

Rhodium-Catalyzed B–H Activation of 1,2-Azaborines: Synthesis and Characterization of BN Isosteres of Stilbenes

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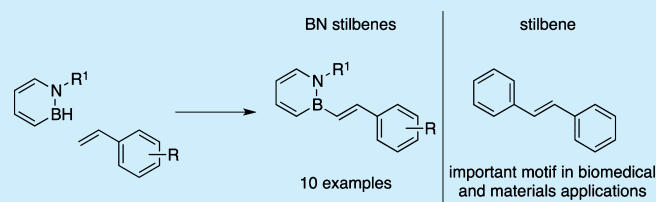
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S Supporting Information

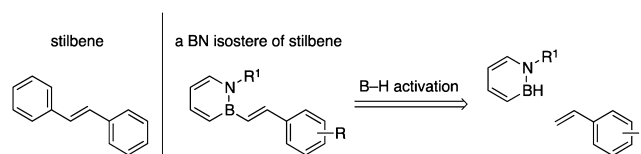
ABSTRACT: The first example of catalytic B–H activation of azaborines leading to a new family of stilbene derivatives through dehydrogenative borylation is reported. Ten 1,2-azaborine-based BN isosteres of stilbenes have been synthesized using this method, including a BN isostere of a biologically active stilbene. It is demonstrated that BN/CC isosterism in the context of stilbenes can lead to significant changes in the observed photophysical properties such as higher quantum yield and a larger Stokes shift. Direct comparative analysis of BN stilbene **3g** and its carbonaceous counterpart **6g** is consistent with a stronger charge-transfer character of the excited state exhibited by **3g** in which the 1,2-azaborine heterocycle serves as a better electron donor than the corresponding arene.



Stilbene and its derivatives are ubiquitous in biologically active molecules¹ and materials science applications. For instance, stilbenoid compounds such as resveratrol have demonstrated anti-inflammatory, anticancer, and cardioprotective activities.² Similarly, the interaction of radiation with stilbenoid compounds has been intensively investigated³ for applications in nonlinear optics⁴ and as light-emitting diodes,⁵ scintillators,⁶ photoresists,⁷ and optical brighteners.^{8,9} Our group has been focusing on developing BN/CC isosterism¹⁰ as a strategy to expand the chemical space of compounds relevant to biomedical research¹¹ and materials science.^{12–14} In view of the versatile applications exhibited by stilbene derivatives, we sought to develop a general method for the synthesis of BN isosteres of stilbene. In this paper, we report the first examples of 1,2-azaborine-based BN stilbenes including a BN isostere of 4-methoxy-*trans*-stilbene, a compound with in vitro activity against MCF-7/6 mammary carcinoma¹⁵ and human colon adenocarcinoma cancer (HT-29)¹⁶ cells. Furthermore, we demonstrate that 1,2-azaborine-based BN stilbenes exhibit photophysical properties that are distinct from their carbonaceous counterparts.

A retrosynthetic analysis revealed that B–H activation of 1,2-azaborines coupled with C–H activation of styrenes through dehydrogenative borylation could furnish the desired 1,2-azaborine-based BN stilbene compounds (Scheme 1). The use of styrenes as direct coupling partners appears particularly attractive due to their ready commercial availability.¹⁷ However, despite some recent progress in the late-stage functionalization of 1,2-azaborines,¹⁸ no systematic study of the B–H activation chemistry of azaborines has been performed.¹⁹ We reported previously that the B–H bond in 1,2-azaborines is relatively nonhydridic.²⁰ Indeed, no reaction is observed between our model *N*-benzyl-*B*-H-1,2-azaborine **1** and *p*-methoxystyrene **2** in

Scheme 1. BN Stilbene and Its Retrosynthetic Analysis



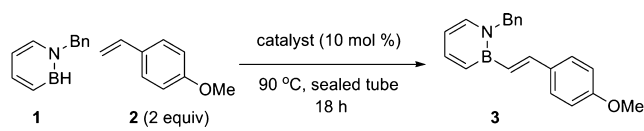
the absence of promoters even at elevated temperatures (up to 110 °C). We thus surveyed a number of commercially available catalysts known to promote B–H activation and dehydrogenative borylations²¹ to facilitate the formation of BN stilbene **3a**.²²

As can be seen from Table 1, Wilkinson's catalyst gave the desired stilbene as the major product in just 15% yield (Table 1, entry 1). Other phosphine-ligated rhodium complexes generally used in B–H activation reactions were ineffective for this reaction (Table 1, entries 2 and 3). On the other hand, Crabtree's complex furnished the product in 51% yield (Table 1, entry 4). Gratifyingly, we found that phosphine-free rhodium alkene complexes such as [Rh(cod)₂]BF₄ or [Rh(nbd)(Cl)]₂ are suitable catalysts for our model dehydrogenative borylation reaction (Table 1, entries 5 and 6). We thus chose those two complexes for further solvent optimization studies. We determined that methylene chloride was the best performing solvent for both rhodium complexes (Table 1, entries 7–12), providing the desired product in up to 98% HPLC yield (83% isolated yield) in the case of [Rh(nbd)(Cl)]₂ (Table 1, entry 12). A reduction of the catalyst loading to 2.5 mol % [Rh(nbd)(Cl)]₂ was not detrimental with respect to the isolated yield of **3a**.

