Title: Synthesis and reactivity of an N-heterocyclic carbene-stabilized diazoborane

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Abstract: Diazo compounds and organic azides are widely used as reagents for accessing valuable molecules in multiple areas of fundamental and applied chemistry. Their capacity to undergo versatile chemical transformations arises from the reactive nature of an incipient dinitrogen molecule at the terminal position. Herein we report synthesis and characterization of an N-heterocyclic carbene (NHC)-stabilized diazoborane, a boron-centered analog of organic azides and diazoalkanes. The diazoborane displays a strong tendency to release N_2, thus serving as a borylene source, in analogy to organic azides and diazoalkanes serving as nitrene and carbene sources, respectively. Also reminiscent of diazoalkane and organic azide reactivity, the diazoborane serves as a 1,3-dipole that undergoes uncatalyzed [3 + 2] cycloaddition with an unactivated terminal alkyne, affording a five-membered heterocycle after a two-step rearrangement.

Main Text: Since their discovery by Griess in the mid to late 1800s, compounds with a N_2 unit at the terminal position have become indispensable chemical reagents across industry and academic laboratories.(*1-4*) Diazo compounds ($R_2C=N=N$) and organic azides ($RN=N=N$), as two classes of nitrogen-rich molecules, form the basis of textbook organic chemistry.(*5-7*) Due to their instability and distinct resonance contributors, these molecules mediate versatile chemical transformations, including multiple organic name reactions, such as the Wolff rearrangement,(*8*) Staudinger reaction,(*9*) and Curtius rearrangement.(*10*) They are also excellent carbene (R_2C:) and nitrene ($R\ddot{N}$:) precursors. Upon N_2 loss, initiated by irradiation or metal catalysts, the generated transient subvalent species or metal complex undergoes group transfer to organic frameworks, facilitating the construction of molecules with material and medicinal value.(*1-3*) In addition, these compounds manifest 1,3-dipoles that engage in [3+2] cycloaddition reactions with alkenes or alkynes, affording five-membered heterocycles. The 1,3-dipolar cycloaddition of organic azides with terminal alkynes catalyzed by Cu is the most classic example of "click chemistry"–the subject of the 2022 Nobel Prize in chemistry.(*4, 11*)

Although numerous transition-metal N_2 complexes have been synthesized since Allen and Senoff's 1965 report of the Ru-N_2 complex,(*12, 13*) boron or heavier main-group diazo compounds have gone unrealized for almost two centuries (Fig. 1A). Considering that boron-containing small molecules continue to experience rapid development for small-molecule activation,(*14*) catalysis,(*15*) materials science,(*16*) and medicinal chemistry,(*17*) we postulate that a compound with a terminal N_2 group linked to boron (i.e., a diazoborane) would present attractive synthetic utility. Indeed, borylation reactions have remained a hot topic since the discovery of hydroboration in 1956 and Suzuki coupling in 1979,(*18-20*) and we propose that diazoborane compounds represent excellent borylene precursors for borylating organic skeletons. Notably, Braunschweig and co-workers recently reported dinitrogen activation by dicoordinate borylene wherein a diazoborane species is a proposed key intermediate.(*21-25*) Stabilization of such a diazoborane and mapping its reactivity patterns has the potential to reveal a wealth of hitherto untapped chemical space.

Efforts to synthesize diazoborane compounds and their analogues have been made by several groups,(*21-28*) and to date, examples of the diazoborane functional group have only been detected under matrix isolation conditions,(*28*) or as proposed transient intermediates.(*23-27*) Although the carboranyl diazonium analogues were isolated in 1982,(*29-31*) their electronic structure, properties, and reactivity differ widely from those anticipated for neutral diazoboranes. Herein, starting from Carpino's hydrazine,(*32*) we report the successful isolation of a N-heterocyclic carbene-stabilized diazoborane via a two-step synthesis. An initial reactivity survey illustrates that the diazoborane serves as a borylene source and 1,3-dipole, a reactivity profile comparable to those of organic azides and diazoalkanes.

