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Dynamic Behavior of N-Heterocyclic Carbene Boranes: Boron–Carbene Bonds in *B,B*-Disubstituted *N,N*-Dimethylimidazol-2-ylidene Boranes Have Substantial Rotation Barriers

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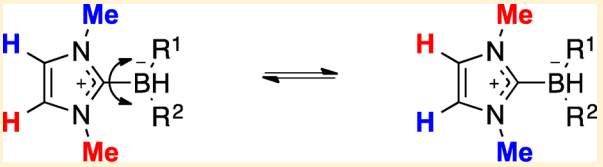
Supporting Information

ABSTRACT: Dynamic NMR spectroscopy has been used to measure rotation barriers in five *B,B*-disubstituted 1,3-dimethylimidazol-2-ylidene boranes. The barriers are attributed to the sp^2–sp^3 bond between C(1) of the N-heterocyclic carbene ring and the boron atom. Bonds to boron atoms bearing a thexyl (1,1,2-trimethylpropyl) group show especially high barriers, ranging from 75–86 kJ mol^{-1}. 2-Isopropyl-1,3,5-trimethylbenzene is used as a comparable to help understand the nature and magnitude of the barriers.



INTRODUCTION

N-Heterocyclic carbene boranes have garnered interest in diverse areas such as main group chemistry,[1] organic synthesis,[2] and polymer chemistry[3] because they blend chemical stability with an interesting reactivity profile.[4] This profile does not include hydroboration,[5] the most common reaction of B–H bonds in boranes, because free boranes are not easily released. With hydroboration excluded, a wealth of other interesting reactions of B–H bonds materialize.

The static structures of many NHC-boranes are understood thanks to the complementary techniques of NMR spectroscopy, X-ray crystallography, and calculations.[3a,6] However, little is known about the dynamic behavior of NHC-boranes.[7] NMR spectra of *N,N*-dialkyl NHC boranes **1** with stereogenic boron atoms (X ≠ Y) typically show chemical shift equivalence of groups on either side of the imidazolylidene ring (for example, the groups R^A in Figure 1a exhibit one resonance). This means that rotation of the bond between the NHC ring and boron is fast on the NMR time scale, as expected for such an sp^2–sp^3 bond.

1,3-(2,6-Diisopropylphenyl)imidazol-2-ylidene boranes **2** exhibit slow rotation around the N–Ar bonds, a feature shared by many *N*-aryl substituted NHC complexes of both metals and main group elements.[8] For example, achiral molecules such as dipp-Imd-BH_2Cl[9] **3** and dipp-Imd-$BHCl_2$[10] **4** shown in Figure 1b exhibit two doublets for the isopropyl methyl groups in their ^1H NMR spectra. One resonance represents the four "A" Me groups, the other, the four "B" Me groups. This slow N–Ar rotation is a variant of standard biaryl rotation that involves Csp^2–Nsp^2 bonds.[11]

The chemical shift equivalence is reduced for molecules like dipp-Imd-BHClOTf **5**,[10] which now has a stereogenic boron atom. The ^1H NMR spectrum of this compound exhibits four Me doublets, each representing pairs of Me groups (A–D). The bond between the boron atom and C2 of the imidazolylidene ring must be rotating rapidly on the NMR time scale; otherwise, there would be eight Me doublets.

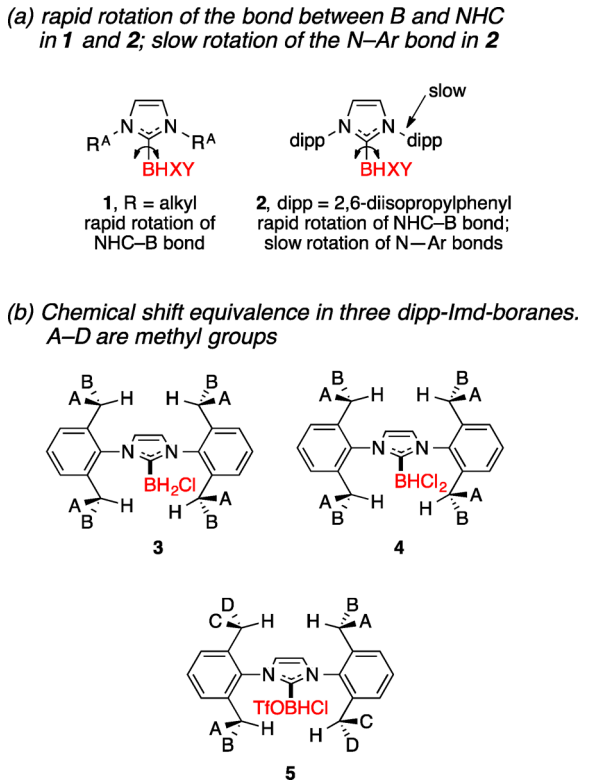


Figure 1. Dynamic aspects of representative NHC-boranes (formal charges omitted).