Received: May 12, 2014

Published: June 11, 2014

Table 1. Survey of Catalysts and Solvents for the Dehydrogenative Borylation Reaction between 1,2-Azaborine 1 and Styrene 2^a



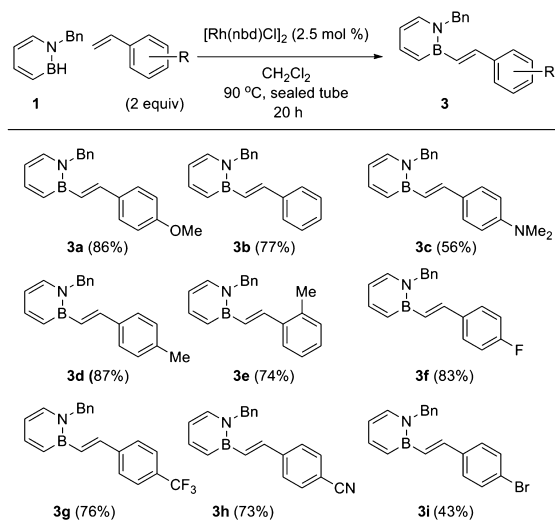
entry	catalyst	solvent	yield ^b (%)
1	RhCl(PPh ₃) ₃	THF	15
2	RhH(CO)(PPh ₃) ₃	THF	0
3	Rh(dppb)(cod)BF ₄	THF	0
4	Ir(cod)(py)(PCy ₃)PF ₆	THF	51
5	[Rh(cod) ₂]BF ₄	THF	64
6	[Rh(nbd)(Cl)] ₂	THF	80
7	[Rh(cod) ₂]BF ₄	toluene	60
8	[Rh(cod) ₂]BF ₄	acetonitrile	23
9	[Rh(cod) ₂]BF ₄	CH ₂ Cl ₂	75
10	[Rh(nbd)(Cl)] ₂	toluene	94
11	[Rh(nbd)(Cl)] ₂	acetonitrile	52
12	[Rh(nbd)(Cl)] ₂	CH ₂ Cl ₂	98 (83) ^c
13	[Rh(nbd)Cl] ₂ (2.5 mol %)	CH ₂ Cl ₂	(86) ^{c,d}

^aAbbreviations: dppb (diphenylphosphinobutane), cod (cyclooctadiene), py (pyridine), nbd (norbornadiene). ^bDetermined by HPLC versus a calibrated internal standard, average of two runs. ^cIsolated yields in parentheses, average of two runs. ^d20 h reaction time.

(Table 1, entry 13). Two equivalents of the styrene were necessary to achieve full conversion to the BN stilbene because one equivalent of styrene was hydrogenated during the catalytic cycle.

With the optimized conditions determined, we next turned our attention to the scope of the dehydrogenative borylation reaction (Scheme 2). The reaction with the parent styrene furnished **3b** in 77% yield. While the electron-rich *p*-methoxystyrene was a suitable substrate for the reaction (**3a**, 86% yield), *p*-(dimethylamino)styrene produced the corresponding BN stilbene **3c** in moderate 56% yield. Steric influences on styrene do not appear to affect the yield of BN stilbene

Scheme 2. Synthesis of BN Stilbenes through Rh-Catalyzed Dehydrogenative Borylation^a

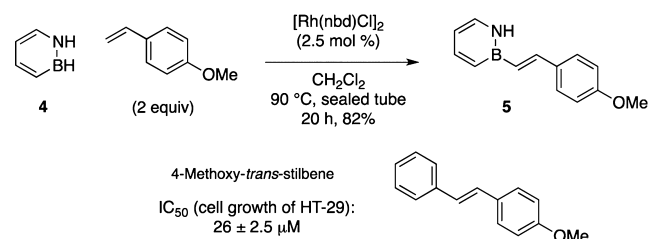


^aThe yields of isolated products are given as the average of two runs.

products as both *p*- and *o*-tolylstyrene are suitable substrates (**3d** and **3e**). Electron-withdrawing substituents are tolerated (**3f**, **3g**, and **3h**). Finally, *p*-bromostyrene couples with **1** to generate a BN stilbene that can be potentially further functionalized through cross-coupling (**3i**).²³

