Reactions of Dihaloboranes with Electron-Rich 1,4-Bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadienes

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Abstract: The reactions of electron-rich organosilicon compounds 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (1), 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (2), and 1,1′-bis(trimethylsilyl)-1,1′-dihydro-4,4′-bipyridine (12) with B-amino and B-aryl dihaloboranes afforded a series of novel B=N-bond-containing compounds 3–11 and 13. The B=N rotational barriers of 7 (>71.56 kJ/mol), 10 (58.79 kJ/mol), and 13 (58.65 kJ/mol) were determined by variable-temperature 1H-NMR spectroscopy, thus reflecting different degrees of B=N double bond character in the corresponding compounds. In addition, ring external olefin isomers 11 were obtained by a reaction between 2 and DurBBr₂. All obtained B=N-containing products were characterized by multinuclear NMR spectroscopy. Compounds 5, 9, 10a, 11, and 13a were also characterized by single-crystal X-ray diffraction analysis.

Keywords: 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadienes; salt-free reduction; rotational barrier; B=N bond

1. Introduction

Low-valent boron compounds are a class of highly reactive species that have been the focus of intense research because of their unique electronic properties [1,2] as well as their diverse and fascinating reactivity patterns such as inert bond activation [3,4], cycloaddition reaction [5–7], and small molecule activation [8]. The progress in this research area is highlighted by the very recent results in terms of borylene-mediated N₂ activation [9] and N₂ coupling [10]. Nonetheless, the synthetic approach to low-valent boron species is severely limited [11–13]. Almost all of the reported synthetic strategies require a strong metallic reducing agent (e.g., Li, K, Na, KC₈) [3,4,14–23], harsh reaction conditions, and a strict moisture- and oxygen-free atmosphere. Therefore, the exploration of metal-free reductants to access low-valent boron species is highly desirable [24–26].

Mashima et al. reported a class of electron-rich organosilicon compounds 1, 2, and 12, which can serve as versatile reducing reagents for the group 4–6 metal chloride complexes. The corresponding low-valent metal species were prepared in a salt-free manner [27–33]. The reducing power mainly derives from the aromatization of the central 1,4-diaza-2,5-cyclohexadiene ring. Deeply inspired by the advantage of the salt-free reduction protocol and easy workup, we decided to examine the ability of the organosilicon compounds 1, 2, and 12 for the reduction of trivalent dihaloboranes. Based on the published results, the disubstituted compounds ArXB(N₂C₄R₄)BXAr are proposed as the reduction products. We hypothesized two possible bonding modes (i.e., A and B in Scheme 1) between the C₄N₂ ring and the boron atoms. In the first manner, B=N is bound by an electron-precise σ bond (A, Scheme 1) and an additional N—B dative π bond. In the second manner, two nitrogen atoms each
provide a π-electron for 6π-aromatization, while the remaining two valence electrons form a lone pair on each N atom, donating to the empty sp²-hybridized orbital of boron, thus leading to the divalent boron radical centers (B, Scheme 1).

Scheme 1. Proposed products from the reactions of ArBX₂ with 1 and 2, and two possible bonding modes A and B between the central C₄N₂ ring and the boron centers.

