis of Bench-Stable Silyldimesitylboranes and Bissilylaminoboranes

Following the finding from our initial DFT study that a bulky silyl group can be expected to stabilize silylboranes, we investigated

the synthesis of novel bench-stable silylboranes with aryl groups on the boron atom via a nucleophilic introduction of bulky silyl groups to an alkylsilyl lithium compound (Table 3). Organoboron compounds with a BAr_2 group, such as $MePh_2Si–BMes_2$,[12] are much less stable compared to those with B(pin) and B(dan) groups, and thus it would be interesting to investigate whether a bulky silyl group can stabilize these silylboranes. We have previously succeeded in developing a method for the synthesis of silylboranes with bulky silyl groups, and these silylboranes can be used to provide the corresponding silyl anion by using an alkyl lithium reagent in a boron-metal exchange reaction.[4a,13] Applying this method to *i*-Pr_3Si–B(pin) (**1c**) and methyllithium as the starting materials, we generated *i*-Pr_3Si lithium (**3c**) via boron-metal exchange. Subsequently, a diarylfluoroborane ($Ar_2B–F$) electrophile was added to the reaction mixture for the formation of a Si–B bond. The product was isolated using column chromatography over silica gel. When dimesitylfluoroborane ($Mes_2B–F$, **4**) was used as the boron electrophile, unprecedented silylboranes with *i*-Pr_3Si (**5a**) or *t*-$BuMe_2Si$ (**5b**) groups were obtained in 66% and 56% yield, respectively. The obtained air-stable silylborane **5a** exhibited solid-state blue luminescence upon UV irradiation and is sufficiently air-stable to allow the recording of its photochemical properties (λ_{ex} = 395 nm, λ_{em} = 476 nm, φ_{em} = 6.2%; Table 3). The fluorescence character of **5a** was determined by measuring its emission lifetime (τ = 3.15 ns). These results showcase the potential materials applications for $R_3Si–BAr_2$-type compounds with high bench stability. The less bulky silyl groups (Et_3Si and *t*-Bu_2HSi) failed to stabilize the corresponding silylboranes (**5c**, **5d**) sufficiently to make them bench-stable, as exemplified by their decomposition during column chromatography over silica gel. Other bulky silyl groups, such as the aryl-di-*i*-propylsilyl group (5e), provided the corresponding products in high yield.

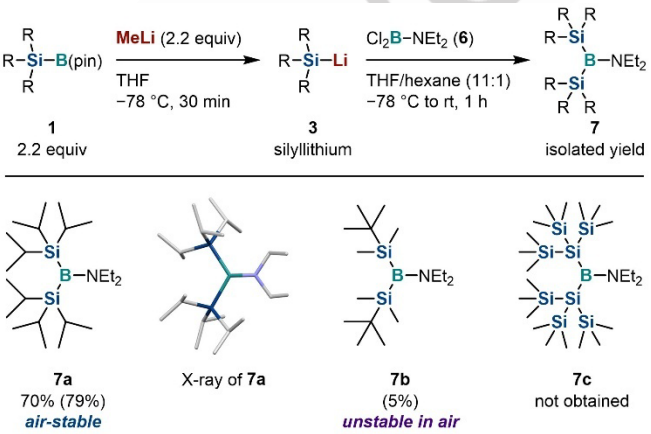
Table 3. Scope of the mono-silylated products.[a]



[a] Reactions were performed on the 0.2-mmol scale in THF under an Ar atmosphere. NMR yields based on CH_2Br_2 as an internal standard are shown in parentheses.

