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Relation	

B(MIDA)-Containing Diborons

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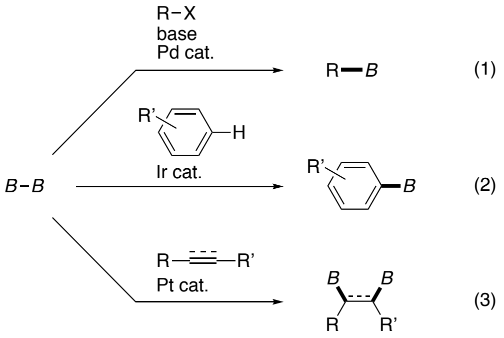
ABSTRACT: Unsymmetrical B(MIDA)-containing diborons of potential synthetic utility were found to be synthesized from readily available (neop)B–B(neop) and $(HO)_2B$–$B(OH)_2$, and the procedure was extended to generation of symmetrical (MIDA)B–B(MIDA). NMR and X-ray crystal structure studies revealed that B(MIDA) units of all diborons obtained in this study were in rigid tetrahedral environment.

INTRODUCTION

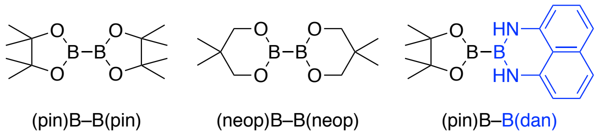
Compounds having a boron–boron σ-bond, diborons (alternatively termed diboron(4) and diborane(4)),[1] have proven to be essential reagents for synthesizing diverse organoboron compounds, which play a pivotal role in modern synthetic organic chemistry,[2] through Miyaura–Ishiyama borylation (C–X borylation, X: halogen, OTf, …) (eq 1, Scheme 1),[3] Hartwig–Miyaura C–H borylation (eq 2),[4] diborylation of unsaturated C–C bonds (eq 3),[5] etc..[6]

Scheme 1. Synthesis of Organoboron Compounds with Diborons



Among various diborons thus far prepared, bench-stable and easy-to-handle tetraalkoxydiborons such as bis(pinacolato)diboron [(pin)B–B(pin)][7] and bis(neopentyl glycolato)diboron [(neop)B–B(neop)][8] have been the mainstay in the above borylation reactions (Figure 1), and recent attention has also been directed toward the use of unsymmetrical diborons[1a,9] aiming at installation of different boryl groups into organic frameworks and opposite regioselectivities to those with (pin)B–B(pin), thus leading to enlarged structural diversity of organoboron compounds to be accessed.

Figure 1. Representative diborons employed in various borylation reactions.



In particular, we have been engaged on synthetic utilization of (pin)B–B(dan)[10] (dan: 1,8-diaminonaphthalene) for copper-catalyzed B(dan)-installing reactions including hydroboration,[11a,b] borylstannylation,[11c] carboboration[11d] and substitutional borylation[11e] (Scheme 2), where their unique site- and regioselectivities are mainly governed by the diminished Lewis acidity of the B(dan) moiety.[12] In this context, our efforts have been continuously devoted to synthesizing new diborons having a boron moiety of diminished Lewis acidity, and we report herein on the first synthesis of unsymmetrical diborons containing a B(MIDA) unit (MIDA: *N*-methyliminodiacetic acid) (Figure 2),[13] whose Lewis acidity is substantially reduced by tetrahedralization of a boron center via intramolecular coordination with an amine moiety, and on their structural properties based upon NMR and X-ray crystal structure analysis. Further application to the synthesis of a sp^3–sp^3 diboron,[14] (MIDA)B–B(MIDA), is also documented.

Scheme 2. Cu-Catalyzed B(dan)-Installing Reactions with (pin)B–B(dan)

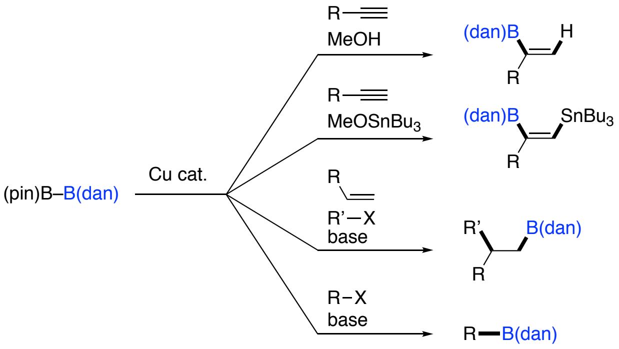
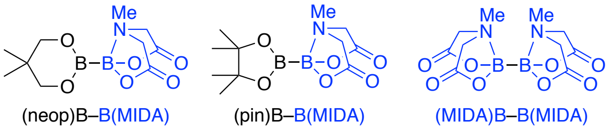


