

Direct 1,2-Carboboration

Mechanistic Study of Highly Efficient Direct 1,2-Carboboration of Alkynes with 9-Borafluorenes

Yoshiaki Shoji,^[a] Naoki Shigeno,^[a] Kumiko Takenouchi,^[a] Manabu Sugimoto,^[b] and Takanori Fukushima^{*[a]}

Abstract: We recently reported a new one-pot transformation of alkynes into 9,10-diarylphenanthrene derivatives, which proceeds through efficient catalyst-free 1,2-carboboration of alkynes with 9-chloro-9-borafluorene (1_{cl}) , which yields a chlorodibenzoborepin, followed by oxidative deborylation/C–C coupling of the resultant chlorodibenzoborepin. Herein, based on new experimental observations for the catalyst-free 1,2-carboboration by using diphenylacetylenes and 1_{Br} or 1_{OTF} as well as results from theoretical investigations, we show how the substituent on the boron atom of 9-borafluorene affects the reactivity toward alkynes. Kinetic studies indicated that the 1,2-carboboration of diphenylacetylene with the borafluorenes can be described as a second-order reaction. The reaction rates became larger with the increase

in the acceptor numbers of the borafluorenes $(1_{Br} > 1_{OTF} > 1_{CI})$, which was evaluated by the Gutmann–Beckett method based on a Lewis acid/base complexation in solution. Interestingly, thermodynamic parameters obtained experimentally indicated that the term of activation entropy, rather than the term of activation enthalpy, largely contributes to the reaction rate. This experimental result was also supported by DFT calculations. Overall, among the borafluorenes examined, 1_{Br} exhibited the highest reactivity toward a wide variety of substituted diarylacetylenes. Similar to the case of chlorodibenzoborepin, when the dibenzoborepin obtained from 1_{Br} or 1_{OTF} was oxidized by using FeCl₃, an efficient deborylation/C–C coupling took place to give the corresponding 9,10-diarylphenanthrene derivatives in high yields.

Introduction

The insertion reactions of unsaturated and/or polarized substrates into a B–C bond of organoboranes have attracted considerable attention for organic transformation.^[1–8] Among them, the carboboration of alkynes with organoboron compounds, which is accompanied by the simultaneous formation of C–C and C–B bonds, represents a useful boron-mediated organic transformation, particularly for the regio- and stereoselective synthesis of substituted alkenes (Figure 1a).^[1,2] Although there are many examples of metal-catalyzed carboboration,^[2,3] catalyst-free direct carboboration has recently received growing attention because of their high cost efficiency and low environmental load.^[1a,4,5] However, as long as alkynes are not activated by, for example, heteroatom or transitionmetal substituents, catalyst-free alkyne carboboration can be achieved only when strongly electrophilic boranes such as

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1.2-Carboboration 1.1-Carboboration (b) One-electron Oxidant (1 equiv.) 9,10-Diarylphenanthrene Borepin 2 9-Chloro-9-borafluorene (2ci: R = H) FeCl₃ (1ci) (excess) Dibenzo[g,p]chrysene (c) CE

Figure 1. (a) Schematic representation of 1,2- or 1,1-carboboration of alkynes. (b) 1,2-Carboboration of alkynes with borafluorene (1_{cl}) that yields borepin **2** and subsequent oxidative deborylation/C–C coupling of the borepin product that leads to an extended π -conjugated system with a 9,10-diarylphenanthrene skeleton. (c) Chemical structures of three borafluorene derivatives with a Cl (1_{cl}), Br (1_{Br}), or OTf (1_{OTf}) group used in this study.

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1_{OTf}



(C₆F₅)₃B are employed.^[1,4] Furthermore, previously reported examples of catalyst-free alkyne carboboration are mostly 1,1type (Figure 1a),^[1,4] and 1,2-type carboboration has been known to occur in only limited cases, where specific boron species such as diarylchloroborane,^[5a] borenium ion $[R_2B^+(:L)]$,^[5b,c] and borinium ion $[R_2B^+]^{[5d]}$ were used. Pentaarylborole derivatives have also been reported to show a formal 1,2-carboboration reaction of alkynes without catalysis.^[9] This reaction proceeds through sequential steps involving the Diels-Alder reaction between alkyne and borole, a sigmatropic shift of the resulting boryl group, and electrocyclic ring-opening, eventually giving rise to a boron-containing unsaturated seven-membered ring compound, that is, a borepin.^[9] Although catalyst-free, direct 1,2-carboboration has rarely been explored to date, the development of readily available and efficient 1,2-carboboration reagents would substantially expand the synthetic utility for substituted alkenes and in turn the scope of boron-mediated organic transformations.