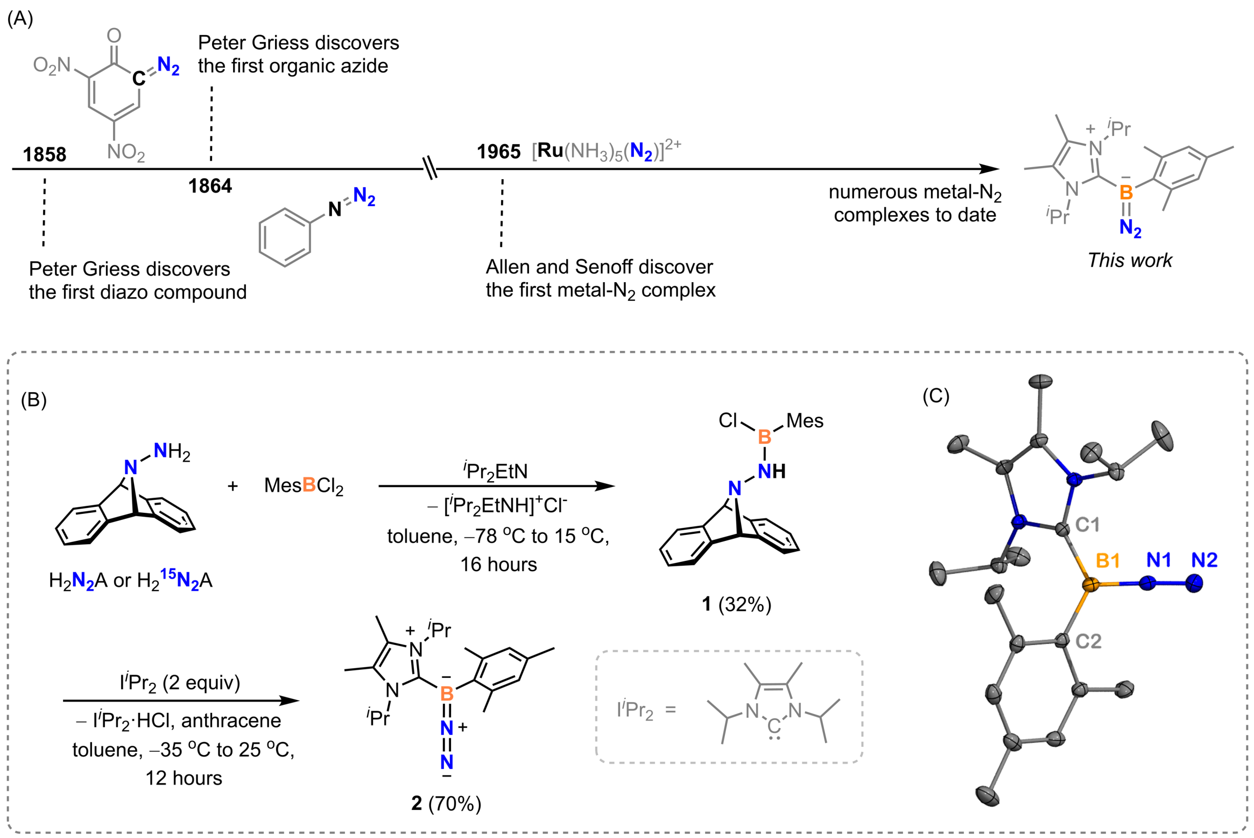

Fig.1. Background and synthesis of 2.
(A) Timeline of the discovery for terminal N_2 compounds. (B) Synthesis of **1** and **2**. (C) The solid-state structure of **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. ^{i}Pr, isopropyl; Mes, mesityl.

The reaction of Carpino's hydrazine with mesitylboron dichloride in the presence of diisopropylethylamine (DIPEA) resulted in the formation of an *N*-amino aminoborane **1** (Fig. 1B). DIPEA scavenges the eliminated HCl and forms the ammonium salt $[^i\mathrm{Pr}_2\mathrm{EtNH}]^+\mathrm{Cl}^-$. The use of an NHC to dehydrohalogenate from borylhydrazine was inspired by the work of Kong and co-workers.(*33*) Compound **1** was separated from the salt by filtration and purified by crystallization from a toluene/hexanes solution in 32% yield. Treatment of **1** with 4,5-dimethyl-1,3-diisopropyl-imidazol-2-ylidene ($\mathrm{I}^i\mathrm{Pr}_2$, 2 equiv) resulted in an immediate color change to dark green. The proton NMR spectrum of the reaction mixture contained signals indicative of compound **2**, free anthracene, and imidazolium cation $[\mathrm{I}^i\mathrm{Pr}_2\text{-H}]^+$. Compound **2** was separated from the imidazolium salt by filtration and purified by recrystallization from diethyl ether. Compound **2** co-crystallizes with the anthracene byproduct and was isolated as a mixture (60 to 70 w%). The anthracene was removed by sublimation at 30 ºC (0.04 torr) to give pure **2** in 71% yield. Compound **2** is heat-sensitive and displays a second-order decay at 50 ºC in C_6D_6 ($k = 0.0094\ \mathrm{mol}^{-1}\cdot\mathrm{L}\cdot\mathrm{min}^{-1}$).