To summarize, *N,N*-dialkylimidazolylidene boranes typically exhibit simple NMR spectra consistent with rapid rotation of all bonds. ^1H NMR spectra of dipp and related *N,N*-diary-

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limidazolylidene boranes commonly exhibit features of slow rotation that can be attributed to the N−Ar bonds.

Within this backdrop, we were initially surprised when we observed evidence of dynamic behavior in the ^{1}H NMR spectrum of a chiral *B*,*B*-disubstituted *N*,*N*-dimethylimidazol-2-ylidene borane. Here, we report the results of experiments conducted to understand and quantify this phenomenon. We have measured the barriers for dynamic processes of five representative *B*,*B*-disubstituted NHC-boranes and can confidently attribute the barriers to slow rotation of the Csp^2−Bsp^3 bond rather than dissociation or epimerization at boron. The barriers are substantial, 56.4 kJ mol^{-1} (13.5 kcal mol^{-1}) and up.

RESULTS AND DISCUSSION

We encountered slow rotation in one of the products of Rh-catalyzed insertions of diazoesters into the B−H bonds of substituted NHC-boranes.[2b] Reaction of α-NHC-boryl ester **6** with methyl 2-diazo-2-phenylacetate and 1% $Rh_2(esp)_2$,[12] as shown in Figure 2a, provided a 56/44 mixture of two separable

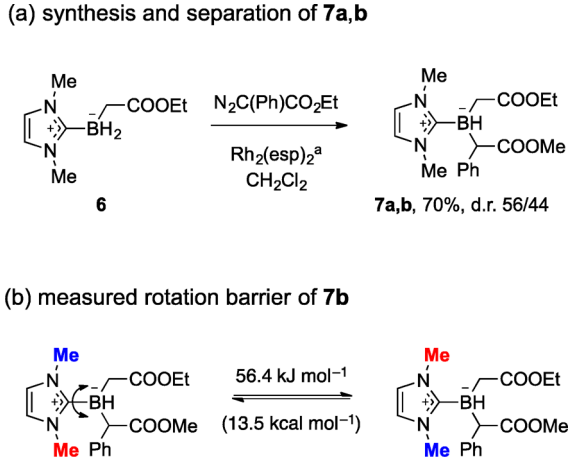

Figure 2. Synthesis and dynamic features of a *B*,*B*-disubstituted NHC-borane. (a) esp is 1,3-benzenedipropanoate, C_6H_4-1,3-$(CH_2CH_2CO_2)_2$.

diastereomers of **7a**,**b** in 70% yield. The diastereomers arise because both the boron atom and one of its substituents are stereocenters. Neither of the isomers is crystalline, and NMR spectroscopy did not provide a clear indication of relative configuration. Interestingly, while the ^{1}H NMR spectrum of the major diastereomer **7a** was standard, the ^{1}H NMR spectrum of the minor diastereomer **7b** lacked the usual six-proton singlet for the two *N*-methyl groups of the imidazolylidene ring. In its place was a very broad hump at about 3.7 ppm that integrated for about six protons. This suggests that slow rotation is interconverting the two *N*-methyl groups of **7b**, as shown in Figure 2b. Apparently, the rt spectrum happens to be very close to the coalescence point at 400 MHz.

A series of ^{1}H NMR spectra were then recorded at five temperatures ranging from 260 to 301 K. As projected, the broad 6 H resonance at 298 K (room temperature) resolved into two broad 3 H signals at 260 K. These signals then gradually coalesced on rewarming. The data were processed by line shape analysis in the usual way to provide rate constants at the various temperatures (see the Supporting Information). Further treatment including an Eyring plot of this data provided the activation free energy $\Delta G^{\ddagger}$, 56.4 kJ mol^{-1} (13.5 kcal mol^{-1}), and the corresponding enthalpy $\Delta H^{\ddagger}$, 38.0 kJ mol^{-1}, and the entropy $\Delta S^{\ddagger}$, −67.7 J K^{-1}.

These data cannot be understood either by dissociation of the boron from the NHC ring (decomplexation) or by epimerization at boron or carbon because all three processes would result in interconversion of the two diastereomers **7a**,**b**, not coalescence of resonances in one of the diastereomers. Further, chiral NHC-boranes with boron stereocenters have been resolved and shown to be thermally stable well above room temperature.[2b] Thus, the rotation of the bond between the boron atom and the imidazolylidene ring is responsible for the 56.4 kJ mol^{-1} activation barrier.