We sought to demonstrate the utility of this dehydrogenative coupling in the synthesis of a BN isostere of a biologically active molecule. We identified the BN isostere of 4-methoxy-*trans*-stilbene as a suitable target.^{15,16} Treatment of the parent 1,2-azaborine **4** with *p*-methoxystyrene under the optimized conditions results in the formation of the BN stilbene **5** in 82% isolated yield (Scheme 3). Thus, the reaction conditions are

Scheme 3. Synthesis of a BN Isostere of 4-Methoxy-*trans*-stilbene



compatible with the protic N-H functional group in **4**. We performed oxygen and water stability studies of compound **5** using published procedures.²⁴ BN stilbene **5** showed <5% decomposition under an oxygen atmosphere in C₆D₆ at 50 °C for 4 h or at room temperature under ambient atmosphere for 16 h. The compound was also stable (<5% decomposition) to 8.5 equivalents of water in DMSO-*d*₆ at room temperature for 2 h, then 50 °C for 2 h.

We were able to isolate only the *trans*-BN stilbene isomers among possible reaction products under our optimized conditions (e.g., hydroboration adducts and *cis*-BN stilbene isomers).²⁵ Single-crystal X-ray diffraction analysis unambiguously confirms our structural assignment for **3a**, which is also consistent with the relatively large ³J_{HH} coupling constant of 18 Hz observed by ¹H NMR.²⁶

Figure 1 illustrates the ORTEP of BN stilbene **3a** along with selected bond distances. The molecule adopts a relatively planar

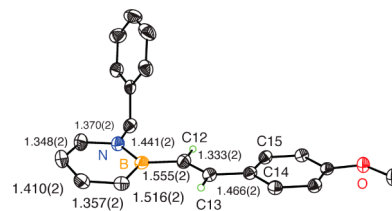


Figure 1. ORTEP illustration, with thermal ellipsoids drawn at the 35% probability level, of BN stilbene **3a**. All hydrogens except for the alkenyl hydrogens at C12 and C13 have been omitted for clarity.

structure in the solid state. The ∠N-B-C12-C13 and ∠C12-C13-C14-C15 dihedral angles are 170.4(1)° and 2.3(2)°, respectively. The heterocyclic intraring distances are consistent with a typical 1,2-azaborine motif.²⁷ The C12-C13 distance of 1.333(2) Å is also consistent with typical distances observed in stilbenes.²⁸ On the other hand, the B-C12 distance of 1.555(2) Å is significantly longer than a typical arene C(sp²)-alkene C(sp²) single-bond distance of ~1.47 Å.²⁹ On the other hand, the B-C12 distance observed in **5** is slightly shorter compared to a

perpendicularly oriented 1,2-azaborine B–C(sp²)–arene single bond distance of $\sim 1.57 \text{ \AA}$.¹⁸

We then investigated the impact of BN/CC isosterism on the photophysical properties of stilbene derivatives. We chose a representative set of BN stilbenes containing an electron-withdrawing (**3g**, (–CF₃) black in Figure 2), electron-neutral

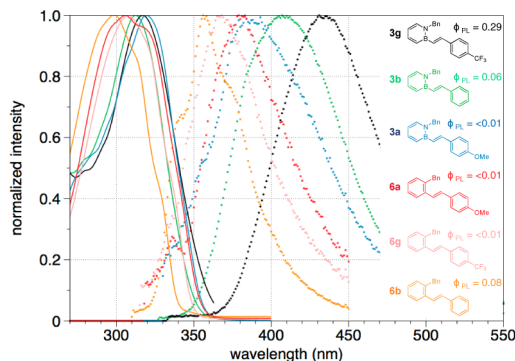


Figure 2. Normalized absorption and emission spectra (in MeCN) of select BN stilbenes in direct comparison with their corresponding carbonaceous counterparts. Quantum yields were determined in EtOH at room temperature.

(**3b**, (–H) green in Figure 2), and electron-rich (**3a**, (–OMe) blue in Figure 2) arene for direct comparison with the corresponding carbonaceous stilbene analogues (**6g** (–CF₃, pink), **6b** (–H, orange), **6a** (–OMe, red)). As can be seen from Figure 2, BN stilbenes exhibit a bathochromic shift in both the absorption and emission spectra. The substituent effect is more pronounced in the emission relative to the absorption. In particular, the effect of the substituents on the emission peak is significantly stronger in BN stilbenes (**3a** (λ_{em}): 390 nm; **3g** (λ_{em}): 431 nm; Δ : 2439 cm^{–1}) than in all-carbon series **6b** (λ_{em}): 357 nm; **6a** (λ_{em}): 380 nm; Δ : 1695 cm^{–1}). The photophysical properties of BN stilbene **3g** (–CF₃, black trace) is particularly intriguing. Compound **3g** exhibits a large Stokes shift (8340 cm^{–1}) and the highest quantum yield (Φ_{PL} : 0.29) among the stilbene compounds that we have investigated.