Spectroscopic characterization. The ^{11}B NMR spectrum of **2** displays a resonance at –11.4 ppm, which lies in the range of tricoordinate borylene species (commonly ca. –30-0 ppm). In comparison, a carbonyl borylene ArB(IMe)(CO) (Ar = 2,6-bis(2,4,6-triisopropylphenyl)phenyl, IMe = 1,3-dimethyl-imidazol-2-ylidene) displays an ^{11}B NMR resonance at –22.5 ppm(*34*) and an isocyanide borylene (alkyl)B(IMe)(CNMes*) (alkyl = 2-methylpropyl, Mes* = 2,4,6-tri(*tert*-butyl)phenyl) shows a resonance at –10.4 ppm.(*35*) In the ^{15}N NMR spectrum of ^{15}N-**2**, the terminal nitrogen displays a doublet at 627.1 ppm ($^1J_{N\text{-}N}$ = 15.3 Hz) and the boron-bound nitrogen atom displays a broad signal at 425.4 ppm (relative to liquid NH_3, –380.5 ppm relative to neat $MeNO_2$, 0 ppm).(*36*) In comparison, the terminal nitrogen and the carbon-bound nitrogen of diphenyldiazomethane (Ph_2CN_2) display ^{15}N NMR resonances at 439 and 303 ppm, respectively (relative to liquid NH_3).(*37*)

The N-N stretching vibrations in **2** (1891 cm^{-1}) and ^{15}N-**2** (1836 cm^{-1}) are remarkably red-shifted compared to common diazo (~2000 cm^{-1}) and azide compounds (~2100 cm^{-1}). In order to understand the intrinsic N–N bond strength of **2**, we calculated the relaxed force constants(*38*) for the relevant oscillators, and those of Mes_2CN_2 and $MesN_3$ for comparison (Fig. S40). Intriguingly, the relaxed N–N, C–N, and B–N force constants (N, 10.2 mdyn/Å; C, 8.1 mdyn/Å; B, 5.2 mdyn/Å) and their corresponding terminal N=N constants (N, 18.9 mdyn/Å; C, 18.2 mdyn/Å; B, 16.9 mdyn/Å) both follow the sequence N > C > B, indicating that the B–N bond and N=N bonds in **2** are both weaker than the corresponding linkages in common diazo and azide compounds.

The UV-visible spectrum of **2** in tetrahydrofuran (THF) features two broad peaks at 370 and 444 nm (Fig. S26). Based on time-dependent density functional theory (TD-DFT) calculations, these peaks mainly arise from electronic transitions of the highest occupied molecular orbital (HOMO)→lowest unoccupied molecular orbital +2 (LUMO+2, 69%) and HOMO→LUMO+1 (91%), respectively.

Crystallography and electronic structure. Storage of a concentrated diethyl ether solution of **2** afforded single crystals suitable for x-ray diffraction analysis (Fig. 1C). The B–N–N moiety evinces a nearly linear geometry (177.7(1) º). The N1–N2 bond length (1.147(1) Å) is slightly longer than a N≡N triple bond (1.10 Å) but shorter than an N=N double bond (1.25 Å).(*39*) The B1–N1 distance (1.406(1) Å) is consistent with that predicted for a B=N double bond (1.39 Å) and shorter than that of a B–N single bond (1.49 Å).(*40*) Therefore, the bond order for the B–N bond is between 1 and 2 while the N–N bond is between 2 and 3. Indeed, the calculated Wiberg bond order is 1.24 for the B–N bond and 2.35 for the N–N bond.

The optimized structure of **2** (PBE0-D3BJ/def2-TZVPP level of theory) is consistent with its solid-state structure. Analysis of the frontier molecular orbitals of **2** yields notable insights (Fig. 2A). In the HOMO the electron pair on the boron atom delocalizes to the adjacent N-N π^* orbital, indicating the nucleophilic nature of the boron center and the terminal nitrogen. The LUMO displays dominant N-N π^* orbital character and the LUMO+1 and LUMO+2 both display partial contribution from the N-N π^* orbital. We also calculated the orbital-weighted dual descriptor of **2** (Fig. 2C),(*41*) to more clearly depict its nucleophilic (in blue) and electrophilic sites (in green).