The difference between **7b** and other *B*,*B*-disubstituted NHC-boranes **1** that do not show dynamic NMR behavior is that one of the carbon atoms bonded to boron is secondary in **7b**. To further increase the rotation barrier of the B−C bond, we prepared four new *B*,*B*-disubstituted NHC-boranes with one of the boron substituents being a tertiary carbon. The precursor for these substrates, *B*-thexylborane **8** (thexyl is 1,1,2-trimethylpropyl), is itself readily available by borenium-catalyzed hydroboration of tetramethylethylene (2,3-dimethyl-2-butene).[5]

Rh-catalyzed insertion reactions of **8** with ethyl diazoacetate and trimethylsilyl diazomethane provided products **9** and **10** in 36% and 15% yields, respectively, after purification by flash chromatography. The ester substituent on the diazo compound increased the yield of **9** relative to **10**. This is sensible given that NHC-boranes are relatively nucleophilic[13] and prefer to insert into transient metal carbenes that are derived from electrophilic diazo precursors.

Two compounds with B−S bonds were also made by reaction of **8** with the corresponding benzothiazole 2-thiol or *N*-phenyltetrazole disulfide.[14] Heating of **8** and benzothiazole 2-thiol (BtSH) in benzene at 80 °C, followed by evaporation and automated flash chromatography, gave boryl sulfide **11** in 58% yield. In the reaction between **8** and *N*-phenyltetrazole disulfide (PtSSPt), the corresponding boryl sulfide **12** formed at room temperature in 59% isolated yield. The four new compound **9**−**12** were fully characterized (Scheme 1).

All four compounds **9**−**12** exhibited doubled resonances in their ^{1}H NMR spectra for either (or both) the *N*-methyl groups or the pair of protons on the imidazolylidene ring at room temperature. This doubling (as opposed to broadening) already

Scheme 1. Synthesis of Four *B*-Thexyl NHC-boranes

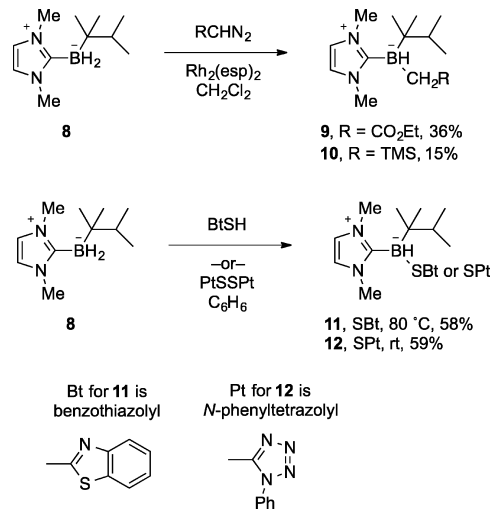

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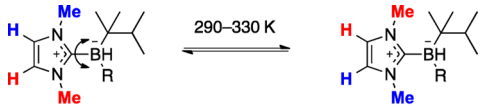
Table 1. Activation Parameters for *B*-Thexyl NHC-boranes 9−12 As Measured by Temperature- and Time-Dependent 1D or 2D EXSY Experiments



9, R = CH_2CO_2Et
10, R = CH_2TMS
11, R = S–benzothiazolyl
12, R = S–(*N*-phenyltetrazolyl)

entry	cmd	resonance[a]	$\Delta G^{\ddagger}$, kJ mol^{-1} (kcal mol^{-1})	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1}
1	**9**	Me	81.8 (19.6)	71.5	−34.6
2	**10**	Me	86.4 (20.7)	81.3	−17.0
3	**11**	H	74.9 (17.9)	60.9	−46.9
4	**12**	H	77.7 (18.6)	62.6	−50.5

[a]The doubled resonances used for the line shape analysis; Me for the *N*-methyl groups, H for the imidazolylidene CH's.

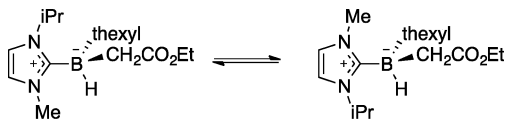
suggests higher rotation barriers for **9**−**12** compared to **7b**. Further, the doubling of the NHC ring protons is consistent with the slow rotation of the NHC−B bond. Because the processes were too slow for coalescence experiments, 1D and 2D EXSY experiments with variable mixing times were used to collect data sets for the barrier measurements.

Sets of spectra were recorded at appropriate temperatures in the range of 290−330 K, and the data were processed to give rate constants and energies of activation (see the Supporting Information). In the spectra of **9** and **10**, the degree of exchange between the two *N*-methyl singlets was assessed in 2D EXSY experiments to provide the data in Table 1. In the spectra of **11** and **12**, the degree of exchange between the two imidazolylidene doublets was assessed in 1D EXSY experiments.