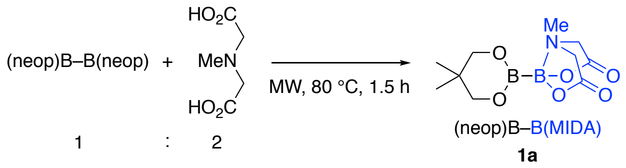
Figure 2. B(MIDA)-containing diborons synthesized in this study.



RESULTS AND DISCUSSION

We first conducted the reaction of (neop)B–B(neop) with MIDA in DMSO at 80 °C under microwave irradiation conditions (entry 1, Table 1), and observed that one of the neop moieties on the boron atom was smoothly substituted by MIDA to give an unsymmetrical diboron, (neop)B–B(MIDA) (**1a**) in 55% yield. The use of DMSO as a solvent was found to be crucial for the formation of **1a**, and thus the reaction in other solvents was totally unsuccessful (entries 2–9). Microwave irradiation was not always required for synthesizing **1a**, and conventional heating in DMSO under slightly modified conditions increased the yield up to 74% (entry 10).

Table 1. Synthesis of (neop)B–B(MIDA)[a]



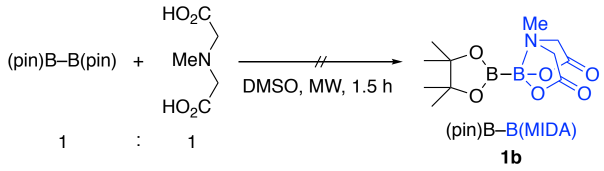
entry	solvent	yield (%)[b]
1	DMSO	55
2	DMF	0
3	EtOH	0
4	EtOH/H_2O (4:1)	0
5	Et_2O	0

6	CH_2Cl_2	0
7	MeCN	trace
8	acetone	trace
9[c]	THF	trace
10[d]	DMSO	74

[a] Reaction conditions unless specified otherwise: (neop)B–B(neop) (1 mmol), MIDA (2 mmol), solvent (2 mL), 80 °C, microwave heating, 1.5 h. [b] Isolated yield. [c] 12 h. [d] Conventional heating, 6 h.

In marked contrast to the case with (neop)B–B(neop), direct substitution of a B(pin) moiety of (pin)B–B(pin) by MIDA turned out to be impracticable even under harsh conditions (DMSO, 250 °C, microwave irradiation) or with an acidic (conc. HCl)/basic (NaOH) additive, and no trace of (pin)B–B(MIDA) (**1b**) was produced (Scheme 3). On the other hand, treatment of $(HO)_2B–B(OH)_2$ with MIDA and pinacol in DMSO resulted in the facile formation of **1b** in 58% yield (Scheme 4).

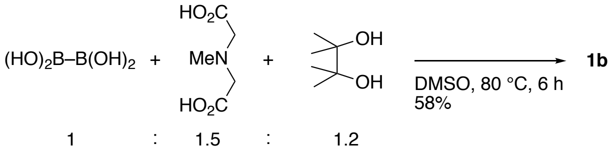
Scheme 3. Reaction of (pin)B–B(pin) with MIDA



conditions

a) no additive, 250 °C
b) NaOH (3 equiv), 200 °C
c) conc. HCl (1 drop), 100 °C, conventional heating, 72 h
(diboron:MIDA = 1.5:1)

Scheme 4. Synthesis of (pin)B–B(MIDA)



While preparing B(MIDA)-containing unsymmetrical diborons **1a** and **1b**, we became aware of the generation of (MIDA)B–B(MIDA) (**1c**) as a side-product (Scheme 5). As described in entry 1 of Table 2, the symmetrical diboron was accessible in 50% yield by treating (neop)B–B(neop) with an excess of MIDA in DMSO at 120 °C, whereas a similar reaction under milder conditions (3 equiv of MIDA, 100 °C) scarcely gave **1c** (entry 2). It should be noted that addition of water significantly promoted the reaction, affording **1c** in 58 or 57% yield under otherwise identical conditions (entries 3 and 4). In addition, an 86% yield of **1c** was also accessible by treating $(HO)_2B–B(OH)_2$ with MIDA (3 equiv) in the absence of water (Scheme 6), which implies that the presence of water may facilitate hydrolysis of (neop)B–B(neop) and/or (neop)B–B(MIDA) intermediate (**1a**) during the reaction process, resulting in the efficient formation of **1c** (entries 3 and 4, Table 3).