2. Results and Discussion

First, we examined compound 1 for its ability to reduce ArBX₂. The results are summarized in Scheme 2. Compound 1 [34] and ArBX₂ (Ar = 2,3,5,6-tetramethylphenyl (Dur), 2,4,6-trimethylphenyl (Mes)) [35] were prepared according to the literature. The reaction of 1 with an equimolar amount of DurBB₂ and MesBC₂ at ambient temperature afforded the expected monosubstituted products 3 and 4, respectively. Adding the second equiv. of dihaloboranes to the reaction mixture led to the disubstituted products 5 and 6. In stark contrast, the reaction of 1 with an equimolar amount of the less sterically demanding PhBC₂ caused precipitation, which is insoluble in all ordinary solvents. This is most likely due to the polymerization of PhCIBC₄N₂H₄SiMe₃ by chlorosilane elimination. Hence, the stepwise synthetic protocol is unsuitable for the synthesis of 7. Instead, 1 was directly treated with 2 equiv. of PhBC₂ to room temperature (RT), affording 7 in an acceptable yield (48%). Hence, the reaction of the monosubstituted intermediate (i.e., PhCIBC₄N₂H₄SiMe₃) with PhBC₂ should be much faster than the self-polymerization process. Compounds 3–7 were confirmed by NMR spectroscopic (Figures S1–S15) and HRMS studies. Furthermore, the multinuclear NMR spectroscopic study revealed that the isolated 5–7 all consist of ca. 1:1 cis-trans isomers in the solution phase at ambient temperature due to the nonrotatable B=N double bond (see Electronic Supporting Information (ESI)).

Suitable single crystals of 5 for X-ray diffraction analysis were obtained by slow evaporation of a saturated hexane solution. Two isomers, 5a and 5b, co-crystallized in the unit cell. The result is depicted in Figure 1 and Figure S37. The central C₄N₂ ring is nearly planar. The endocyclic N1–C2 (1.385(7) Å), N2–C3 (1.415(7) Å), C1–C2 (1.311(9) Å), and C3–C3* (1.326(8) Å) distances lie in the expected range for N–C single bonds and C=C double bonds. The bond lengths of B1–N1 (1.423(8) Å) and B2–N2 (1.400(8) Å) are shorter than that of a B–N single bond, which is indicative of a significant B=N double bond character. All these geometric parameters suggest the bonding mode A in Scheme 1. Therefore, both boron centers adopt a formal oxidation state of +3.
Compound 2, which features a less-negative redox potential (+0.10 V) with respect to 1 (−0.24 V), was further examined to reduce PhBCl₂ and DurBBr₂ (Scheme 2). Differing from the aforementioned reactions with 1, both monosubstituted products 8 and 9 could be prepared upon a 1:1 ratio reaction of 2 with PhBCl₂ and DurBBr₂, respectively. Upon the reaction of 2 with two equiv. of PhBCl₂ at RT, the disubstituted compounds 10a and 10b were obtained as 1:1 cis-trans isomers. Surprisingly, treatment of 2 with two equiv. of DurBBr₂ at ambient temperature led to the formation of 11, which can be regarded as the product from an isomerization of 11' [36,37]. Compounds 8–11 were confirmed by NMR spectroscopic (Figures S16–S28) and HRMS studies. There were two sets (intensity ratio of ca. 1:0.3) of ¹H signals between 4 and 6 ppm, each consisting of three multiplets with the integration ratio of 1:1:1, which can be assigned to the migrated H and two remaining olefinic protons. These are the
most characteristic signs for the formation of the isomerized product. After assigning each peak (with the help of the NOE spectrum, see the ESI Figure S26 for more details), we could determine that the ratio of isomers 11a and 11b was 77:23. Furthermore, the isomerization was also observed upon the treatment of the isolated 9 with an equimolar amount of DurBBr₂ at RT.

The structures of 9, 10a, 11a, and 11b were confirmed by single-crystal X-ray diffraction analysis (Figure 2 and Figures S38–S40). All four compounds adopt a boat conformation, which could be explained by the small energy difference between the planar and nonplanar geometry of the C₄N₂ ring, and the steric congestion between the central exocyclic methyl groups and the bulky boron substituents. Bond lengths (Å) of 9 (B₁–N₁ 1.376(7), N₁–C₁ 1.451(6), C₁–C₂ 1.343(7), N₂–C₂ 1.434(6), N₂–Si₁ 1.759(5)), 10 (B₁–N₁ 1.401(2), N₁–C₂ 1.449(17), C₁–C₂ 1.328(2), N₁–C₁* 1.4513(18)) are all as expected. The overall structures of 11a and 11b resemble that of 10a. However, since the C₃ position in 11a and 11b accepted one H atom from the methyl group at the C₂ position, respectively, and thus became sp²-hybridized, the torsion angles C₄–C₃–N₂–B₂ (11a: 94.25°; 11b: 94.69°) are notably greater than those at the other three carbon positions (57°–63°) in the central six-membered ring. Due to the disordered nature of the crystal, the bond lengths of 11a and 11b cannot be further discussed.