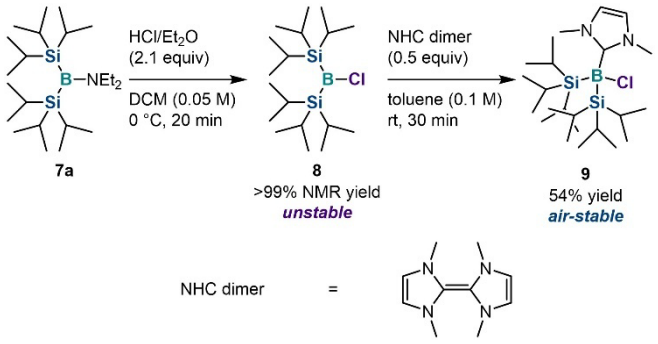
The bis-silylation of dichloro-diethylaminoborane (**6**) with bulky silyl anions for the synthesis of the corresponding bissilylaminoborane was also investigated (Table 4).[14] Here, (*i*-$Pr_3Si)_2B–NEt_2$ (**7a**) was obtained in high yield, while (*t*-$BuMe_2Si)_2B–NEt_2$ (**7b**) was formed but not isolated due to decomposition upon attempted purification. On the other hand, the use of a sterically extremely hindered tris(trimethylsilyl)silyl group also failed to furnish the desired bissilylaminoborane (**7c**), instead providing a complex mixture. Thus, the *i*-Pr_3Si group exhibits the appropriate steric hindrance required to obtain an air-stable bissilylaminoborane.

Table 4. Scope of the bissilylated products.[a]



[a] Reactions were performed on the 1.0-mmol scale in THF and hexane under an Ar atmosphere. NMR yields based on CH_2Br_2 as an internal standard are shown in parentheses.

Then, we conducted further investigations into the transformation of bissilylaminoborane **7a** (Scheme 1). As it is known that a B–N bond can be converted to a B–Cl bond, we conducted a chlorination reaction of the bissilylaminoborane using a hydrogen-chloride solution.[15] While bissilylchloroborane **8** was obtained in quantitative yield, it was not sufficiently stable to be isolated. In order to stabilize the bissilylchloroborane product, an *N*-heterocyclic-carbene ligand was introduced to occupy the vacant p-orbital using a 1,3-dimethylimidazolylidene dimer (NHC dimer), and the resulting complex (**9**) could be handled under atmospheric conditions.[16] Attempts to synthesize trisilylated boranes, such as $(i\text{-}Pr_3Si)_3B$, failed despite many attempts.



Scheme 1. Transformation of bissilylaminoborane **7a**. [a] Reaction was performed on the 0.1-mmol scale.

Chemical Reactivity of *i*-Pr$_3$Si–BMes$_2$ toward Carbon Monoxide (CO)

To investigate the reactivity of the air-stable silylborane *i*-Pr$_3$Si–BMes$_2$ (**5a**), we treated **5a** with CO and observed the formation of a spirocyclic compound (**10**). This represents the first reported reaction between an Si–B bond and CO.[17] The reaction of **5a** with CO in hexane solution gave fused borate **10**, which contains three molecules of CO and two molecules of **5a** (Figure 3a). Interestingly, in **10**, the triple bond of CO was cleaved, and one of the two mesityl groups is dearomatized, forming a spirocyclic ring consisting of five- and six-membered rings.

The proposed reaction mechanism, based on DFT calculations, is shown in Figure 3b (for details, see the Supporting Information).[18] First, CO coordinates to the boron atom (**int 3**), followed by migration of the silyl group with an effective barrier of only +5.8 kcal/mol. As the silyl group migrates, a borylsilylketone (**int 4**) is formed, followed by the formation of siloxycarbene **int 5** (**int4** → **TS4**; $\Delta G^{\ddagger}$ = +28.7 kcal/mol). Considering the entire energy profile, this step serves as the rate-determing step of this reaction. This intermediate is converted into boraalkene **int 6** (**int5** → **TS5**; $\Delta G^{\ddagger}$ = +7.2 kcal/mol). Isomerization then exchanges the mesityl and siloxy groups to generate key intermediate **int 8** (**int6** → **TS6, int 7** → **TS7**; $\Delta G^{\ddagger}$ = +11.9 and +1.7 kcal/mol, respectively).[19] Another molecule of CO then coordinates to the isomerized boraalkene to form **int 9** (**int 8** → **TS8**; $\Delta G^{\ddagger}$ = +6.4 kcal/mol), and an electrophilic dearomatization reaction leads to five-membered ring **int 10** (**int9** → **TS9**; $\Delta G^{\ddagger}$ = +15.5 kcal/mol). Finally, another key intermediate (**int 8**) approaches, with its boron atom coordinated by the carbonyl oxygen of **int 10**. The formed intermediate (**int 11**) then undergoes a subsequent electrophilic dearomatization reaction that leads to the formation of a six-membered ring and provides spirocyclic **10** (**int11** → **TS10**; $\Delta G^{\ddagger}$ = +16.8 kcal/mol).