These four compounds have significantly higher rotation barriers than **7b**. The two compounds with B−S bonds, **11** and **12**, have barriers of 74.9 kJ mol^{-1} (17.9 kcal mol^{-1}) and 77.7 kJ mol^{-1} (18.6 kcal mol^{-1}) (Table 1, entries 3 and 4). The two compounds with B−CH_2 bonds, **9** and **10**, have even higher barriers of 81.8 kJ mol^{-1} (19.6 kcal mol^{-1}) and 86.4 kJ mol^{-1} (20.6 kcal mol^{-1}) (Table 1, entries 1 and 2). The larger barriers in **9** and **10** compared to **11** and **12** presumably arise because B−C bonds are shorter than B−S bonds.

All the compounds so far have stereocenters at boron, but the local plane of symmetry in the NHC ring renders the two rotamers identical. If the symmetry of the NHC ring is broken, then the slow rotation should engender diastereomers. The highest barriers observed in this work, 82 and 86 kJ mol^{-1} with **9** and **10**, are just below the level needed for chromatographic separation of diastereomers (atropisomers) at room temperature.

To test the prediction that diastereomers would result, NHC-borane **13** (Figure 3) was made starting from 1-isopropyl-1-methylimadozol-2-ylidene borane by a two-step sequence of borenium-catalyzed hydroboration of tetramethylethylene, followed by Rh-catalyzed B−H insertion with ethyl diazoacetate.



13, thexyl is 1,1,2-trimethylpropyl
Equilibrium ratio is 70/30 (unassigned)
partially separable by HPLC

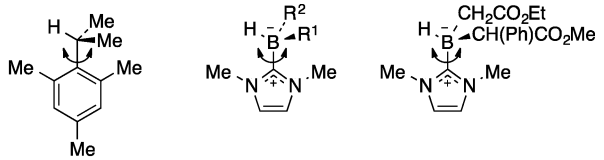
Figure 3. Rotational isomers of **13**.

Both ^{1}H and ^{13}C NMR analysis showed that **13** was about a 70/30 mixture of rotamers; however, the sample could not be resolved into its component atropisomers at room temperature by flash chromatography. On the other hand, HPLC injection resulted in partial separation, with the minor rotamer eluting before the major rotamer. The chromatogram exhibited features of atropisomers that partially equilibrate during the time scale of the experiment (see the Supporting Information).

Thus, unsymmetrical NHC-borane **13** probably has a rotation barrier close to that of the related symmetric sample **9**. Its rotamers can only be partially resolved at room temperature, and they then reequilibrate rather quickly. Nonetheless, the observation of the diastereomeric rotamers and their equilibrium on the time scale of some minutes at rt is consistent with the picture of NHC-B bond rotation that emerged from the data in Table 1.

As far as we know, these are the first measurements of rotation barriers for bonds between N-heterocyclic carbenes and a main group element.[15] Touchstones in other areas of NHC chemistry include a number of interesting metal complexes that exhibit slow rotation of the NHC−metal bond that have been prepared by Enders and others.[16] Chiral complexes of this type have been used in catalysis.[17] However, most such complexes have a square-planar metal atom and are, therefore, geometrically different from the tetrahedral boron atom of **7** and **9**−**12**.

Simple touchstones in carbon chemistry include 2-isopropyl-1,3,5-trimethylbenzene **14** and related molecules with a secondary alkyl group bonded to a benzene ring and flanked by two ortho substituents (Figure 4).[18] The rotation barrier of the Csp^2−Csp^3 bond between the benzene ring and the isopropyl group of **14** is 53.6 kJ mol^{-1} (12.8 kcal mol^{-1}). In this simple analogy, the 1,3-dimethyl-substituted benzene ring of **14** maps onto the *N*,*N*-dimethyl imidazolylidene ring of NHC-boranes like **15**, while the central isopropyl carbon atom of **14** maps onto the boron atom of **15**. The first of the NHC-boranes



14 $\Delta G^{\ddagger}$ = 53.6 kJ mol^{-1} | **15** | **7b** $\Delta G^{\ddagger}$ = 56.4 kJ mol^{-1}

Figure 4. 2-Isopropyl-1,3,5-trimethylbenzene **13** as a touchstone.

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7b has the closest structure to **14**, and indeed the rotation barriers of **7b** and **14** are roughly comparable.

According to this analogy, larger *N*-alkyl groups or larger boron substituents should result in higher rotation barriers. Axial chirality results if the two, the imidazolyl nitrogen or carbon substituents, are different, and stable atropisomers are within reach based on the barriers reported herein. Suitably substituted NHC-boranes with three boron substituents should surely show features of slow rotation in their NMR spectra. Indeed, Braunschweig, Stephan, and co-workers have recently observed doubling of resonances in NMR spectra of a trisubstituted NHC-borane[7a] and a hindered disubstituted NHC-borane.[7b] Both groups assigned the doubling to slow rotation of the NHC−B bond. These observations mesh nicely with the barriers reported here.