![Figure 2](image)

**Figure 2.** Molecular structures of 9, 10a, and 11 in the solid state (ellipsoids set at 50% probability). Hydrogen atoms, except for the C(sp³)–H and the olefinic H in 11a and 11b, are omitted for clarity. Selected bond lengths (Å) and angles (°) for 9: B₁–N₁ 1.376(7), N₁–C₁ 1.451(6), C₁–C₂ 1.343(7), N₂–C₂ 1.434(6), N₂–Si₁ 1.759(5), C₂–C₁–N₁ 115.3(4), C₁–N₁–C₁* 111.1(4); for 10a: B₁–N₁ 1.401(2), N₁–C₂ 1.449(17), C₁–C₂ 1.328(2), N₁–C₁* 1.4513(18), C₁–C₂–N₁ 116.25(12), C₂–N₁–C₁* 110.63(11).

The reaction of (SiMe₃)₂NBCl₂ with 12 [38] of greater reducing power (redox potential of −0.40 V) [39] was performed at ambient temperature in C₄D₆. After the removal of the solvent and extraction with hexane, an NMR spectroscopically pure product 13 was obtained with a yield of 75%. Compound 13 was confirmed by NMR spectroscopic (Figures S29–S31) and HRMS studies. Suitable single crystals of 13a for X-ray diffraction analysis were obtained upon storage of the reaction mixture overnight at RT (Figure 3 and Figure S41). The N₁–C₁/N₁–C₅ (1.402(8)–1.414(8) Å), C₁–C₂/C₅–C₄ (1.332(8)–1.347(9) Å), C₂–C₃/C₃–C₄ (1.444(9)–1.452(9) Å), C₃–C₃* (1.376(12) Å) distances are in line with the Lewis structure depicted in Scheme 3.
Figure 3. Molecular structure of 13a in the solid state (ellipsoids set at 50% probability). Selected bond lengths (Å) and angles (°) for 13a: B1–N1 1.459(8), B1–N2 1.392(10), Si1–N2 1.757(5), Si2–N2 1.770(5), N1–C1 1.402(8), N1–C5 1.414(8), C1–C2 1.332(8), C4–C5 1.347(9), C2–C3 1.452(9), C3–C4 1.444(9), C3–C3* 1.376(12), C1–N1–C5 115.7(5), C2–C1–N1 123.3(6), C1–C2–C3 122.9(6), C4–C3–C2 112.7(5), C5–C4–C3 123.3(6), C4–C5–N1 122.1(6).

Scheme 3. Synthesis of 13.

Apparently, both the RT-NMR spectroscopic and crystallographic studies failed to prove any successful reduction of the trivalent borane to divalent boron radical. Since the rotational barrier around an N–B dative bond should be lower than that of a B=N double bond, we assumed that any contribution from the bonding mode B (Scheme 1) should slightly lower the rotational barrier around the exocyclic B–N bond. In this context, we conducted a variable-temperature 1H-NMR experiment to provide further insight. Toluene-d8 was selected as the solvent with a temperature ranging from −60 °C to 80 °C. In general, the exocyclic H or Me as marked in Figure 4 (top right) should display two signals if the B=N bond is nonrotatable. The separated signals will coalesce at an elevated temperature when the B–N bond overcomes the rotational barrier and begins to rotate. Determination of the separation (Hz) of two signals and the coalescent temperature allows calculation of the B–N rotational barrier. The results of the VT-NMR experiments and assignment of the signals of interest are depicted in Figure 4 and Figures S32–S36. The obtained ΔG‡ values are summarized in Table 1. Analysis of the VT-NMR spectra revealed 7 with a strong B=N bond, and 10 and 13 with weak B=N bonds, as reflected by their rotational barriers >71.56 kJ/mol (7), 58.79 kJ/mol (10), 58.65 kJ/mol (13) when compared with ordinary B=N double bonds (71–100 kJ/mol) [40]. When taking the aforementioned assumption into account, the remarkably lower B–N rotational barrier of 10 compared to that of 7 is not in line with the fact that the reducing power of 2 is slightly weaker than that of 1, according to the CV data. Therefore, the lower B–N rotational barrier in 10 should be mainly due to its boat conformation, which allows for less steric hindrance. Furthermore, although the central C4N2 rings of 7 and 13 both adopt a planar structure, the B–N rotational barrier in 13 is significantly lower than that of 7. This finding could be explained by the competition in π donation from another B-amino function (–N(SiMe3)2) in 13.
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10 should be mainly due to its boat conformation, which allows for less steric hindrance. Furthermore, although the central C4N2 rings of 
7 and 13 both adopt a planar structure, the B–N rotational barrier in 13 is significantly lower than that of 7. This finding could be explained by the competition in π donation from another B-amino function (–N(SiMe3)2) in 13.

