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Synthesis of Amine–Borane Intramolecular Complexes through Palladium-Catalyzed Rearrangement of Ammonioalkynyltriarylborates

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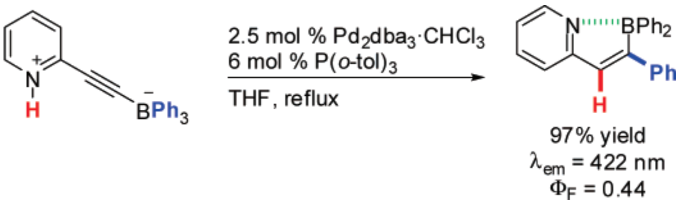
ABSTRACT



The palladium-catalyzed rearrangement reaction of alkynyltriarylborates having a tertiary ammonium moiety stereoselectively afforded amine–borane intramolecular complexes, some of which exhibited significantly strong fluorescence.

Boron-modified π-conjugated compounds have attracted much attention because they exhibit unique photophysical and electrochemical properties.[1] For example, when a nitrogen-containing π-conjugated skeleton forms an intramolecular complex with a triarylborane moiety suitably positioned within the molecule, it is constrained into a planar structure which leads to considerable lowering of the LUMO level.[2] Thus, this class of compounds has become an intriguing synthetic target with the aim of developing novel electron-transporting materials. We recently reported a palladium-catalyzed reaction of alkynyltriarylborates with aryl halides, which resulted in the stereoselective synthesis of (trisubstituted alkenyl)diarylboranes via a 1,2-migration of an aryl group from boron to the α-carbon.[3] We attempted to employ this reaction for the synthesis of an intramolecular amine-borane complex by using an alkynylborate bearing a tethered amine. However, the reaction failed to proceed, likely due to the strong coordination of the nitrogen atom to palladium. This hypothesis led us to employ an alkynyborate in which the amino group is in the form of an ammonium salt instead of a free amine, to mask the coordinating character of the nitrogen atom. Herein, we report the successful application of this strategy to the stereoselective synthesis of amine−borane intramolecular complexes.

Thus, zwitterionic alkynyltriarylborate **1a**[4] was treated with a catalytic amount of $Pd_2dba_3·CHCl_3$ and P(*o*-tol)$_3$ in refluxing THF. A rearrangement reaction took place, and after 1 h, the cyclic alkenylborane **2a**, in which the unmasked tertiary amino group was coordinated to boron, was isolated by column chromatography on silica gel in 91% yield (eq 1). In this product, the ammonium proton on nitrogen had migrated onto the *sp* carbon β to boron, whereas the phenyl group on boron migrated to the α *sp* carbon. The hydrogen atom and phenyl group were incorporated across the carbon−carbon double bond in a cis fashion to give the (*E*)-isomer,

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[1] Reviews: (a) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574. (b) Yamaguchi, S.; Wakamiya, A. *Pure Appl. Chem.* **2006**, *78*, 1413. (c) Jäkle, F. *Coord. Chem. Rev.* **2006**, *250*, 1107.

[2] (a) Wakamiya, A.; Taniguchi, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170. (b) Yoshino, J.; Kano, N.; Kawashima, T. *Chem. Commun.* **2007**, 559. (c) Jaska, C. A.; Piers, W. E.; McDonald, R.; Parvez, M. *J. Org. Chem.* **2007**, *72*, 5234.

[3] Ishida, N.; Miura, T.; Murakami, M. *Chem. Commun.* **2007**, 4381. For related migration reactions of alkynyltriorganylborates, see references therein.

[4] The alkynylborate **1a** was prepared in 83% yield by the reaction of the corresponding lithium acetylide with triphenylborane-pyridine complex followed by treatment with pyridinium chloride.

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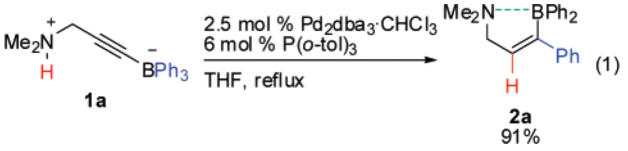
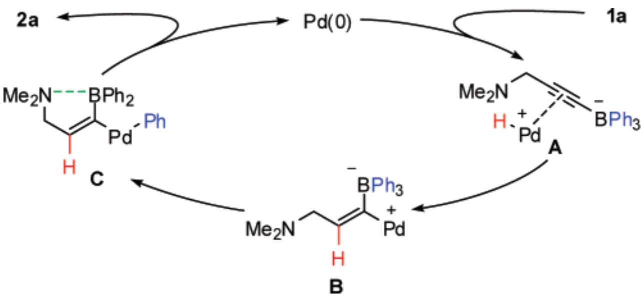
which was the only stereoisomer detected in the ^{1}H NMR spectrum of the reaction mixture. Of note is that the observed stereochemistry in which hydrogen and boron are vicinally attached across a carbon−carbon double bond in a trans fashion is difficult to access by conventional hydroboration reactions of alkynes. In the absence of a palladium catalyst, **1a** remained unchanged in refluxing THF. On the other hand, a complex mixture resulted when **1a** was treated with Brønsted acids such as acetic acid or methanesulfonic acid.[5]