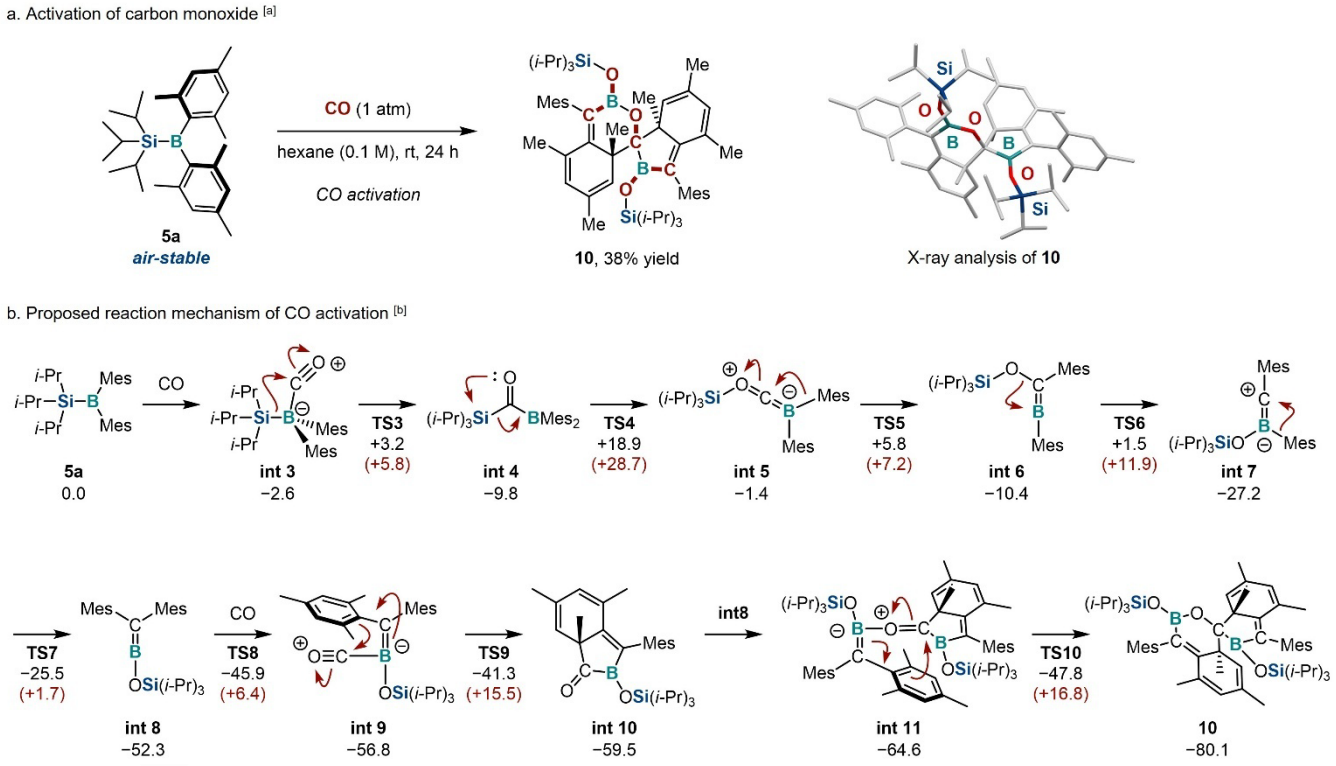


Figure 3. Chemical reactivity between *i*-Pr$_3$Si–BMes$_2$ (**5a**) and CO. [a] Reactions were performed on the 0.1-mmol scale in hexane under a CO atmosphere. [b] Values refer to relative free energies, and values shown in the parentheses represent the effective free-energy barrier associated with that step (in kcal/mol). Calculation methods: B3LYP-D3BJ/6-311G(d,p)/SMD(toluene)//B3LYP-D3/6-311G(d,p)/SMD(toluene).