In summary, substantial barriers have been measured for five different *B,B*-disubstituted N-heterocyclic carbene boranes that bear one primary and either one secondary or one tertiary substituent on the boron atom. The barriers are attributed to slow rotation around the bond between the NHC ring and the boron atom and range for 56 kJ mol^{-1} (secondary boron substituent) up to 75−86 kJ mol^{-1} (tertiary boron substituents).

EXPERIMENTAL SECTION

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-ethoxy-2-oxoethyl)(2-methoxy-2-oxo-1-phenylethyl)hydroborate (7a,b). (1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-ethoxy-2-oxoethyl)dihydroborate **6** (38.0 mg, 0.19 mmol, 1.0 equiv) and the $Rh_2(esp)_2$ (1.4 mg, 0.0019 mmol, 0.01 equiv) were dissolved in dry DCM (2 mL) under argon. The solution was dark green. The reaction mixture was heated to reflux. A solution of methyl 2-diazo-2-phenylacetate (66.7 mg, 0.38 mmol, 2.0 equiv) in dry DCM (2 mL) was added via syringe pump over a period of 4 h. The color of the solution turned orange. After 4 h, the solvent was removed and the crude ^{1}H NMR and ^{11}B NMR were taken. The mixture was concentrated and purified by flash chromatography (Hex:EA = 1:2) to give two diastereomers as a colorless oil. Diastereomer **7a** (25.6 mg, 0.075 mmol, 39%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.20 (m, 2H), 7.06−7.10 (m, 2H), 6.90−6.99 (m, 1H), 6.58 (s, 2H), 3.87 (qd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2H), 3.62 (s, 3H), 3.47 (s, 6H), 3.22 (br, 1H), 1.75 (br, 2H), 1.03 (t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 178.6, 144.0, 127.5, 127.5, 124.2, 121.0, 58.7, 50.8, 49.0 (br), 36.4, 28.0 (br), 14.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ −16.4 (d, J_{BH} = 96 Hz); IR (film) 2950, 2377, 1703, 1482, 1453, 1434, 1363 cm^{-1}; HRMS (ESI) m/z (M^+ + H) calcd for $C_{18}H_{26}BN_2O_4$ 345.1980, found 345.1974. Diastereomer **7b** (20.1 mg, 0.059 mmol, 31%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.27 (m, 2H), 7.11−7.19 (m, 2H), 6.99−7.02 (m, 1H), 6.73 (s, 2H), 3.74−3.85 (m, 2H), ∼3.7 (very broad, 6H), 3.40 (s, 3H), 3.24 (br, 1H), 1.53 (br, 2H), 0.97 (t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 178.9, 143.3, 128.5, 127.6, 124.4, 121.2, 58.6, 50.6, 49.0 (br), 36.7, 26.5 (br), 14.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ −16.5 (d, J = 95 Hz); IR (film) 3134, 2950, 2376, 1703, 1598, 1577, 1481, 1453, 1432 cm^{-1}; HRMS (ESI) m/z (M^+ + H) calcd for $C_{18}H_{26}BN_2O_4$ 345.1980, found 345.1990. The minor diastereomer shows slow rotation.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)(2-ethoxy-2-oxoethyl)hydroborate 9. (1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)dihydroborate **8** (58.2 mg, 0.30 mmol, 1.0 equiv) and $Rh_2(esp)_2$ (2.3 mg, 0.0030 mmol) were dissolved in dry DCM (2 mL) under argon. The solution was dark green. The reaction mixture was heated to reflux. A solution of ethyl 2-diazoacetate (0.089 mL, 0.60 mmol, 2.0 equiv) in dry DCM (2 mL) was added via syringe pump over a period of 4 h. The color of the solution turned orange. After 4 h, the solvent was removed and the crude ^{1}H NMR and ^{11}B NMR were taken. The conversion was estimated by crude ^{11}B NMR as 55%. The mixture was concentrated and purified by flash chromatography to give the product (30.3 mg, 0.11 mmol, 36%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (ABq, 2H, $\Delta\delta_{AB}$ = 0.012, J_{AB} = 2.0 Hz), 3.94 (s, 3H), 3.84 (q, J = 6.8 Hz, 2H) 3.79 (s, 3H), 1.67−1.76 (m, 2H), 1.36 (sep, J = 6.8 Hz, 1H), 0.98 (t, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H), 0.74 (s, 3H), 0.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 121.1, 121.0, 58.2, 37.8, 37.4, 37.0, 26.6, 24.9, 18.9, 18.1, 14.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ −16.3 (d, J_{BH} = 87 Hz); IR (film) 3121, 2951, 2857, 2353, 1694, 1472 cm^{-1}; HRMS (ESI) m/z (M^+) calcd for $C_{15}H_{28}BN_2O_2$ 279.2238, found 279.2229.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)((trimethylsilyl)methyl)hydroborate 10. The (1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)dihydroborate **8** (62 mg, 0.32 mmol, 1.0 equiv) and $Rh_2(esp)_2$ (2.4 mg, 0.0032 mmol) were dissolved in dry DCM (2 mL) under argon. The solution was dark green. The reaction mixture was heated to reflux. A solution of trimethylsilyldiazomethane (0.24 mL, 0.47 mmol, 1.5 equiv) in dry DCM (2 mL) was added via syringe pump over a period of 4 h. The color of the solution turned orange. After 4 h, the solvent was removed and the crude ^{1}H NMR and ^{11}B NMR were taken. The conversion was estimated by crude ^{11}B NMR as 18%. The mixture was concentrated and purified by flash chromatography to give the product (13 mg, 0.046 mmol, 15%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, 1H, J = 2.0 Hz), 6.72 (d, 1H, J = 2.0 Hz), 3.84 (s, 3H), 3.79 (s, 3H), 1.46 (sep, J = 6.8 Hz, 1H), 0.86 (t, J = 6.4 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H), 0.70 (s, 3H), 0.49 (s, 3H), −0.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.0, 120.5, 37.5, 37.3, 36.5, 26.8, 24.3, 19.1, 17.9, 0.25; ^{11}B NMR (128 MHz, $CDCl_3$) δ −18.7 (d, J_{BH} = 83 Hz); IR (film) 2926, 2854, 1718, 1556, 1468, 1379 cm^{-1}; HRMS (ESI) m/z (M^+) calcd for $C_{15}H_{32}BN_2Si$ 279.2422, found 279.2421.