According to natural resonance theory (NRT) analysis,(*42-44*) four major resonance structures are depicted in Fig. 2D. 35.8% of the resonance structures contain a N≡N triple bond and a B–N single bond, the predominant structural representation of the two bonds, while 20.9% of the resonance structures suggest a N=N double bond and a B=N double bond, a more classical way to represent diazo compounds.

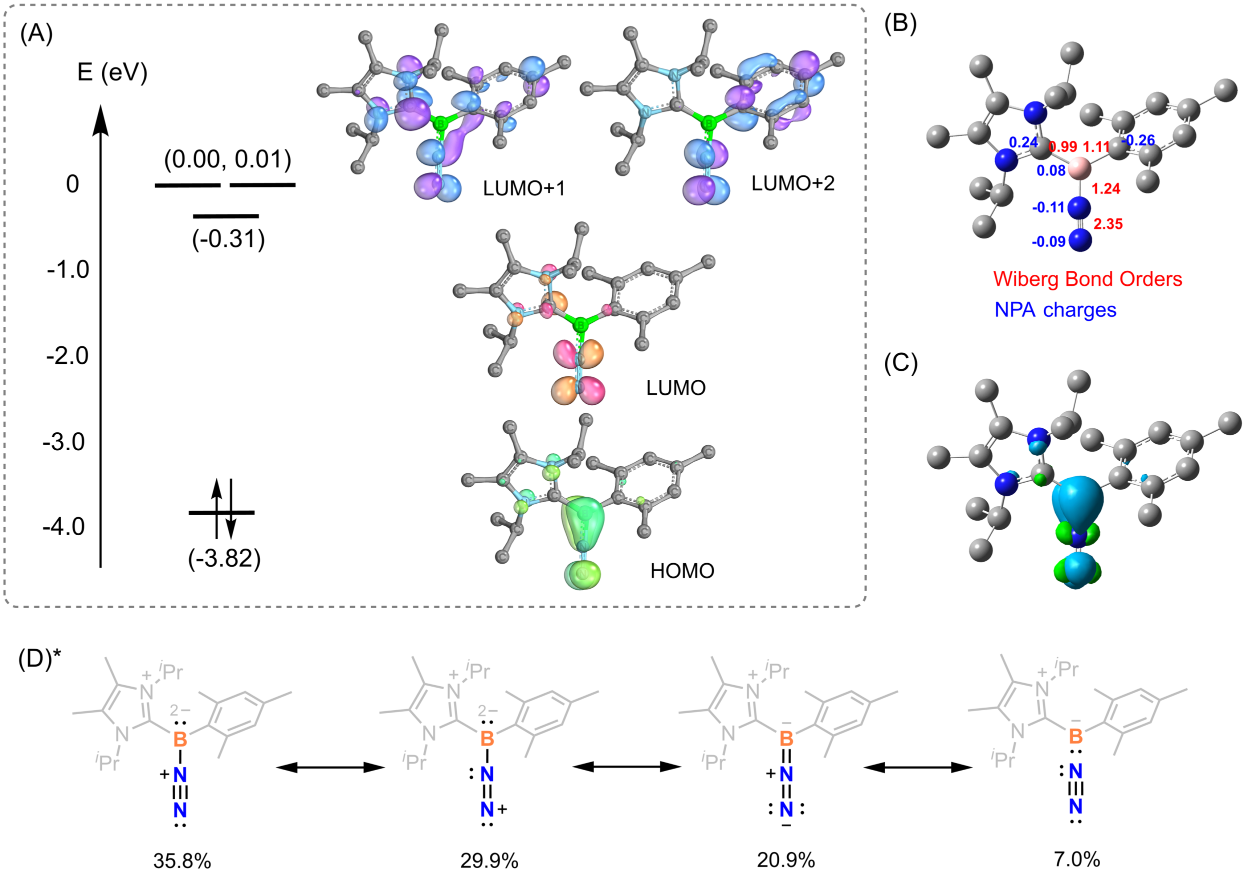

Fig. 2. Theoretical analysis of 2.
(a) Calculated HOMO, LUMO, LUMO+1, and LUMO+2 of **2**. An isovalue of 0.05 (e/au^3)$^{1/2}$ was used in the isosurface contour plots. (b) Optimized structure of **2** with selected Wiberg bond orders and natural charges in natural population analysis (NPA). (c) Orbital-weighted dual descriptor of **2**. Nucleophilic sites are depicted in blue and electrophilic sites are depicted in green. An isovalue of 0.003 e/au^3 was used in the isosurface contour plots. (d) Four resonance structures with their weight percentages. Different resonance structures are summarized to highlight the boron–nitrogen and nitrogen–nitrogen bonds with minor resonance structures omitted. *The last 6% of the resonance structures are a variety of very minor contributors including Mes(I^{i}Pr$_2$)B≡N–N.