**Figure 4.** Variable-temperature 1H-NMR (400 MHz, toluene-d8) spectra of 7, 10, and 13.

**Table 1.** Rotational barrier of 7, 10, and 13.

| Compound | Tc       | Δν     | ΔG (kJ/mol) |
|----------|----------|--------|-------------|
| 7        | >80 °C (353 K) | 85.0 Hz | >71.56 | |
| 10       | 32 °C (305 K)  | 243.5 Hz | 58.79 | |
| 13       | 20 °C (293 K)  | 96.0 Hz  | 58.65 | |

Tc = coalescence temperature; Δν = the separation in hertz between the two singlets in the absence of exchange; ΔG (kJ/mol) = rotational barrier.
3. Materials and Methods

3.1. General Information

All manipulations were performed under dry argon using standard Schlenk line or glovebox techniques. Solvents were purified by distillation from Na under dry argon. C₆D₆ was dried over an Na/K alloy and then degassed by freeze–pump–thaw cycles. PhBCl₃ was purchased from Beijing MREDA Technologie Co., Ltd., without any special treatment before use. The NMR spectra were acquired on a Bruker AVANCE 400 (¹H: 400 MHz, ¹³C[¹H]): 101 MHz, ¹⁹B: 128 MHz) NMR spectrometer at 298 K. Variable-temperature NMR experiments were conducted on a Bruker AVANCE 400 NMR spectrometer (¹H: 400 MHz, 213–353 K). Chemical shifts are given in ppm. ¹H and ¹³C[¹H] NMR spectra were referenced to an external tetramethylsilane (TMS) via the residual protons of the solvent (¹H) or the solvent itself (¹³C[¹H]). ¹⁹B NMR spectra were referenced to the external BF₃·OEt₂. High-resolution mass spectrometry (HRMS) was performed with a Thermo Fisher Scientific Q Exactive Mass Spectrometer (MS) system.

3.2. Synthesis of 3 and 4:

In the glove box, DurBBr₂ (30.3 mg, 0.1 mmol, 1.0 equiv.) and 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (1) (22.6 mg, 0.1 mmol, 1.0 equiv.) were added into C₆D₆ (0.6 mL) in a J. Young NMR tube. The mixture was rested for 10 min prior to the removal of the volatiles under vacuum to get 3 as a pale yellow solid (23.6 mg, 72 mmol, 63%). Compound 4 was synthesized in a similar manner, with a yield of 64%.

3: ¹H-NMR (400 MHz, C₆D₆): δ = 6.86 (s, 1H, H of Dur), 6.35 (d, J = 6.6 Hz, 1H, H of C₆N₂), 5.13 (d, J = 6.5 Hz, 1H, H of C₆N₂), 4.91 (d, J = 6.6 Hz, 1H, H of C₆N₂), 4.64 (d, J = 6.5 Hz, 1H, H of C₆N₂), 2.29 (s, 6H, Me of Dur), 2.06 (s, 6H, Me of Dur). Compound 4 was synthesized in a similar manner, with a yield of 64%.