Scheme 5. Formation of (MIDA)B–B(MIDA) as a Side-product

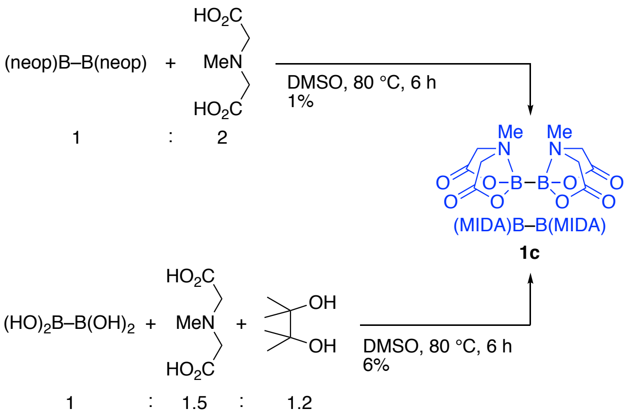
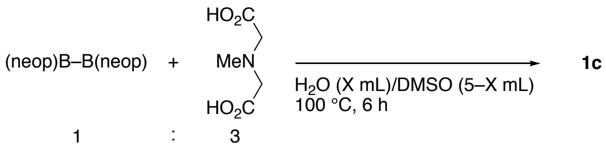


Table 2. Synthesis of (MIDA)B–B(MIDA)[a]

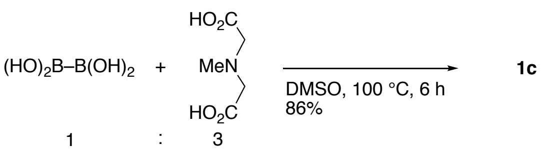


entry	X (mL)	yield (%)[b]
1[c]	0	50
2	0	2

3	0.25	58
4	1	57

[a] Reaction conditions unless specified otherwise: (neop)B–B(neop) (1 mmol), MIDA (3 mmol), H_2O (X mL), DMSO (5–X mL), 100 °C, 6 h. [b] Isolated yield. [c] MIDA (5 mmol), DMSO (2 mL), 120 °C, 6 h.

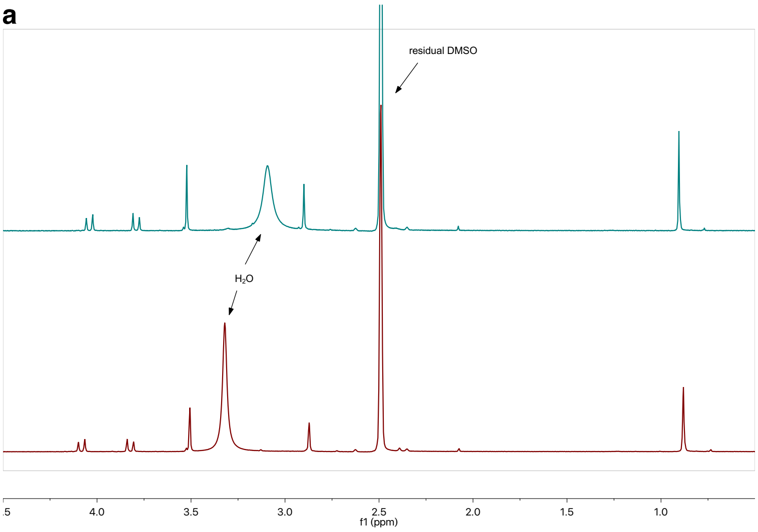
Scheme 6. Synthesis of (MIDA)B–B(MIDA) Using $(HO)_2B–B(OH)_2$



