BN Heterocycles

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Monobenzofused 1,4-Azaborines: Synthesis, Characterization, and Discovery of a Unique Coordination Mode**

*Senmiao Xu, Fredrik Haeffner, Bo Li, Lev N. Zakharov, and Shih-Yuan Liu**

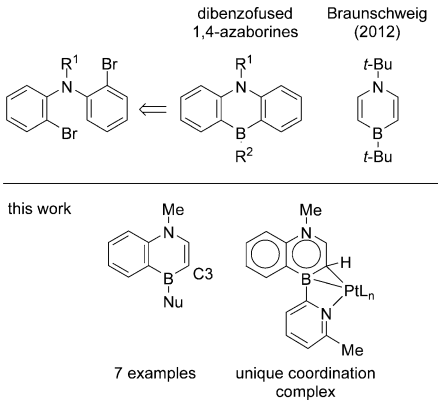
Abstract: *We report the first general synthesis of boron-substituted monobenzofused 1,4-azaborines using ring-closing metathesis of an enamine-containing diene as a key synthetic strategy. As part of our investigations, we discovered that the B-C3 moiety in a 1,4-azaborine can serve uniquely as a η^2-L-type ligand. This functionality is exemplified by two κ^2-N-η^2-BC Pt complexes of a boron-pyridyl-substituted monobenzofused-1,4-azaborine. Single-crystal X-ray diffraction analysis of the Pt complexes shows a strong structural contribution from the iminium resonance form of the monobenzofused-1,4-azaborine ligand. We also demonstrate that a palladium(0) complex supported by a 1,4-azaborine-based phosphine ligand can catalyze hydroboration of 1-buten-3-yne with unique selectivity. In view of the importance of arene–metal π-interactions in catalytic applications, this work should open new opportunities for ligand design involving the 1,4-azaborine motif as an arene substitute.*

BN/CC isosterism has emerged as a viable strategy to broaden the chemical diversity of compounds relevant to materials science and biomedical research.[1] The replacement of two carbon atoms in benzene with a boron and a nitrogen atom leads to three BN isosteres of benzene: 1,2-azaborine,[2,3] 1,3-azaborine,[4] and 1,4-azaborine.[5] The chemistry of 1,3- and 1,4-azaborines has been less explored than that of 1,2-azaborines, arguably because of a lack of general synthetic approaches to those BN heterocycles. Specifically, the development of 1,4-azaborines has been primarily limited to polycyclic dibenzofused derivatives because of the ready availability of versatile halogenated diarylamine synthons (Scheme 1, top).[6] Braunschweig and co-workers reported the only synthesis of a non-dibenzofused 1,4-azaborine to date, prepared by a rhodium-catalyzed cyclization of *N*-*t*Bu-*B*-*t*Bu-iminoborane with acetylene.[7] Despite the elegant simplicity of this method, the reported synthetic scope is currently limited to one example.

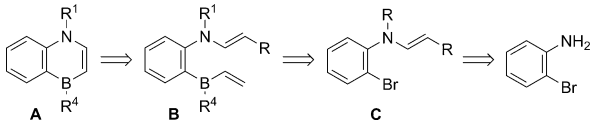
We sought to develop a more general synthesis toward non-dibenzofused 1,4-azaborine compounds. Herein, we describe a synthetic route toward boron-substituted monobenzofused 1,4-azaborines. The new procedure enabled the unexpected discovery that the B–C3 moiety in a 1,4-azaborine can uniquely serve as η^2-L-type ligand. This ligand functionality is shown by the preparation of a platinum complex of a boron-pyridyl-substituted monobenzofused-1,4-azaborine (Scheme 1, bottom). We also demonstrate that a palladium(0) complex supported by a 1,4-azaborine-based phosphine ligand can catalyze the hydroboration of 1-buten-3-yne with distinct regio- and diastereoselectivity.

In our work on 1,2-[8] and 1,3-azaborines,[4a] we have shown that ring-closing metathesis (RCM) is a powerful synthetic tool to construct the corresponding BN heterocyclic core. We envisioned that a non-dibenzofused 1,4-azaborine **A** could also be produced using RCM (Scheme 2). The diene precursor **B** should be accessible from commercially available 2-bromoaniline via *N*-vinyl aniline **C**.