4: ¹H-NMR (400 MHz, C₆D₆): δ = 6.75 (s, 2H, H of Mes), 6.17 (d, J = 6.6 Hz, 1H, H of C₆N₂), 5.07 (d, J = 6.5 Hz, 1H, H of C₆N₂), 4.91 (d, J = 6.6 Hz, 1H, H of C₆N₂), 4.65 (d, J = 6.5 Hz, 1H, H of C₆N₂), 2.37 (s, 6H, Me of Mes), 2.15 (s, 3H, Me of Mes), 0.21 (s, 9H, Me of TMS). ¹³C[¹H]-NMR (101 MHz, C₆D₆): δ = 139.2, 137.8, 127.5, 119.4, 118.5, 112.4 (1C, C of C₆N₂), 112.8 (1C, C of C₆N₂), 21.3 (2C, o-CH₃ of Mes), 20.9 (C, p-CH₃ of Mes). The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. ¹⁹B-NMR (128 MHz, C₆D₆): δ = 34.1. HRMS: calc. for [M]+ C₁₇H₂₃BBrN₂Si+ 378.1362; found: 378.1363.

3.3. Synthesis of 5–7

In the glove box, DurBBr₂ (60.4 mg, 0.2 mmol, 2.0 equiv.) and 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (1) (22.6 mg, 0.1 mmol, 1.0 equiv.) were added into C₆D₆ (0.6 mL) in a J. Young NMR tube. The mixture was rested overnight prior to the removal of the volatiles under vacuum to get 5 as a yellow oil with a 45% yield. Mixture 5 contains the cis-structure 5a and trans-structure 5b, and the ratio of the cis-trans isomers was about 1:1. Compounds 6–7 were synthesized in a similar manner, with a cis-trans ratio of about 1:1 (yield: 52% (6) and 48% (7)).

5a + 5b: ¹H-NMR (400 MHz, C₆D₆): δ = 6.86 (s, 2H), 6.82 (s, 2H), 6.52 (s, 2H), 6.26 (d, 3JH-H = 1.6 Hz, 1H), 6.24 (d, 3JH-H = 1.6 Hz, 1H), 5.36 (d, 3JH-H = 1.6 Hz, 1H), 5.34 (d, 3JH-H = 1.6 Hz, 1H), 4.99 (s, 2H), 2.09 (s, 12 H), 2.07 (s, 12 H), 2.03 (s, 12 H), 2.01 (s, 12 H). ¹³C[¹H]-NMR (101 MHz, C₆D₆): δ = 134.0, 133.9, 133.6, 133.5, 132.5, 132.3, 118.2, 117.7, 117.2, 116.6, 19.2, 19.1, 18.5, 18.4. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. ¹⁹B-NMR (128 MHz, C₆D₆): δ = 38.9. HRMS: calc. for [M]+ C₁₆H₂₄B₂ClN₂Si+ 526.09564; found: 526.09549.

6a + 6b: ¹H-NMR (400 MHz, C₆D₆): δ = 6.69 (s, 4H), 6.67 (s, 4H), 6.34 (s, 2H), 6.09 (d, 3JH-H = 1.6 Hz, 1H), 6.08 (d, 3JH-H = 1.6 Hz, 1H), 5.32 (d, 3JH-H = 1.6 Hz, 1H), 5.30 (d, 3JH-H = 1.6 Hz, 1H), 4.94 (s,
2H), 2.19 (s, 12H), 2.16 (s, 12H), 2.13 (s, 6H), 2.12 (s, 6H). $^{13}$C$^1$H-NMR (101 MHz, C$_6$D$_6$): δ = 138.9, 138.8, 138.6, 138.5, 127.6, 127.6, 117.3, 116.4, 116.3, 115.5, 21.2, 21.1, 20.9, 20.8. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. $^{11}$B-NMR (128 MHz, C$_6$D$_6$): δ = 38.5. HRMS: calc. for [M]+ C$_{22}$H$_{32}$N$_2$B$_2$Cl$^+$ 410.16537; found: 410.16492.