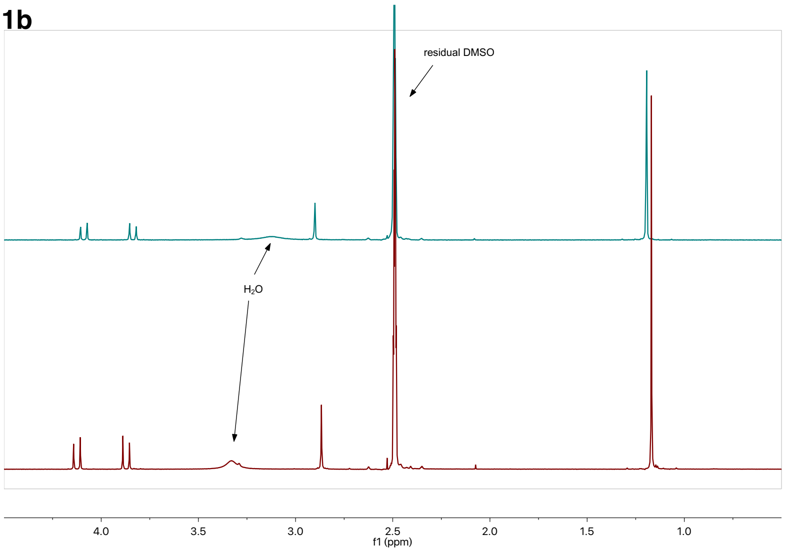
^1H NMR spectra of **1** showed AX-coupling pattern for the methylene protons of the B(MIDA) moiety in each case, which denotes tetrahedral environment of the boron center arising from intramolecular N–B coordination (Figure 3).[15] In addition, the B(MIDA) moieties of **1c** were found to be magnetically equivalent (Figure 3c), which indicates symmetrical sp^3–sp^3 bonding between two boron atoms. The bicyclic structures of the B(MIDA) proved to be rigid, as the methylene protons did not coalesce at all upon heating (up to 70 °C) in variable-temperature NMR experiments. Interestingly, a little shift in the methylene protons (upfield) and the methyl protons (on nitrogen, downfield) were observed at the higher temperature in all cases.[16] Furthermore, the sp^3 hybridization in the B(MIDA) was also confirmed by ^{11}B NMR, where their δ values lie in the range of 10–11 ppm, being similar to those of related diboron[9a] and B(MIDA) boronates.[15,17]

Figure 3. Variable-temperature ^{1}H NMR (DMSO-d_6) spectra of **1**. 23 °C (red) and 70 °C (green).

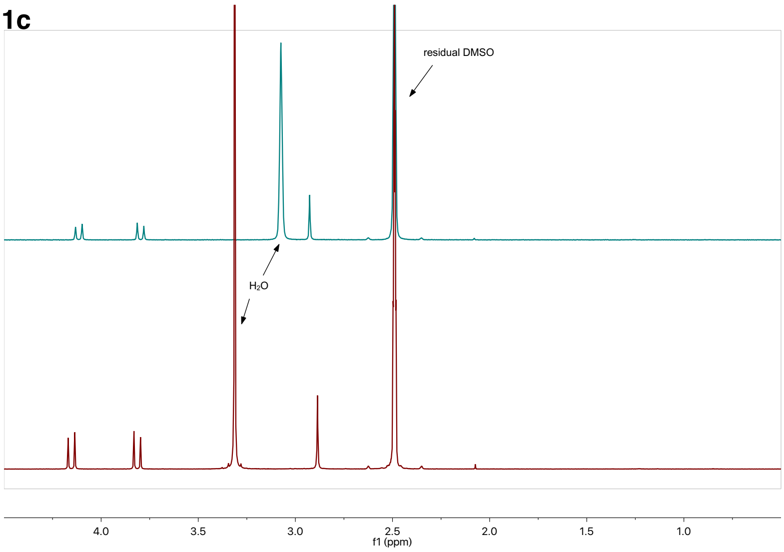
1a


residual DMSO
H_2O
5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

1b


residual DMSO
H_2O
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

1c


residual DMSO
H_2O
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

The molecular structures of diborons (**1a** and **1c**) were also determined by X-ray crystal structure analysis, which reveals the pyramidalized environment around the B(MIDA) moieties (Figures 4 and 5). The N–B coordination is evident from their bond length (1.660 Å on average) (Table 3), being similar to those of R–B(MIDA) compounds[16,17] and picoline-coordinated (cat)B–B(cat),[18] and the B(sp^3) centers deriving therefrom have proven to be somewhat distorted from ideal sp^3 hybridization (Tetrahedral character: 62.8% (**1a**) and 62.4% (**1c**)).[19] In addition, the B–B bond in these diborons slightly elongates (1.721 Å on average) as compared with that in (pin)B–B(pin) (B(sp^2)–B(sp^2): 1.710 Å)[9b,20] owing to the boron-tetrahedralization.