Scheme 3 illustrates our synthesis of monobenzofused 1,4-azaborine **6**. Successive N-substitution of 2-bromoaniline afforded *N*-allyl-*N*-methyl-2-bromoaniline **2**. Subsequent



Scheme 1. 1,4-Azaborine synthesis: Previous and present work. Nu = nucleophile.



Scheme 2. Retrosynthetic analysis of non-dibenzofused 1,4-azaborine **A**.

[*] Dr. S. Xu, Dr. F. Haeffner, Dr. B. Li, Prof. Dr. S.-Y. Liu
Department of Chemistry, Boston College
Chestnut Hill, MA 02467 (USA)
E-mail: shihyuan.liu@bc.edu
Dr. L. N. Zakharov
Center for Advanced Materials Characterization in Oregon
University of Oregon, Eugene, OR 97403-1253 (USA)

[**] Correspondence concerning X-ray crystallography should be directed to Lev N. Zakharov (lev@uoregon.edu) and Bo Li (complex **8h**, **11**; bo.li.5@bc.edu). Correspondence concerning electronic structure calculations should be directed to Fredrik Haeffner (jan.haeffner@bc.edu). Portions of this work were carried out at the University of Oregon. Support for this work has been provided by the National Science Foundation (CHE-1212346) and by Universal Display Corporation.

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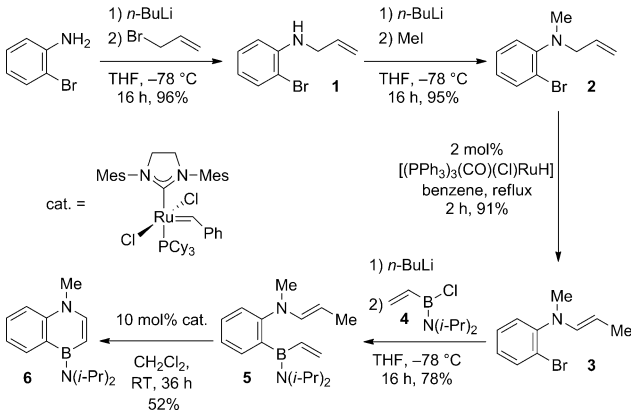
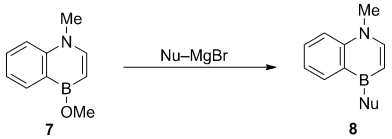


Scheme 3. Synthesis of monobenzofused 1,4-azaborine **6**. Cy = cyclohexyl. Mes = mesityl.

alkene isomerization of **2** in the presence of $[(PPh_3)_3(CO)(Cl)RuH]$ (2 mol%) produced the *N*-vinyl aniline **3** in 85% yield ($E/Z > 19:1$).[9] Exchange of the bromide in the aryl–Br bond in **3** for lithium, followed by quenching with vinylboron chloride **4**, generated diene intermediate **5**. Our preliminary investigation of the RCM of **5** with Grubbs first-generation and Schrock catalysts were unsuccessful.[10,11] To our delight, we found that in the presence of Grubbs 2nd generation catalyst (10 mol%), diene **5** converted into the desired product **6** in 52% yield.[12]

The boron-diisopropylamino substituent in **6** can be quantitatively replaced by the methoxy group by treating **6** with MeOH (1 equiv). In view of the relatively better leaving-group ability of the methoxy substituent, we envisioned that compound **7** would serve as a general synthetic precursor toward boron-substituted monobenzofused 1,4-azaborines. As can be seen from Table 1, aryl-, vinyl-, alkyl-, and alkynyl-based Grignard reagents (entries 1–4) serve as suitable nucleophiles to furnish the corresponding products **8a**–**d**, respectively. Organolithium reagents such as mesityllithium also displace the boron-methoxy group in precursor **7** (entry 5).