(Benzo[*d*]thiazol-2-ylthio)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)hydroborate 11. Benzothiazole-2-thiol (17.6 mg, 0.10 mmol) was added to a benzene (0.5 mL) solution of diMe-Imd-BH_2thexyl **8** (19.4 mg, 0.10 mmol). The colorless solution was charged to a sealed tube and heated in an oil bath at 80 °C for 12 h. The mixture was cooled to room temperature; then, the solvent was evaporated and the title product (21.0 mg, 58%) was obtained as an oil after flash chromatographic purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.0, 0.4 Hz, 1H), 7.57 (dd, J = 7.2, 0.4 Hz, 1H), 7.30−7.23 (m, 1H), 7.12 (td, J = 7.2, 0.8 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 4.05 (s, 3H), 4.04 (s, 3H), 3.70−3.30 (m, 1H), 1.71 (sep, J = 6.8 Hz, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.95 (s, 3H), 0.88 (d, J = 6.8 Hz, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 154.2, 135.7, 125.2, 122.4, 122.0, 121.5, 120.4, 120.1, 38.0, 37.5, 36.4, 27.0, 23.6, 19.2, 17.7; ^{11}B NMR (128.4 MHz, C_6D_6) δ −11.0 (d, J = 84.7 Hz); FTIR (thin film, CH_2Cl_2) ν = 2952, 1578, 1454, 1416, 1234, 1115, 998, 756, 727 cm^{-1}; HRMS (ESI) m/z (M^+ + H) calculated for $C_{18}H_{27}BN_3S_2$ 360.1739, found 360.1743.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)((1-phenyl-1*H*-tetrazol-5-yl)thio)hydroborate 12. 1-Phenyl-tetrazoldisulfide (35.4 mg, 0.10 mmol) was added to a solution of diMe-Imd-BH_2thexyl **8** (19.4 mg, 0.10 mmol) in benzene (0.5 mL). The colorless solution was charged to a sealed tube. The sealed tube was stirred at rt for 1 day. After all the NHC-borane was consumed, the solvent was evaporated, and the title product (22.2 mg, 59%) was obtained as an oil after flash chromatographic purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.47 (d, J = 7.2 Hz, 1H), 6.92 (d, J = 1.6 Hz, 1H), 6.78 (d, J = 1.6 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 1.65 (br s, 1H), 1.55 (sep, J = 6.8 Hz, 1H), 0.93−0.91 (m, 6H), 0.85 (d, J = 6.8 Hz, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 135.2, 129.1, 128.9, 124.2, 121.9, 121.3, 37.9, 37.7, 36.9, 27.0, 24.1, 19.1, 17.9; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ −10.9 (br s); FTIR (thin film, CH_2Cl_2) ν = 2954, 1597, 1499, 1477, 1375, 1232, 1090, 1005, 760, 694 cm^{-1}; HRMS (ESI) m/z (M^+ + H) calculated for $C_{18}H_{28}BN_6S$ 371.2189, found 371.2192.