Reactivity. We then sought to explore the reactivity of **2** (Fig. 3). In order to compare the propensity of the N_2 fragment to dissociate from boron with reference to carbon and nitrogen, we tested its reactivity with diphenyldiazomethane (Ph_2CN_2) and phenyl azide (PhN_3). Treatment of **2** with these two reagents results in immediate violent bubbling (*Explosion attention!*), indicating the evolution of N_2 during the reaction. The corresponding products of the reactions were identified by single-crystal x-ray diffraction analyses (Figs. S36 and 37). The reaction with Ph_2CN_2 yields a bora-azine **3**. A ^{15}N labeling experiment further confirmed that the "N_2" unit in **3** originates from Ph_2CN_2. Interestingly, a similar reaction proceeded upon treatment of a rhodium(I)-N_2 complex with diphenyldiazomethane,(*45*) showing the metallomimetic nature of borylene.(*46, 47*) The reaction with PhN_3 affords compound **4**, which contains a new BN_4 five-membered ring. The formation of **4** is rationalized from the [3+2] cycloaddition of an NHC-coordinated iminoborane (Mes(I^{i}Pr$_2$)B=NPh) with PhN_3.(*48-52*) In contrast to the reaction with Ph_2CN_2, the NHC ligand dissociates from the boron center and is isolated as a nitrene addition adduct. Based on these results, diazoborane has a higher propensity to undergo N_2 loss with respect to the diazo and azide compounds. Borylene transfer to an organic skeleton occurs either with the NHC associated or dissociated.

Although azide compounds display no reaction with terminal alkynes without a metal catalyst, and diazo compounds commonly require polar alkynes for the reaction to proceed without catalysts, compound **2** undergoes [3+2] dipolar cycloaddition with phenylacetylene at 25 ºC. Surprisingly, the formed five-membered ring undergoes further rearrangements, finally affording a *1H*-5-bora-pyrazole (Fig. S38), with the formation of an aromatic ring being the presumed driving force for the reaction. The position of the acidic hydrogen in **5** was located in the Fourier difference map.

As analyzed above, the frontier molecular orbitals suggest nitrene character for the diazoborane terminal nitrogen atom. Treatment of **2** with an N,N′-diamidocarbene (DAC) results in the immediate fading of the green color.(*51*) Single-crystal x-ray diffraction analysis confirms the formation of the nitrene addition product **6** (Fig. S39).

Dinitrogen and isocyanide are commonly regarded as isoelectronic ligands.(*52*) Treatment of **2** with 2,6-dimethylphenyl isocyanide resulted in a slow color change from dark green to dark red, indicating isocyanide-N_2 exchange in compound **2** to form **7**. The central boron atom of the product gives a signal at –8.9 ppm in its ^{11}B NMR spectrum, comparable to that observed for the aforementioned isocyanide borylene complex (alkyl)B(IMe)(CNMes*) (–10.4 ppm).(*36*)

During the last two centuries, rich chemistry has been developed based on diazoalkanes and organic azide reagents for accessing valuable molecules. We therefore anticipate an exciting future for the diazoborane functional group, now that proof of its structure and accessible reactivity has been provided.