We performed emission solvatochromism studies on BN stilbene **3g** and its carbonaceous analogue to elucidate the nature of the excited state. Figure 3 illustrates a significant positive solvatochromism on the emission maxima of BN stilbene **3g** (a red shift of 2457 cm^{–1} going from cyclohexane (λ_{em} : 393 nm) to DMSO (λ_{em} : 435 nm)) as compared to the carbonaceous stilbene **6g** (a red shift of 674 cm^{–1} from cyclohexane to

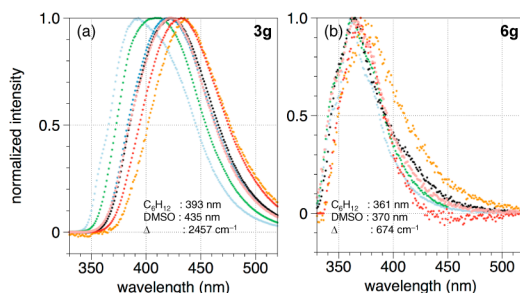


Figure 3. Normalized emission spectra of (a) BN stilbene **3g** and (b) carbonaceous analogue **6g** in various solvents (DMSO, orange; MeCN, red; black, CH₂Cl₂; pink, EtOH; blue, THF; green, Et₂O; cyclohexane, pale blue). All measurements were taken at $1 \times 10^{-5} \text{ M}$.

DMSO).³⁰ The solvatochromic study is consistent with a stronger charge transfer character of the excited state for **3g** than for **6g**, which also presumably involves a larger structural reorganization from ground state leading to the large observed Stokes shift for **3g**. The relatively high photoluminescence quantum yield for BN stilbene **3g** may be due to destabilization of biradical states relative to the charge-transfer state and subsequent deactivation of nonradiative decay pathways associated with the biradical states.³¹ Time-dependent density functional theory (TD-DFT) calculations for compound **3g** reveal that the HOMO–LUMO transition is the predominant one with an oscillator strength of 0.57 (see Supporting Information for details of the calculations).

Figure 4 shows that the *N*-benzyl group does not significantly impact the HOMO–LUMO transition. The HOMO–LUMO

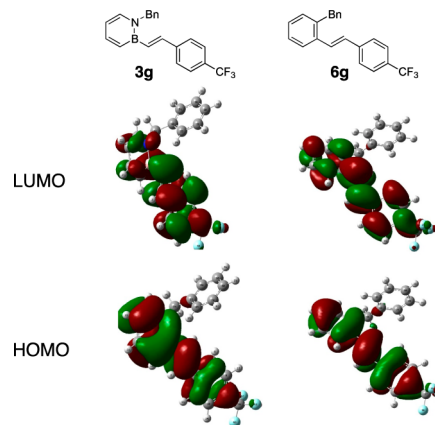


Figure 4. HOMO and LUMO (B3LYP Kohn–Sham orbitals) of **3g** and **6g**.

diagrams are also consistent with **3g** exhibiting a stronger charge transfer character than the carbonaceous **6g**. Thus, our studies suggest that BN/CC isosterism in the context of stilbenes can promote charge transfer transitions in which the 1,2-azaborine heterocycle can be considered a better electron donor than the corresponding arene.

In summary, we have established the first example of catalytic B–H activation of azaborines leading to a family of BN stilbenes through dehydrogenative borylation of styrenes. Ten examples of BN stilbenes have been synthesized using this method, including a BN isostere of a biologically active stilbene. Catalytic activation of the relatively unreactive aromatic B–H bond in these systems expands the basic synthetic utility of the 1,2-azaborines. This study has enabled the discovery that BN/CC isosterism in the context of stilbenes can lead to significant changes in observed photophysical properties such as higher quantum yield and a larger Stokes shift. Direct comparative analysis of BN stilbene **3g** and its carbonaceous counterpart **6g** is consistent with a stronger charge transfer character of the excited state exhibited by **3g** in which the 1,2-azaborine heterocycle serves as a better electron donor than the corresponding arene.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic data, electronic structure calculations, and crystallographic data (CIF). 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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■ ACKNOWLEDGMENTS

Support has been provided by the National Institutes of Health (National Institute General Medical Sciences, R01-GM094541). Funding for the University of Oregon Chemistry Research and Instrumentation Services has been provided in part by the NSF (CHE-0923589). D.A.D thanks the Robert Ramsay Chair Fund of The University of Alabama for support.

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