(2,3-Dimethylbutan-2-yl)(3-isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)dihydroborate. Triflimide (56.6 mg, 0.19 mmol, 0.2 equiv) was added to a solution of (3-isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)trihydroborate (0.134 g, 0.96 mmol, 1.1 equiv) and 2,3-dimethylbut-2-ene (0.13 mL, 1.05 mmol, 1.1 equiv) in DCM (2 mL). The reaction mixture was refluxed overnight. Then, the solvent was removed and the crude ^{1}H NMR and ^{11}B NMR were taken. The

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conversion was estimated by crude ^{11}B NMR as 65%. The mixture was concentrated and purified by flash chromatography to give the product (113 mg, 0.50 mmol, 53%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (ABq, 2H, $\Delta\delta_{AB}$ = 0.085, J_{AB} = 1.6 Hz), 5.22 (sept, J = 6.8 Hz, 1H), 3.80 (s, 3H), 1.38 (d, J = 6.8 Hz, 6H), 0.91 (d, J = 6.8 Hz, 6H), 0.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.8, 114.8, 49.6, 39.9, 36.4, 28.3, 23.0, 18.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ −23.9 (t, J_{BH} = 83 Hz); IR (film) 3172, 3111, 2938, 2282, 1573, 1428, 1408 cm^{-1}; HRMS (ESI) m/z (M^+) calcd for $C_{13}H_{26}BN_2$ 221.2184, found 221.2181.

(2,3-Dimethylbutan-2-yl)(2-ethoxy-2-oxoethyl)(3-isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)hydroborate 13. (1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2,3-dimethylbutan-2-yl)dihydroborate (49 mg, 0.22 mmol, 1.0 equiv) and $Rh_2(esp)_2$ (1.6 mg, 0.0022 mmol) were dissolved in dry DCM (2 mL) under argon. The solution was dark green. The reaction mixture was heated to reflux. A solution of ethyl 2-diazoacetate (0.27 mL, 2.2 mmol, 10 equiv) in dry DCM (2 mL) was added via syringe pump over a period of 10 h. The color of the solution turned orange. After 10 h, the solvent was removed and the crude ^{1}H NMR and ^{11}B NMR were taken. The conversion was estimated by crude ^{11}B NMR as 61%. The mixture was concentrated and purified by flash chromatography to give two inseparable diastereomers (with a ratio of 73/27, 23 mg, 0.074 mmol, 34%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82−6.94 (m, 2H), 5.45 (sept, J = 6.8 Hz, 0.73H), 4.97 (sept, J = 6.8 Hz, 0.27H), 3.94 (s, 2.2H), 3.87−3.72 (m, 2H), 3.75 (s, 0.8H), 1.86 (br, 2H), 1.51 (d, J = 6.8 Hz, 0.81H), 1.47 (d, J = 6.8 Hz, 0.81H), 1.41 (d, J = 6.8 Hz, 2.19H), 1.23 (d, J = 6.8 Hz, 2.19H), 1.40−1.25 (m, 1H), 1.02−1.00 (m, 3H), 0.86−0.78 (m, 6H), 0,73 (s, 3H), 0.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 121.8, 121.8, 115.3, 115.0, 58.3, 49.9, 49.3, 38.2, 37.7, 37.4, 36.9, 26.6, 25.4, 24.8, 24.1, 23.6, 23.4, 22.0, 19.0, 19.0, 18.5, 18.0, 14.4, 14.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ −16.3 (d, J_{BH} = 86 Hz); IR (film) 3119, 2936, 2856, 2355, 1740, 1696, 1559, 1453 cm^{-1}; HRMS (ESI) m/z (M^+) calcd for $C_{17}H_{32}BN_2O_2$ 307.2551, found 307.2544.

■ ASSOCIATED CONTENT

Supporting Information

Contains general information on the synthesis and NMR experiments, data from the NMR analyses, and copies of ^{1}H, ^{11}B, and ^{13}C NMR spectra of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Wang, Y.; Robinson, G. H. *Inorg. Chem.* **2011**, *50*, 12326−12337. (b) Braunschweig, H.; Dewhurst, R. D.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. *Science* **2012**, *336*, 1420−1422. (c) Braunschweig, H.; Dewhurst, R. D. *Organometallics* **2014**, *33*, 6271−6277.

(2) (a) Eisenberger, P.; Bestvater, B. P.; Keske, E. C.; Crudden, C. M. *Angew. Chem., Int. Ed.* **2015**, *54*, 2467−2471. (b) Li, X.; Curran, D. P. *J. Am. Chem. Soc.* **2013**, *135*, 12076−12081. (c) Taniguchi, T.; Curran, D. P. *Org. Lett.* **2012**, *14*, 4540−4543. (d) Pan, X.; Lacôte, E.; Lalevée, J.; Curran, D. P. *J. Am. Chem. Soc.* **2012**, *134*, 5669−5675. (e) Merling, E.; Lamm, V.; Geib, S. J.; Lacôte, E.; Curran, D. P. *Org. Lett.* **2012**, *14*, 2690−2693.