7a + 7b: $^1$H-NMR (400 MHz, C$_6$D$_6$): δ = 7.86 (s, 2 H), 7.51–7.46 (m, 8 H), 7.19–7.15 (m, 10 H), 6.29 (s, 2H), 6.08 (d, $^3$J$_{H-H}$ = 1.68 Hz, 1H), 6.06 (d, $^3$J$_{H-H}$ = 1.64 Hz, 1H), 5.78 (d, $^3$J$_{H-H}$ = 1.60 Hz, 1H), 5.76 (d, $^3$J$_{H-H}$ = 1.70 Hz, 1H), 5.54 (s, 2 H). $^{13}$C$^1$H-NMR (101 MHz, C$_6$D$_6$): δ = 133.3, 133.2, 130.2, 130.1, 127.9, 127.8, 118.0, 117.5, 116.8, 116.5. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. $^{11}$B-NMR (128 MHz, C$_6$D$_6$): δ = 36.5. HRMS: calc. for [M]+ C$_{16}$H$_{14}$N$_2$B$_2$Cl$_2$ + 326.07147; found: 326.07069.

3.4. Synthesis of 8 and 9

Compounds 8 and 9 were synthesized in a similar manner as 3 and 4, with yields of 65% and 75%, respectively.

8: $^1$H-NMR (400 MHz, C$_6$D$_6$): δ = 7.93–7.90 (m, 2H), 7.85–7.83 (m, 1H), 7.24–7.13 (m, 2H), 2.14 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H), 1.52 (s, 3H), 0.19 (s, 9H). $^{13}$C$^1$H-NMR (101 MHz, C$_6$D$_6$): δ = 132.5, 132.2, 131.9, 131.9, 131.6, 128.6, 128.0, 122.8, 121.8, 16.8, 16.7, 16.7, 16.5, 0.2. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. $^{11}$B-NMR (128 MHz, C$_6$D$_6$): δ = 35.9. HRMS: calc. for [M+H]+ C$_{17}$H$_{27}$N$_2$BClSi + 333.17196; found: 333.17233.

9: $^1$H-NMR (400 MHz, C$_6$D$_6$): δ = 6.88 (s, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), Me of Durr, 2.10 (s, 2H), 2.06 (s, 3H), 1.71 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H), 0.25 (s, 9H). $^{13}$C$^1$H-NMR (101 MHz, C$_6$D$_6$): δ = 133.8, 133.2, 133.1, 133.0, 132.8, 131.6, 131.4, 122.5, 122.0, 19.6, 19.4, 19.3, 19.2, 18.1, 18.0, 16.1, 1.8. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. $^{11}$B-NMR (128 MHz, C$_6$D$_6$): δ = 37.7. HRMS: calc. for [M+H]+ C$_{21}$H$_{35}$N$_2$BBrSi + 433.18405; found: 433.18483.

3.5. Synthesis of 10

In the glove box, PhBCl$_2$ (31.6 mg, 0.2 mmol, 2.0 equiv.) and 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (2) (28.2 mg, 0.1 mmol, 1.0 equiv.) were added into C$_6$D$_6$ (0.6 mL) in a J. Young NMR tube. The mixture was rested overnight prior to the removal of the volatiles under vacuum to get 10 as a pale yellow solid (24.9 mg, 0.53 mmol, 53%).

10a + 10b: $^1$H-NMR (400 MHz, toluene-d$_8$): δ = 7.72–7.20 (m, 8H), 7.11–7.06 (m, 12H), 1.95 (br, 12H), 1.45 (br, 12H). $^{13}$C$^1$H-NMR (101 MHz, toluene-d$_8$): δ = 133.2, 130.2, 129.1, 128.6, 128.2, 128.0, 127.9, 127.7, 125.4, 124.9, 20.8, 20.7, 20.3, 20.1. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. $^{11}$B-NMR (128 MHz, toluene-d$_8$): δ = 36.9. HRMS: calc. for [M+H]+ C$_{20}$H$_{23}$N$_2$B$_2$Cl$_2$ + 383.14189; found: 383.14083.