Figure 4. Solid-state structure of **1a** with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity.

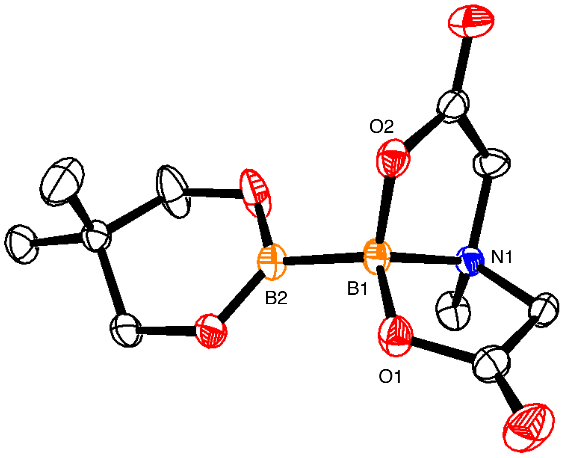


Figure 5. Solid-state structure of **1c** with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity.

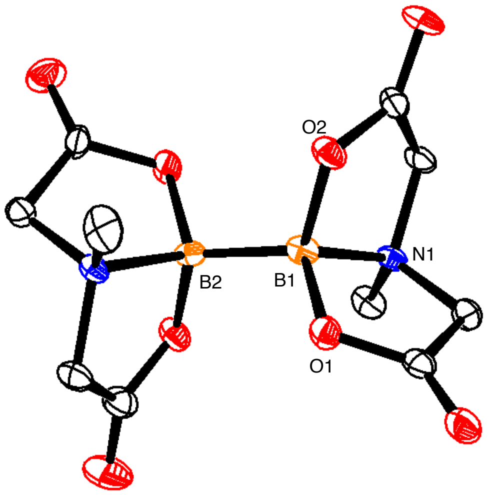


Table 3. Selected Bond Distances, Bond Angles and Calculated THC[a] of 1a and 1c[b]

	1a	**1c**
Bond distance (Å)		

B1–N1	1.646(2)	1.674(6)
B1–B2	1.723(3)	1.719(7)
B1–O1	1.502(2)	1.471(6)
B1–O2	1.467(2)	1.490(6)
Bond angle (°)		
B2–B1–N1	117.1(1)	116.3(4)
B2–B1–O1	111.9(1)	115.1(4)
B2–B1–O2	115.2(1)	113.1(4)
N1–B1–O1	99.5(1)	101.8(3)
N1–B1–O2	101.9(1)	100.7(3)
O1–B1–O2	109.7(1)	108.2(4)
THC (%)		
	62.8	62.4

[a]THC = Tetrahedral character. [b]The metrics for both B(MIDA) units in **1c** are effectively identical, and thus only one set was provided in Table 3. Furthermore, **1c** was found to

exist as two molecular structures having different N–B–B–N torsion angles in solid state, and Figure 5 shows one of them for simplification. See Figure S4 for details.

CONCLUSIONS

We have demonstrated that unsymmetrical B(MIDA)-containing diborons [(neop)B–B(MIDA) and (pin)B–B(MIDA)] can facilely be synthesized by simply substituting (neop)B–B(neop) or $(HO)_2B–B(OH)_2$ of high availability with MIDA, and that a modified method leads to efficient generation of (MIDA)B–B(MIDA) having a B(sp^3)–B(sp^3) bond. The NMR and X-ray crystal structure studies revealed that all of the B(MIDA) moieties were in tetrahedral environment, and these sp^3-hybridized boron structures were found to be rigid even upon heating. Moreover, the B–B bonds are elongated by introducing the B(MIDA) unit as compared with those of B(sp^2)–B(sp^2) diborons such as (pin)B–B(pin) and (cat)B–B(cat),[21] which would result from the increased p-character in the B–B bonding. Further studies on synthetic application of the diborons to various borylation reactions as well as on synthesis of other B(MIDA)-containing diborons are in progress.