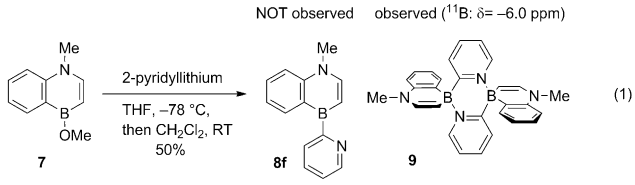
Table 1: Synthesis of boron-substituted monobenzofused 1,4-azaborines through nucleophilic substitution.



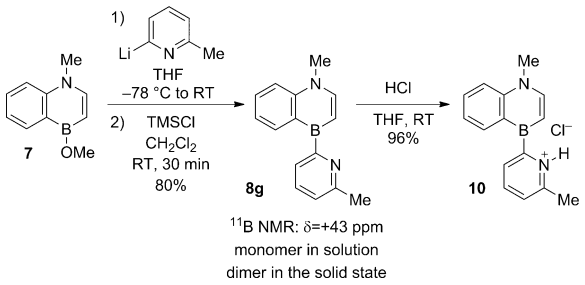
Entry	Nu-MgBr	Product	*T* [°C]	Yield [%][a]
1	Ph-MgBr	**8a**	RT	80
2	vinyl-MgBr	**8b**	RT	89
3	isopropyl-MgBr	**8c**	RT	91
4	PhC≡C-MgBr	**8d**	RT	77
5	Mesityl-MgBr	**8e**	-78	70

[a] Yield of isolated product.

We are particularly interested in boron-2-pyridyl-substituted 1,4-azaborine because of its potential to serve as a novel κ^2-N,C-bidentate ligand. When the substitution reaction, illustrated in Table 1, was applied to 2-pyridyllithium as the nucleophile, the target 1,4-azaborine **8f** was not detected. Instead, the dimeric molecule **9**, with a ^{11}B resonance signal (in CH_2Cl_2) at $\delta = -6$ ppm, was observed, which presumably originated from the target monomer **8f** [Eq. (1)]. The dimer **9** persists both in solution and in the solid state as evidenced by solution NMR spectroscopy and single crystal X-ray diffraction analysis.[13]



To probe the coordination ability of this new ligand scaffold, we needed to shift the equilibrium toward the monomeric state in solution. Thus, we pursued the synthesis of the 6-methyl-2-pyridyl derivative **8g** as a more sterically encumbered analogue of **8f**. Treatment of precursor **7** with 6-methylpyrid-2-yllithium followed by trimethylsilylchloride furnishes product **8g** in 80% yield (Scheme 4). In contrast to **8f**, compound **8g** exists as a monomer in solution as evidenced by the resonance signal at $\delta = +43$ ppm in its ^{11}B NMR spectrum in CD_2Cl_2 ($K_a = 1.67\ M^{-1}$).[14] However, upon concentration and recrystallization, we found that **8g** is also a dimer in the solid state.[13] Addition of HCl to a solution of **8g** produces the protonated complex **10**, which was structurally characterized using single-crystal X-ray crystallography (Figure 1).[15]



Scheme 4. Synthesis of ligand **8g** and its protonated derivative **10**.

The coordination ability of ligand **8g** was examined by investigating the reaction between **8g** and $[\{PtMe_2(\mu\text{-}SMe_2)\}_2]$.[16] Platinum complex **11** was isolated from the reaction mixture and featured an η^2-coordination to the Pt atom by the B-C3 component of the 1,4-azaborine ring (Figure 1).[17] There are many examples of C–C–metal π complexes (e.g., alkene/arene π complexes),[18,19] however the corresponding η^2-borataalkene ($[R_2B{=}CR_2]^-$) transition-metal complexes are relatively uncommon.[20,21] Ligand **8g** is particularly unique because it is an overall charge-neutral ligand, and the negatively charged borataalkene substructure