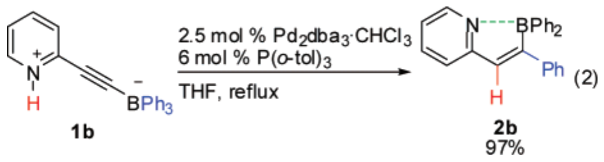


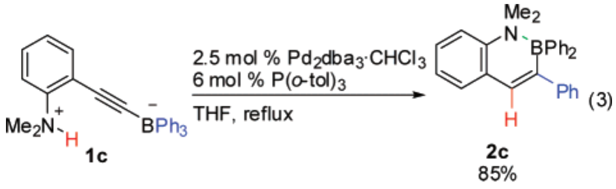
A possible mechanism is depicted in Scheme 1. Transfer of the proton from the tertiary ammonium moiety to palladium(0) takes place initially giving cationic palladium species **A**. Then, regioselective *cis*-hydropalladation across the carbon−carbon triple bond takes place,[6] affording the zwitterionic intermediate **B**. One of the phenyl groups migrates from boron to palladium, furnishing the triorganylborane, which spontaneously forms a complex with the unmasked tertiary amino group to give diorganopalladium species **C**. Finally, the cyclic amine−borane adduct **2a** is released through reductive elimination with the regeneration of palladium(0).[7]

Scheme 1. Possible Mechanism

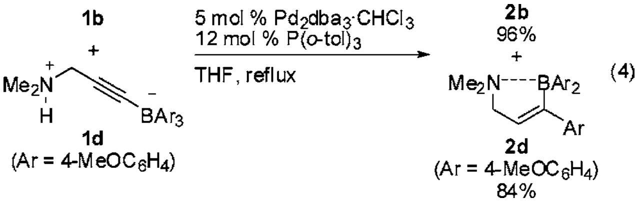


Substrate **1b** having a pyridinium group and **1c** having an anilinium group underwent analogous reactions. Six-membered ring aniline−borane complex **2c** as well as five-membered ring pyridine−borane complex **2b** were produced in good to excellent yields (eqs 2 and 3). Interestingly, the pyridine-borane complex **2b** exhibited strong fluorescence (vide infra).



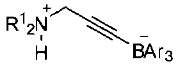
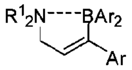
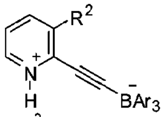
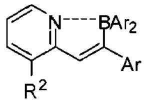
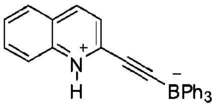
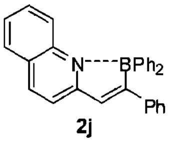


A crossover experiment was carried out as shown in eq 4, and proved that the aryl migration occurs intramolecularly, as with the previous case.[3] A mixture of **1b** and **1d** was treated with the palladium catalyst, resulting in the formation of a mixture of **2b** (96% yield) and **2d** (84% yield). No crossover products were observed by ^{1}H NMR analysis of the reaction mixture.



The reactions of structurally modified substrates are summarized in Table 1. Both electron-donating and -with-

Table 1. Reactions of Various Ammonioalkynyltriarylborates[a]

entry	alkynylborate **1**	product **2**	yield / %[b]
1[c]	 **1e** R^1 = Me, Ar = 4-FC$_6$H$_4$	 **2e**	67
2	**1f** R^1 = Bn, Ar = Ph	**2f**	89
3[d]	 **1g** R^2 = Me, Ar = Ph	 **2g**	92
4	**1h** R^2 = H, Ar = 2-Np	**2h**	98
5	**1i** R^2 = H, Ar = 4-ClC$_6$H$_4$	**2i**	96
6	 **1j**	 **2j**	96

[a] Reaction conditions: 2.5 mol % Pd$_2$dba$_3$·CHCl$_3$, 6 mol % P(*o*-tol)$_3$, THF, reflux, 1 h. [b] Isolated yield. [c] Conducted in refluxing cyclopentyl methyl ether. [d] Conducted in dichloroethane at 70 °C.

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(5) (a) Miyaura, N.; Yoshinari, T.; Itoh, M.; Suzuki, A. *Tetrahedron Lett.* **1974**, *15*, 2961. (b) Pelter, A.; Harrison, C. R.; Subrahmanyam, C.; Kirkpatrick, D. *J. Chem. Soc., Perkin Trans. I* **1976**, 2435.

(6) For previous examples of generation of palladium(II) hydride species by protonation of Pd(0) and a subsequent hydropalladation process, see: (a) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828. (b) Grushin, V. V. *Chem. Rev.* **1996**, *96*, 2011. (c) Zargarian, D.; Alper, H. *Organometallics* **1993**, *12*, 712. (d) Tani, K.; Ono, N.; Okamoto, S.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1993**, 386. (e) Trost, B. M.; Braslau, R. *Tetrahedron Lett.* **1989**, *30*, 4657.