EXPERIMENTAL SECTION

General Information. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 160 MHz) or Varian 400MR (^{1}H, 400 MHz) spectrometer using a residual proton in DMSO-d_6 (^{1}H, δ = 2.49) or DMSO-d_6 (^{13}C, δ = 39.5) as an internal standard, and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. All microwave reactions (Biotage, Initiator+) were conducted in a sealed tube, and the reaction temperature was maintained by an external infrared sensor. Unless otherwise noted, commercially available reagents were used without purification. DMSO was dried over activated molecular sieves 3A.

Synthesis of 1a. A DMSO solution (10 mL) of (neop)B–B(neop) (1.13 g, 5.00 mmol) and MIDA (1.10 g, 7.50 mmol) was stirred at 80 °C for 6 h before removal of DMSO by bulb-to-bulb distillation (3.00-5.00 mmHg, 90 °C). The residue was extracted three times with acetone (70 mL), and an insoluble solid was removed by filtration. Evaporation of the solvent followed by washing with toluene (60 mL) gave **1a** (0.99 g, 74%) as a colorless solid.

mp 249.0-250.8 °C

^{1}H NMR (DMSO-d_6) δ 4.08 (d, J = 16.9 Hz, 2H), 3.82 (d, J = 16.9 Hz, 2H), 3.51 (s, 4H), 2.87 (s, 3H), 0.88 (s, 6H).

^{13}C NMR (DMSO-d_6) δ 169.86, 70.24, 60.64, 47.40, 31.18, 21.67.

^{11}B NMR (DMSO-d_6) δ 31.2, 9.7.

HRMS Calcd for $C_{10}H_{17}B_2NO_6Na$: [M+Na]$^+$, 292.1134. Found: *m*/*z* 292.1132.

Synthesis of 1b. A DMSO solution (5 mL) of $(HO)_2B–B(OH)_2$ (89.7 mg, 1.00 mmol), MIDA (220.0 mg, 1.50 mmol) and pinacol (141.8 mg, 1.20 mmol) was stirred at 80 °C for 6 h before removal of DMSO by bulb-to-bulb distillation (3.00-5.00 mmHg, 90 °C).

The residue was extracted twice with chloroform (25 mL), and an insoluble solid was removed by filtration. Evaporation of the solvent followed by washing with hexane (40 mL) gave **1b** (154 mg, 58%) as a colorless solid.

mp 251.1-252.5 °C

^{1}H NMR (DMSO-d_6) δ 4.13 (d, J = 17.0 Hz, 2H), 3.87 (d, J = 17.0 Hz, 2H), 2.87 (s, 3H), 1.17 (s, 12H).

^{13}C NMR (DMSO-d_6) δ 169.73, 82.54, 60.75, 47.77, 24.81.

^{11}B NMR (DMSO-d_6) δ 33.7, 9.7.

HRMS Calcd for $C_{11}H_{19}B_2NO_6Na$: $[M+Na]^+$, 306.1291. Found: m/z 306.1292.

Synthesis of 1c. A DMSO solution (50 mL) of (neop)B–B(neop) (2.26 g, 10.0 mmol) and MIDA (4.41 g, 30.0 mmol) was stirred at 100 °C for 5 min, and then water (5 mL) was added to the mixture. After stirring at 100 °C for 6 h, the mixture was diluted with acetone (150 mL) and an insoluble solid was collected by filtration. The resulting solid was washed with water and acetone to give **1c** (1.60 g, 50%) as a colorless solid.

mp 362-365 °C (decomposed)

^{1}H NMR (DMSO-d_6) δ 4.15 (d, *J* = 17.0 Hz, 4H), 3.82 (d, *J* = 17.0 Hz, 4H), 2.89 (s, 6H).

^{13}C NMR (DMSO-d_6) δ 169.68, 60.68, 47.31.

^{11}B NMR (DMSO-d_6) δ 11.6.

HRMS Calcd for $C_{10}H_{14}B_2N_2O_8Na$: $[M+Na]^+$, 335.0828. Found: *m/z* 335.0829.

ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C and ^{11}B NMR spectra and single-crystal X-ray diffraction data.

Accession Codes

CCDC 1563699 and 1563700 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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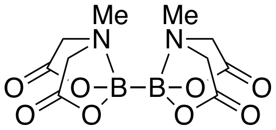

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