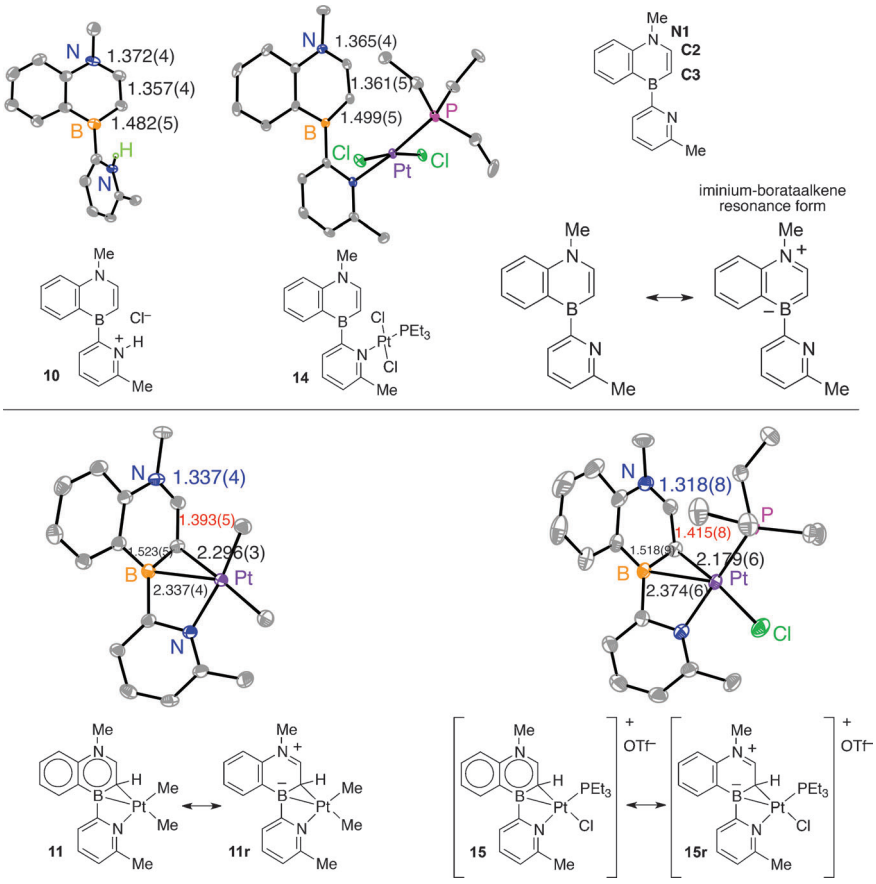
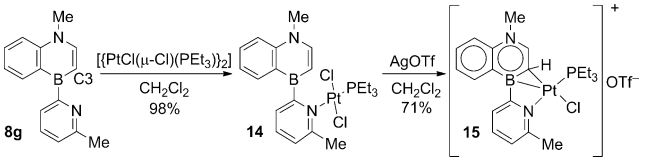


Figure 1. ORTEP illustrations (thermal ellipsoids set at 35% probability) and structural formulas with resonance forms of κ^2-*N*-η^2-BC Pt complexes **11**, **15**, and compounds **10** and **14**. Counteranions in **10** and **15** have been omitted for clarity. Top right: atom numbering scheme.

is revealed in only one of the resonance forms (see Figure 1, top right). Note, under identical reaction conditions the analogous naphthylpyridine complex could not be obtained from the corresponding carbonaceous ligand,[22] suggesting that the observed coordination mode in complex **11** is unique to the 1,4-azaborine motif.

To probe the η^2-BC–metal bonding as a function of the electronic properties of the metal, we separately prepared the cationic Pt complex **15** (Scheme 5). The reaction between ligand **8g** and *trans*-[{PtCl(μ-Cl)(PEt_3)}$_2$] generates the pyridine adduct **14** in excellent yield. Subsequent chloride abstraction with AgOTf furnishes the desired cationic Pt complex **15**.[23]

Figure 1 illustrates the crystal structures of κ^2-*N*-η^2-BC Pt complexes **11** and **15** and the structures of reference compounds **10** and **14**.[24] Changes are evident in the intra-ring bond length of the 1,4-azaborine heterocycle upon η^2-BC



Scheme 5. Synthesis of the cationic Pt complex **15**.