(7) For examples of simple hydroarylation reactions catalyzed by palladium, see: (a) Trost, B. M.; Toste, F. D.; Greenman, K. *J. Am. Chem. Soc.* **2003**, *125*, 4518. (b) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992.

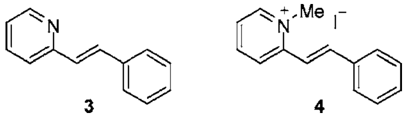
drawing groups were tolerated as the aryl substituents (entry 1 and eq 4). Chloro substituents remained intact under the reaction conditions (entry 5). A reaction of 2-quinolinium derivative **1j**, whose nitrogen atom was more sterically hindered than **1b**, gave a 96% yield of quinoline-borane complex **2j** (entry 6).

The photophysical properties of compounds **2b**, **2h**, and **2j** are summarized in Table 2. The absorption wavelength of **2b** (λ_{abs} = 356 nm in MeOH) was apparently elongated in comparison with those of non-borylated counterparts such as (*E*)-2-styrylpyridine **3** (λ_{abs} = 309 nm) and (*E*)-*N*-methyl-2-styrylpyridinium iodide **4** (λ_{abs} = 340 nm, Figure 1),[8] probably due to the planar structure enforced by the B−N coordination.[2a] In addition, **2b** exhibited strong purple fluorescence in CH_2Cl_2 solution (λ_{em} = 422 nm, Φ_F = 0.44). The extension of π-conjugation from **2b** to the naphthyl analogue **2h** caused a red shift of the emission maxima by 9 nm, whereas π-extension to the quinoline derivative **2j** shifted emission maxima by as much as 51 nm. Thus, it seems possible to tune the emission color by simple structural modifications.

Table 2. Photophysical Properties of Pyridine−Boranes **2**

	UV−vis absorption[a]		fluorescence[a,b]	
pyridine−borane **2**	λ_{abs} / nm	log ϵ	λ_{em} / nm	Φ_F
2b	359 (356)[c]	4.17	422	0.44
2h	372	4.12	431	0.32
2j	395	4.35	473	0.26

[a] Measured in CH_2Cl_2. [b] Determined with reference to 2-aminopyridine in 0.1 N H_2SO_4 and aqueous tryptophan solution (pH = 7.2). Excited at 280 nm. [c] Measured in MeOH.

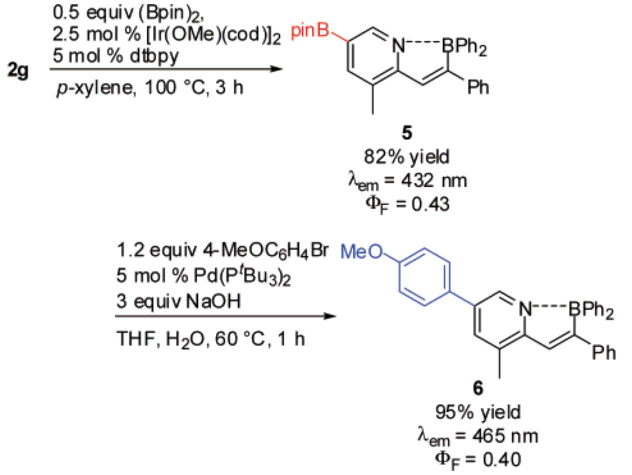


3 **4**

Figure 1. Nonborylated counterparts.

Finally, we examined further functionalization of the produced amine−borane complex. When the pyridine−borane complex **2g** (Scheme 2) was subjected to the Ir-catalyzed C−H borylation reaction,[9] the 5-position of the pyridine ring, which is probably most sterically accessible, was selectively borylated to give boronic ester **5** in 82% yield. A subsequent cross-coupling reaction of **5** with 4-bromoanisole proceeded regioselectively on the pyridine ring to afford biaryl **6** in 95% yield with the other B−C bonds remaining unreacted by virtue of the nitrogen coordination. The resulting pyridine−borane **6** showed sky-blue fluorescence with a maximum wavelength of 465 nm (Φ_F = 0.40).

Scheme 2. Functionalization of **2g**



In summary, we have developed a palladium-catalyzed rearrangement reaction of ammonioalkynyltriarylborates. Hydrogen and boron were stereoselectively installed across the resulting carbon−carbon double bond in a trans fashion to give intramolecular amine−borane complexes, some of which exhibited significantly strong fluorescence. Further investigations on the photophysical properties of these compounds are in progress.

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Supporting Information Available: Experimental details and selected spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] These values were determined in MeOH solutions. Williams, J. L. R.; Webster, S. K.; Van Allan, J. A. *J. Org. Chem.* **1961**, *26*, 4893.

[9] Pyridine ring was preferentially borylated over phenyl C−H bonds. (a) Takagi, J.; Sato, K.; Hartwig, J. F.; Ishiyama, T.; Miyaura, N. *Tetrahedron Lett.* **2002**, *43*, 5649. (b) Mkhalid, I. A. I.; Coventry, D. N.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Perutz, R. N.; Marder, T. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 489.