To gain a better understanding of the chemical reactivity and bench stability of *i*-Pr_3Si–$BMes_2$ (**5a**), we performed further mechanistic studies. First, comparative experiments were performed to evaluate the reactivity of boron compounds stabilized by electron donation and steric hindrance to the vacant p-orbital, such as *i*-Pr_3Si–B(pin) (**1c**) and trimesitylborane (Mes_3B, **11**). **1c** and **11** do not react with CO, whereas the silyldimesitylborane with a bulky *i*-Pr_3Si group (**5a**) is able to react with CO (Figure 4a). To further investigate the origin of the reactivity of **5a** toward CO, CO σ-complexes of **5a** and **11** were compared using DFT calculations (Figure 4b). The change of Gibbs energy to form *i*-Pr_3Si–$B(CO)Mes_2$ (**int 3**) and the $Mes_3B(CO)$ complex (**int 12**) are –2.6 kcal/mol and +16.7 kcal/mol, respectively, indicating the formation of **int 3** is energetically favored. The possible origin of such an energy difference was evaluated based on natural-bond-orbital (NBO) and distortion/interaction-activation (DIA) analyses, which revealed that it results from the hyperconjugation between the Si–B σ-bond and the C–O π*-bond in *i*-Pr_3Si–$B(CO)Mes_2$ (**int 3**). The NBO analysis furthermore showed a significant overlap between the Si–B σ-bond and C–O π*-bond in *i*-Pr_3Si–$B(CO)Mes_2$ (**int 3**), albeit that the overlap between the corresponding C–B σ-bond and C–O π*-bond in $Mes_3B(CO)$ (**int 12**) is minimal. The second-order perturbation energy derived from the NBO analysis also confirmed this strong σ(Si–B) → π^*(C–O) orbital interaction. Further NBO analysis on silylborane **5a** and borane **11** also revealed a stronger π(C–C) → p^*(B) interaction in the latter, making **11** less Lewis-acidic (Table S11). In the DIA analysis, the *i*-Pr_3Si–$B(CO)Mes_2$ complex (**int 3**) exhibited a high interaction energy of –37.3 kcal/mol, probably due to the effect of σ(Si–B) → π^*(C–O) hyperconjugation, whereas the $Mes_3B(CO)$ complex (**int 12**) has a significantly lower interaction energy (–19.6 kcal/mol). In contrast, in this case, the distortion energies, which roughly reflect the steric repulsion upon coordination of CO, were nearly identical for the *i*-Pr_3Si–$B(CO)Mes_2$ complex (**int 3**; +20.6 kcal/mol) and $Mes_3B(CO)$ complex (**int 12**; +22.3 kcal/mol). These results indicate that the contribution of the Si–B bond to the activation of CO is very significant, mainly due to electronic interactions. In the case of the approach of oxygen to the boron center, the oxidation is sensitive to steric hindrance, highlighting the importance of kinetic stabilization. The activation energy for the oxidation of **5a** is relatively high (+27.4 kcal/mol; Figure S11). On the other hand, when CO approaches the boron center, electronic stabilization is crucial for the formation of the σ-complex. In addition, hyperconjugation cannot only stabilize the σ-complex but also activate carbon monoxide as the π^*(C–O) orbital is filled with electrons and therefore weakens the C–O bond. Therefore, the reaction proceeds even in compounds with bulky *i*-Pr_3Si groups.