(3) Lalevée, J.; Telitel, S.; Tehfe, M. A.; Fouassier, J. P.; Curran, D. P.; Lacôte, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 5958−5961.

(4) Curran, D. P.; Solovyev, A.; Makhlouf Brahmi, M.; Fensterbank, L.; Malacria, M.; Lacôte, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 10294−10317.

(5) (a) Pan, X.; Boussonnière, A.; Curran, D. P. *J. Am. Chem. Soc.* **2013**, *135*, 14433−14437. (b) Prokofjevs, A.; Boussonnière, A.; Li, L.; Bonin, H.; Lacôte, E.; Curran, D. P.; Vedejs, E. *J. Am. Chem. Soc.* **2012**, *134*, 12281−12288.

(6) (a) Hioe, J.; Karton, A.; Martin, J. M. L.; Zipse, H. *Chem.—Eur. J.* **2010**, *16*, 6861−6865. (b) Telitel, S.; Vallet, A.-L.; Schweizer, S.; Delpech, B.; Blanchard, N.; Morlet-Savary, F.; Graff, B.; Curran, D. P.; Robert, M.; Lacôte, E.; Lalevée, J. *J. Am. Chem. Soc.* **2013**, *135*, 16938−16947.

(7) (a) Farrell, J. M.; Posaratnanathan, R. T.; Stephan, D. W. *Chem. Sci.* **2015**, *6*, 2010−2015. (b) Braunschweig, H.; Claes, C.; Damme, A.; Dei; Dewhurst, R. D.; Horl, C.; Kramer, T. *Chem. Commun.* **2015**, *51*, 1627−1630.

(8) (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172. (b) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485−496.

(9) Solovyev, A.; Chu, Q.; Geib, S. J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 15072−15080.

(10) Solovyev, A.; Geib, S. J.; Lacôte, E.; Curran, D. P. *Organometallics* **2012**, *31*, 54−56.

(11) (a) Eliel, E. L.; Wilen, S. *Stereochemistry of Organic Compunds*; Wiley-Interscience: New York, 1994. (b) Oki, M. *The Chemistry of Rotational Isomers*; Springer-Verlag: New York, 1993. (c) Oki, M. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E., Wilen, S. H., Eds.; John Wiley & Sons: New York, 1983; Vol. *14*, pp 181. (d) Wolf, C. *Dynamic Stereochemistry of Organic Compounds*; RSC Publishing: Cambridge, U.K., 2008.

(12) Espino, C. G.; Fiori, K. W.; Kim, M.; Du Bois, J. *J. Am. Chem. Soc.* **2004**, *126*, 15378−15379.

(13) Horn, M.; Mayr, H.; Lacôte, E.; Merling, E.; Deaner, J.; Wells, S.; McFadden, T.; Curran, D. P. *Org. Lett.* **2012**, *14*, 82−85.

(14) Pan, X.; Vallet, A.-L.; Schweizer, S.; Dahbi, K.; Delpech, B.; Blanchard, N.; Graff, B.; Geib, S. J.; Curran, D. P.; Lalevée, J.; Lacôte, E. *J. Am. Chem. Soc.* **2013**, *135*, 10484−10491.

(15) (a) Carmalt, C. J.; Cowley, A. H. In *Advances In Inorganic Chemistry*; Academic Press: San Diego, CA, 2000; Vol. *50*, pp 1−32. (b) Kuhn, N.; Al-Sheikh, A. *Coord. Chem. Rev.* **2005**, *249*, 829−857.

(16) (a) Sabater, S.; Mata, J. A.; Peris, E. *Eur. J. Inorg. Chem.* **2013**, *2013*, 4764−4769. (b) Lee, K. M.; Chen, J. C. C.; Lin, I. J. B. *J. Organomet. Chem.* **2001**, *617*, 364−375. (c) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617*, 70−80. (d) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913−919. (e) Enders, D.; Gielen, H.; Breuer, K. *Z. Naturforsch. B* **1998**, *53*, 1035−1038. (f) Enders, D.; Gielen, H.; Breuer, K. *Tetrahedron: Asymmetry* **1997**, *8*, 3571−3574.

(17) Wang, F.; Liu, L.-J.; Wang, W.; Li, S.; Shi, M. *Coord. Chem. Rev.* **2012**, *256*, 804−853.

(18) (a) Ernst, L.; Mannschreck, A. *Chem. Ber.* **1977**, *110*, 3258−3265. (b) Mannschreck, A.; Ernst, L. *Chem. Ber.* **1971**, *104*, 228−247. (c) Mannschreck, A.; Ernst, L. *Tetrahedron Lett.* **1968**, *9*, 5939−5940. (d) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH: Deefield Beach, FL, 1986.

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