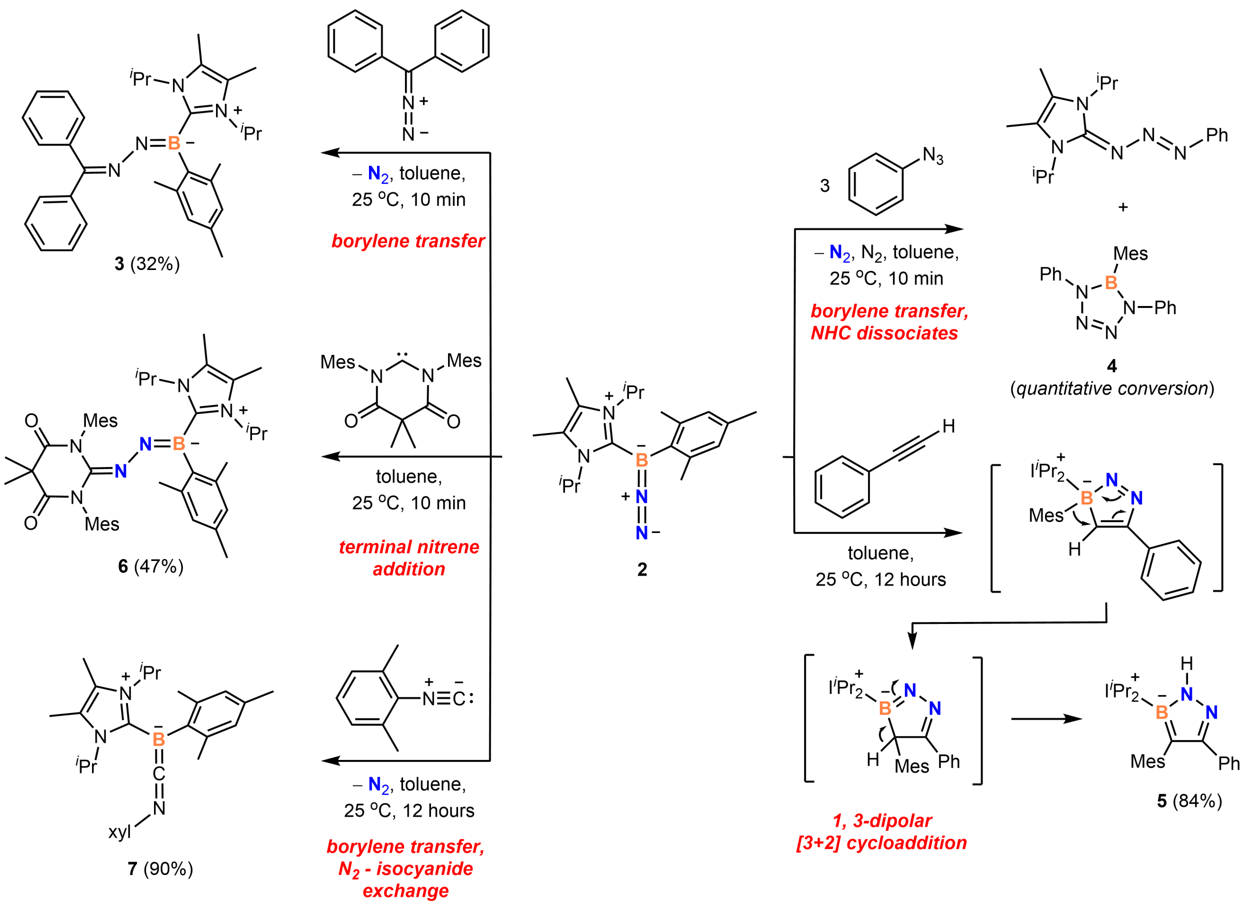

Fig. 3. Reactivity studies of 2.
Compound **2** undergoes borylene transfer, dipolar [3+2] cycloaddition, terminal nitrene addition, and N_2-isocyanide exchange. Compounds **3-6** are characterized by single-crystal X-ray diffraction and the data are provided in the supporting information (Figs. S36-39).

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Acknowledgments: The authors acknowledge Research Computing at Massachusetts Institute of Technology (Engaging Cluster, Supercloud) for providing computational resources and technical support that have contributed to the results reported within this publication. The authors thank Dr. Peter Müller for helping solve problems related to X-ray crystallography data, and DCIF staff for their technical support.

Funding: This study is based upon work supported by the National Science Foundation under Grant No. 2247252 (CCC) and No. 2046544 (RJG).

Author contributions: CZ devised the project, synthesized, and characterized all compounds **1-7**, and drafted the manuscript. CZ and CCC performed the computational work. RJG and CCC supervised the project and revised the manuscript.

Competing interests: The authors declare no competing financial interests.

Data and materials availability: General information, experimental procedures, ^{1}H NMR/^{13}C NMR/^{11}B NMR spectra, high resolution mass spectrometry data, infrared spectrometry data and computational details are provided in the Supplementary Materials. Full crystallographic data for structures **1**, **2**, **3**, **4**, **5**, and **6** are available free of charge from the Cambridge Crystallographic Data Center under reference numbers 2334697, 2334698, 2334699, 2334700, 2334701, and 2334702, respectively.

SUPPLEMENTARY MATERIALS

Materials and Methods
Supplementary Text
Figs. S1 to S44
Tables S1 to S9
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