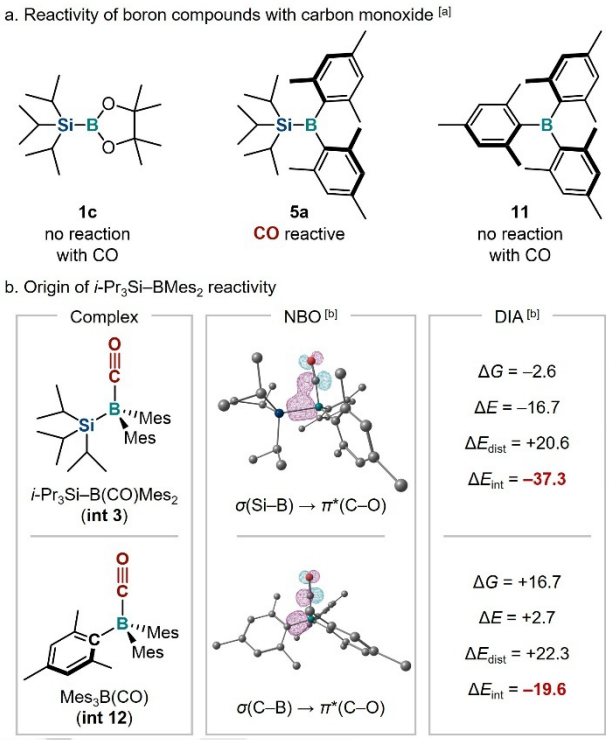


Figure 4. Activation of CO by boron compounds. [a] Reactions were performed on the 0.1-mmol scale in hexane under a CO atmosphere. [b] NBO orbitals were visualized using an isovalue of 0.14. Values refer to Gibbs free energies (G) and electronic energies (E) (in kcal/mol). Calculations were conducted at the B3LYP-D3BJ/6-311G(d,p)/SMD(toluene)//B3LYP-D3BJ/6-311G(d,p)/SMD(toluene) level.

Conclusion

In conclusion, we have demonstrated that introducing an appropriate level of steric hindrance at the silicon atom improves the bench stability of silylboranes of the type R_3Si–BAr_2 and $(R_3Si)_2B$–NR_2, resulting in unique chemical reactivity. Oxidation experiments and density-functional-theory (DFT) calculations revealed that the steric bulk around the silicon atom hinders access of oxygen to the boron center, thus rendering these silylboranes air-stable. Notably, bench stable silylborane *i*-Pr_3Si–$BMes_2$ (**5a**) shows solid-state luminescence upon UV irradiation, indicating potential applicability of R_3Si–BAr_2 derivatives in organic materials. In addition, **5a** shows unprecedented reactivity, such as the formation of spirocyclic compounds with carbon monoxide (CO), driven by the significant hyperconjugation between the Si–B σ-bond and the C–O π*-bond. In addition, bissilylaminoborane (*i*-$Pr_3Si)_2B$–NEt_2 (**7a**) could be transformed into bissilylchloroborane **8**, followed by coordination of an *N*-heterocyclic carbene to produce the air-stable chloroborane **9**. Silylborane **5a** exhibits two features of note, i.e., steric protection around the boron atom providing kinetic stabilization and electronic activation by the Si–B bond, facilitating its reactivity toward CO. The strategy of stabilizing and activating the Si–B bond presented here can be expected to become useful for designing and developing novel materials containing Si–B bonds.

We are convinced that this study will further accelerate the use of silylborane reagents in organic synthesis and organic materials.

Supporting Information

See the supporting information for further details regarding methods and materials, supplementary graphics, characterization data, DFT calculations, and other experiments.

Acknowledgements

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Keywords: Silylboranes • Carbon monoxide activation • Boron-metal exchange • Hyperconjugation • Kinetic stabilization

[1] a) J.-J. Feng, W. Mao, L. Zhang, M. Oestreich, *Chem. Soc. Rev.* **2021**, *50*, 2010; b) K. Kubota, H. Ito, in *Catalytic Generation of Silicon Nucleophiles, Organosilicon Chemistry: Novel Approaches and Reactions* (Eds.: T. Hiyama and M. Oestreich), Wiley-VCH, Weinheim, **2019**, pp. 1–31; c) J. R. Wilkinson, C. E. Nuyen, T. S. Carpenter, S. R. Harruff, R. Van Hoveln, *ACS Catal.* **2019**, *9*, 8961; d) L. B. Delvos, M. Oestreich, in *Science of Synthesis Knowledge Update 2017/1* (Eds.: M. Oestreich), Thieme, Stuttgart, **2017**, pp. 65–176; e) A. B. Cuenca, R. Shishido, H. Ito, E. Fernández, *Chem. Soc. Rev.* **2017**, *46*, 415; f) Y. Tsuji, T. Fujihara, *Chem. Rec.* **2016**, *16*, 2294; g) A. Hensel, M. Oestreich, *Top. Organomet. Chem.* **2016**, *58*, 135; h) M. Sawamura, H. Ito, in *Copper-Catalyzed Asymmetric Synthesis*, Wiley-VCH, Weinheim, Germany, **2014**, pp. 157–178; i) M. Oestreich, E. Hartmann, M. Mewald, *Chem. Rev.* **2013**, *113*, 402. j) T. Ohmura, M. Suginome, *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29.