3.6. Synthesis of 11a and 11b

In the glove box, 9 (37.6 mg, 0.1 mmol, 1 equiv.) and DurBBr$_2$ (30.3 mg, 1 mmol, 1.0 equiv.) were added into C$_6$D$_6$ (0.6 mL) in a J. Young NMR tube. The mixture was rested overnight prior to the removal of the volatiles under vacuum to get 11 as a yellow oil with a yield of 76%. Mixture 11 contains two olefin isomers, 11a and 11b, with a ratio of about 1:3.

11a: $^1$H-NMR (400 MHz, C$_6$D$_6$): δ = 6.91 (s, 1H), 6.89 (s, 1H), 5.14–5.13 (m, 1H), 4.72–4.71 (m, 1H), 4.38 (s, 1H), 2.58 (s, 3H), 2.55 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 2.11 (s, 3H), 2.09 (s, 6H), 2.07 (s, 3H), 1.99 (d, $^3$J$_{H-H}$ = 0.8 Hz, 3H), 1.41 (d, $^3$J$_{H-H}$ = 0.8 Hz, 3H), 0.91 (d, $^3$J$_{H-H}$ = 6.6 Hz, 3H).

11b: $^1$H-NMR (400 MHz, C$_6$D$_6$): δ = 6.89 (s, 1H), 6.88 (s, 1H), 5.75–5.70 (m, 1H), 4.47–4.46 (m, 1H), 4.07–4.06 (m, 1H), 2.54 (s, 3H), 2.52 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 2.10 (s, 3H), 2.09 (s, 9H), 2.07 (s, 3H), 1.98 (d, $^3$J$_{H-H}$ = 1.1 Hz, 3H), 1.45 (d, $^3$J$_{H-H}$ = 1.1 Hz, 3H), 1.13 (d, $^3$J$_{H-H}$ = 8.0 Hz, 3H).

11a + 11b: $^{13}$C$^1$H-NMR (101 MHz, C$_6$D$_6$): δ = 152.0, 151.4, 133.7, 133.6, 133.6, 133.5, 133.4, 133.3, 133.2, 133.2, 132.6, 132.2, 132.1, 132.0, 131.7, 131.4, 131.4, 131.1, 130.8, 129.9, 105.6, 101.7, 61.2,
17.9, 15.4. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening. 

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4. Conclusions

In summary, the reactions of electron-rich organosilicon compounds 1, 2, and 12 with various B-amino and B-aryl dihaloboranes were comprehensively studied. No direct evidence for the presence of divalent boron radical character could be obtained from NMR spectra and single-crystal structures. The rotational barrier around the exocyclic B–N bonds was studied by VT H-NMR spectroscopy, which revealed relatively small barriers for 10 and 13. The steric hindrance as well as the competition from additional B-amino functions were the main factors affecting the B–N rotational barrier. In addition, the reaction between 2 and DurBBr resulted in 11 via an isomerization process. Although this study does not access the desired biradial species, we believe that the novel B=N-containing products could act as RXB• source upon the liberation of the aromatic linker (i.e., pyrazine and 4,4’-bipyridine). Studies of the mechanism of the isomerization reaction, as well as the application of 10 and 13 as RXB• transfer reagents to unsaturated organic substrates, are currently underway in our laboratory, and will be reported in due course.

Supplementary Materials: Supplementary materials are available online. Figures S1–S31: NMR spectra for 3–11, 13. Figures S32–S36: Variable-temperature 1H-NMR spectra for 7, 10, and 13. Figures S37–S41, Single crystal structure for 5, 9–11, and 13. Table S1: Crystal data for 5, 9–11, and 13.

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