coordination to the platinum center. As can be seen from Figure 1, the N1–C2 distances are significantly shorter in complexes **11** and **15** (1.337(4) Å and 1.318(8) Å, respectively; blue numbers in Figure 1) than in reference compounds **10** and **14** (1.372(4) Å and 1.365(4) Å), respectively). Concomitantly, the C2–C3 bond distances in **11** and **15** are longer (1.393(5) Å, 1.415(8) Å; red numbers in Figure 1) than those in compounds **10** and **14** (1.357(4) Å and 1.361(5) Å, respectively). This situation is consistent with a substantial contribution from the iminium resonance form (resonance structures depicted as **11r** and **15r** in Figure 1) to the structures of κ^2-*N*-η^2-BC Pt complexes **11** and **15**. Furthermore, it appears that the iminium resonance contribution becomes more prominent when the Pt center is more electron deficient (cf. **11** vs **15**).[25] This is also consistent with a shorter Pt–C3 distance in **15** (2.179(6) Å) as compared to **11** (2.296(3) Å). It appears that back-bonding occurs between the Pt metal center and the boron atom; the more electron-rich Pt complex **11** features a shorter Pt–B distance (2.337(4) Å) than complex **15** (2.374(6) Å). The boron atom is located out of the square plane in both **11** and **15**, potentially allowing back-donation from one of the filled Pt dπ orbitals to the empty p orbital of boron. The geometry about the boron center remains trigonal planar in both complexes (sum of the bond angles around B are 359.9° and 360.0° for **11** and **15**, respectively). The Pt–B distances observed in complexes **11** and **15** (ca. 2.34–2.37 Å) are significantly shorter than the sum of the corresponding van der Waals radii of 3.67 Å (Pt: 1.75 Å,[26] and B: 1.92 Å),[27] and in agreement with reported dative Pt→B bonding (Pt–B distance: 2.12–2.53 Å).[28,29] The resonance signals in the ^{11}B NMR spectra of **11** and **15** (δ = 16.9 and 22.6 ppm in CD_2Cl_2, respectively) appear significantly more upfield than the signal for the free ligand **8g** (δ = 43 ppm), which is consistent with an appreciable Pt–B interaction.

We have performed preliminary DFT calculations to understand the electronic properties of ligand **8g**. Figure 2 depicts the electrostatic potential surface map and the HOMO orbital of ligand **8g** along with its carbonaceous naphthylpyridine ligand **C8g** for comparison. The strongly negative charge at the C3 center and the large contribution to the HOMO by the C3 carbon in **8g** relative to **C8g** are consistent with the more strongly donating nature of the C3 atom in **8g**.[30]

To demonstrate the utility of our new ligand platform in organic synthesis, we prepared the 1,4-azaborine-based phosphine ligand **8h**[31] and chose to investigate the palladium-

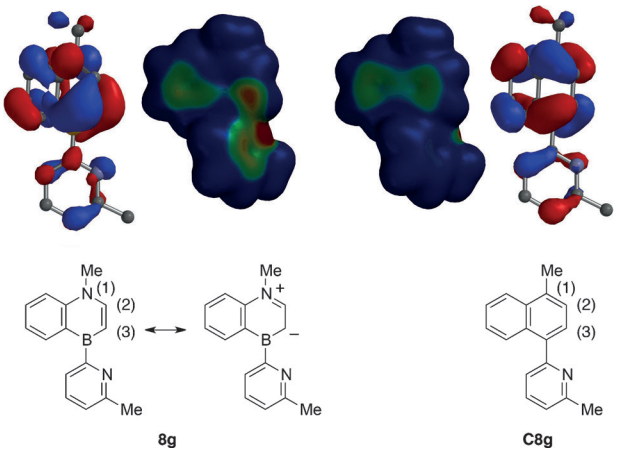
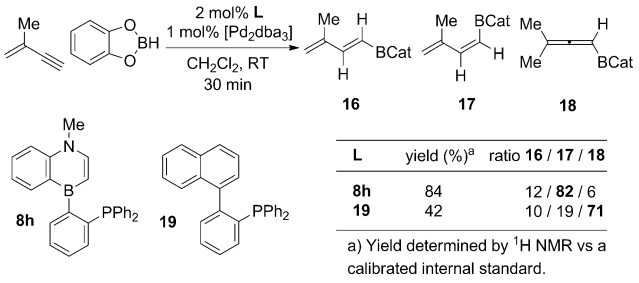