[2] M. Suginome, H. Nakamura, Y. Ito, *Chem. Commun.* **1996**, 2777.

[3] a) T. A. Boebel, J. F. Hartwig, *Organometallics* **2008**, *27*, 6013; b) E. Yamamoto, R. Shishido, T. Seki, H. Ito, *Organometallics* **2017**, *36*, 3019; c) S. Kamio, T. Imagawa, M. Nakamoto, M. Oestreich, H. Yoshida, *Synthesis* **2021**, *53*, 4678.

[4] a) R. Shishido, M. Uesugi, R. Takahashi, T. Mita, T. Ishiyama, K. Kubota, H. Ito, *J. Am. Chem. Soc.* **2020**, *142*, 14125 b) T. Takeuchi, A. Roy, H. Ito, *J. Am. Chem. Soc.* **2023**, *145*, 16249.

[5] a) A. Matsumoto, Y. Ito, *Org. Chem.* **2000**, *65*, 5707. b) M. Kondo, J. Kanazawa, T. Ichikawa, T. Shimokawa, Y. Nagashima, K. Miyamoto, M. Uchiyama, *Angew. Chem., Int. Ed.* **2020**, *59*, 1970. c) N. Takemura, Y. Sumida, H. Ohmiya, *ACS Catal.* **2022**, *12*, 7804. d) S. Ishigaki, Y. Nagashima, D. Yukimori, J. Tanaka, T. Matsumoto, K. Miyamoto, M. Uchiyama, K. Tanaka, *Nat. Commun.* **2023**, *14*, 652.

[6] We have previously reported a decomposition study of silylboranes (*cf.* ref. 3b), but in that paper, we did not determine whether the precise degradation mechanism was oxidation or hydrolysis. To the best of our knowledge, there is only one other paper on the degradation of silylboranes, which describes a side reaction of silylborane activation; for details, see: C. Gryparis, M. Stratakis, *Org. Lett.* **2014**, *16*, 1430.

[7] a) H. Yoshida, Y. Izumi, Y. Hiraoka, K. Nakanishi, M. Nakamoto, S. Hatano, M. Abe, *Dalton Trans.* **2022**, *51*, 6543; b) J. Carlos Araujo Da Silva, M. Birot, J.-P. Pillot, M. Pétraud, *J. Organomet. Chem.* **2002**, *646*, 179; c) M. Birot, J.-P. Pillot, J.-P. Desvergne, J. Araujo da Silva, J.-C. Rayez, M.-T. Rayez, J. Mascetti, D. Liotard, *J. Mol. Struct.* **2003**, *646*, 179; d) E. Yamamoto, K. Izumi, T. Shishido, T. Seki, N. Tokodai, H. Ito, *Chem.-Eur. J.* **2016**, *22*, 17547. e) J. Gilmer, M. Bolte, A. Virovets, H.-W. Lerner, F. Fantuzzi, M. A Wagner, Chem. Eur. J. **2023**, *29*, e202203119. f) J. Gilmer, T. Trageser, L. Čaić, A. Virovets, M. Bolte, H.-W. Lerner, F. Fantuzzi, M. Wagner, Chem. Sci. **2023**, *14*, 4589.

[8] For selected examples of kinetically stable boron compounds, see: a) S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2002**, *124*, 8816; b) L. G. Mercier, W. E. Piers, M. Parvez, *Angew. Chem., Int. Ed.* **2009**, *48*, 6108; c) A. Caruso Jr, M. A. Siegler, J. D. Tovar, *Angew. Chem., Int. Ed.* **2010**, *49*, 4213; d) Y. Shoji, N. Tanaka, Y. Ikabata, H. Sakai, T. Hasobe, N. Koch, H. Nakai, T. Fukushima, *Angew. Chem., Int. Ed.* **2022**, *61*, e202113549.

[9] SC-AFIR is an automated reaction path search method; for details, see: S. Maeda, Y. Harabuchi, M. Takagi, K. Saita, K. Suzuki, T. Ichino, T. Sumiya, K. Sugiyama, Y. Ono, *J. Comput. Chem.* **2018**, *39*, 233. The possible reaction mechanism was calculated using the SC-AFIR method implemented in the global reaction route mapping (GRRM) program combined with the Gaussian 16 program; for details, see the Supporting Information.

[10] S. Maeda, Y. Harabuchi, *J. Chem. Theory Comput.* **2019**, *15*, 2111.

[11] The MECP was calculated using the GRRM program; for details, see the Supporting Information.

[12] We have previously synthesized $MePh_2Si–BMes_2$, but we found that this compound was difficult to synthesize and handle under ambient conditions; see also: ref. 7d.

[13] A. Kawachi, T. Minamimoto, K. Tamao, *Chem. Lett.* **2001**, *30*, 1216.

[14] J. D. Buynak, B. Geng, *Organometallics* **1995**, *14*, 3112.

[15] D. J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke, W. Weuter, *J. Organomet. Chem.* **1989**, *378*, 125.

[16] We used an NHC dimer instead of an isolated NHC monomer, but the coordination of the carbene monomer to the vacant p-orbital of boron was successful. We could not isolate the NHC monomer even when applying reported procedures. For the isolation of the NHC monomer, see: J. Messelberger, A. Grünwald, S. J. Goodner, F. Zeilinger, P. Pinter, M. E. Miehlich, F. W. Heinemann, M. M. Hansmann, D. Munz, *Chem. Sci.* **2020**, *11*, 4138.

[17] Organoboron compounds can react with CO, which results in e.g., carbonyl complexes of boron, carbonyl insertion into C–B bonds, and the cleavage of C–O triple bond of CO by organoboron compounds; for details, see: a) H. C. Brown, *Acc. Chem. Res.* **1969**, *2*, 65. ; b) Y. Katsuma, N. Tsukahara, L. Wu, Z. Lin, M. Yamashita, *Angew. Chem., Int. Ed.* **2018**, *57*, 6109. c) S. Fujimori, S. Inoue, *J. Am. Chem. Soc.* **2022**, *144*, 2034.

[18] All steps were calculated using the Gaussian 16 program, except for the formation of **int 8** from **int 6**, whose formation steps were calculated using the artificial force induced reaction (AFIR) method implemented in the GRRM program combined with the Gaussian 16 program; for details, see the Supporting Information.

[19] It seems feasible to assume that the reaction can proceed even though **int 6** contains a silyl enol ether moiety due to the inherently high reactivity of the boraalkene unit. For a related example demonstrating the high reactivity of a boraalkene, see ref. 17b.

[20] Deposition Numbers: 2429990 (for **5a**), 2429988 (for **7a**), 2429991 (for **9**), 249989 (for **10**), 249992 (for **10'**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe.

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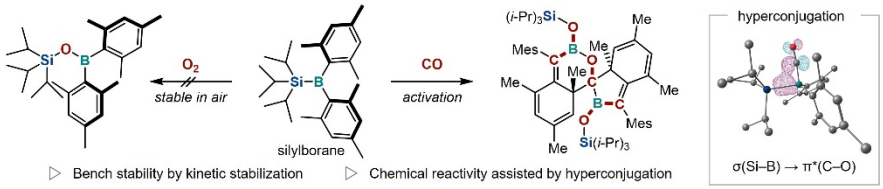

Following initial experimental and theoretical studies that indicated that silylboranes decompose via oxygenation, bulky silyl anions were used to synthesize silylboranes with enhanced bench stability and novel reactivity. These kinetically stabilized silylboranes are stable in air and moderately activate carbon monoxide (CO) to form spirocyclic compounds. DFT calculations suggested that the activation of CO is driven by hyperconjugation.