Figure 2. Electrostatic potential surfaces of **8g** and its carbonaceous analogue **C8g** computed at the 0.002 electron a.u. density isocontour level (−100 to −50 kcal mol^{-1}) and illustrations of their HOMOs.

catalyzed hydroboration of an enyne as a model reaction (Scheme 6). The regio- and diastereoselectivity of this hydroboration reaction largely depends on the nature of the phosphine ligand. The use of a monodentate tertiary phosphine leads to allenylborane formation, while the reaction in



L	yield (%)[a]	ratio **16** / **17** / **18**
8h	84	12 / **82** / 6
19	42	10 / 19 / **71**

a) Yield determined by ^{1}H NMR vs a calibrated internal standard.

Scheme 6. Unique selectivity in Pd-catalyzed hydroboration of 2-methyl-1-buten-3-yne using ligand **8h**.

the presence of bidentate bisphosphine ligands yields predominantly *cis*-hydroboration of the alkyne.[32] Preliminary results show that in the presence of **8h** as the supporting ligand,[33] the hydroboration reaction was completed in 30 minutes to afford the *trans*-hydroboration product **17** as the major product. On the other hand, the carbonaceous ligand **19** furnished allene **18** as the major product under otherwise identical reaction conditions, which is consistent with literature reports on monodentate phosphine ligands.[32] Thus, ligand **8h** provides unique selectivity for *trans*-hydroboration product **17** that has not been achieved with other ligand architectures.

In summary, we have developed the first general synthesis of boron-substituted monobenzofused 1,4-azaborines. As part of our synthetic investigations, we discovered that the B−C3 moiety in a monobenzofused 1,4-azaborine can uniquely act as an η^2-L-type ligand to transition-metal centers. As a demonstration of the utility of the new ligand motif, we showed that palladium-catalyzed hydroboration of enynes supported by a 1,4-azaborine-based phosphine ligand resulted in distinct regio- and diastereoselectivity. In view of the importance of arene–metal π-interactions in catalytic applications, our work opens a pathway for the development of the 1,4-azaborine motif as an arene substitute in the design of ligands for homogenous catalysis. Investigations along this route are currently underway in our laboratories.

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[12] Full conversion was observed by ^{11}B NMR spectroscopy.

[13] See Supporting Information for details.

[14] Monomer **8 f** was not observed at elevated temperature whereas an appreciable amount of [(**8 g**)$_2$] was observed at low temperature. The equilibrium constant was obtained by variable temperature (VT) ^{1}H NMR spectroscopy. See Figure S2–S4, Table S1, and Chart S1 in the Supporting Information for details.

[15] Note, the treatment of **9** with HCl did not lead to the corresponding protonated monomer.

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[22] ^{1}H NMR spectrum of the reaction mixture indicates no reaction occurred between the carbonaceous naphthylpyridine ligand **12** and [{Pt(Me)$_2$(μ-SMe$_2$)}$_2$]. See Figure S5 in Supporting Information for details.

[23] The carbonaceous naphthylpyridine ligand **12** and dibenzofused 1,4-azaborines do not furnish the corresponding η^2-Pt complexes. See Supporting Information for details (Figure S6–S8).

[24] Crystallographic data for **9**, [(**8 g**)$_2$], **8 h**, **10**, **11**, **14**, **15**, **16 a** and **16 b** can be found in the Supporting Information. CCDC 977735 (**9**), 977734 [(**8 g**)$_2$], 990259 (**8 h**), 979025 (**10**), 977460 (**11**), 977857 (**14**), 978486 (**15**), 986967 (**S16 a**), and 986966 (**S16 b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[33] The reaction of **8 h** with [Pd$_2$dba$_3$] at room temperature for two hours resulted in the formation of a complex with a ^{11}B NMR chemical shift of δ = 32.0 ppm, an upfield shift of over 14 ppm from the corresponding resonance signal for the free ligand. The upfield shift in the ^{11}B NMR resonance signal is consistent with our observation in the complexation of **8 g** with platinum and indicates the formation of κ^2-*N*-η^2-BC complex.