We recently reported that 9-chloro-9-borafluorene^[10] ($\mathbf{1}_{cl}$) causes direct 1,2-carboboration of various internal and terminal alkynes to give dibenzoborepin derivatives such as 2_{cl} (Figure 1 b).^[11] Notably, the resultant dibenzoborepin derivatives undergo deborylation/C-C coupling upon one-electron oxidation to transform into aromatic compounds efficiently (Figure 1 b).^[11] The sequential 1,2-carboboration and oxidative deborylation/C-C coupling reactions can be performed in a onepot fashion, thus enabling facile synthesis of a wide variety of extended π -conjugated systems with 9,10-diarylphenanthrene and/or dibenzo[g,p]chrysene skeletons (Figure 1b). The finding of this new direct 1,2-carboboration that proceeds between alkynes and the simple aromatic borane prompted us to further investigate how the Lewis acidity of the borane compound affects the reaction efficiency. Here, we report mechanistic aspects of the direct alkyne 1,2-carboboration through kinetic and theoretical studies on the reactions between diarylacetylenes and three borafluorene derivatives with a Cl, Br, or trifluoromethane sulfonyloxy (OTf) group on the boron atom (1_{cl}) $\mathbf{1}_{Brr}^{[12]}$ and $\mathbf{1}_{OTfr}^{[13]}$ Figure 1 c).

Results and Discussion

We prepared $\mathbf{1}_{Br}$ from 9,9-dimethyl-9-stannafluorene and BBr₃ in 78% yield, according to the procedure reported previously.^[12a,b] Compound $\mathbf{1}_{OTF}$ was obtained as yellow needle crystals in 74% yield by the treatment of $\mathbf{1}_{CI}$ with Me₃SiOTf (5 equiv) in CH₂Cl₂ at 25 °C.^[14] Attempts for elemental analysis of this crystalline product have not been successful because of the highly hygroscopic nature of $\mathbf{1}_{OTF}$. Instead, we confirmed the purity of the product (>97%) by quantitative ¹H NMR analysis in CDCl₃ at 25 °C by using hexamethylbenzene as an internal standard (Figures S14–S16 in the Supporting Information).^[14]

To evaluate the electronic structures of 1_{CI} , 1_{Br} and 1_{OTF} (in vacuum), density functional theory (DFT) calculations were carried out by using the ω B97X-D/[SDD for Cl, Br, and S, 6-31G(d,p) for C, B, O, F, and H] level (Tables S4–S6 in the Supporting Information).^[14] In the optimized geometries of 1_{CI} , 1_{Br} and 1_{OTF} , the highest occupied molecular orbitals (HOMOs) are





Figure 2. Selected molecular orbitals and energies of (a) $1_{CI'}$ (b) $1_{BI'}$ and (c) $1_{\sigma rf}$ in the optimized geometries at the ω B97X-D/[SDD for Cl, Br, and S, 6-31G(d,p) for C, B, O, F, and H] level.

solely located on the phenylene rings (Figure 2) and lie in almost identical energy levels (-8.04, -8.06, and -8.00 eV, respectively). The contributions of the vacant 2p orbitals of boron are reflected in the lowest unoccupied molecular orbitals (LUMOs; Figure 2). Based on the calculated LUMO levels of 1_{Cl} (-0.62 eV), 1_{Br} (-0.72 eV), and 1_{OTf} (-0.37 eV), 1_{Br} is expected to exhibit the highest electron-accepting properties. The calculated natural bond orbital (NBO) charges on the boron atoms of 1_{Cl} , 1_{Br} , and 1_{OTf} are +0.74, +0.64, and +1.05, indicating the higher polarized nature of 1_{OTF} compared with 1_{Cl} and 1_{Br} (Figures S3–S5 in the Supporting Information).

NMR spectroscopy provided insight into the Lewis acidity of the borafluorenes in solution. The ^{11}B NMR spectra of 1_{Clr} 1_{Brr} and $\mathbf{1}_{\text{OTf}}$ in CDCl3 at 25 $^\circ\text{C}$ showed a signal arising from the boron atom at δ = 63.6, 65.7, and 50.2 ppm, respectively (Figure S11 in the Supporting Information).^[14] This observation was consistent with the order of the electron-accepting ability $(1_{Br} > 1_{Cl} > 1_{OTf})$ expected from the calculated LUMO energies. To further evaluate Lewis acidity of the borafluorenes by using the Gutmann-Beckett method,^[15] we measured changes in the ³¹P NMR chemical shift of triethylphosphine oxide (Et₃PO) upon addition of the borafluorene. Although the ³¹P NMR signal of Et₃PO alone was observed at $\delta = 55.2$ ppm in CDCl₃ at 25 °C, it appeared at δ = 81.5, 83.2, or 82.3 ppm in the presence of five equivalents of 1_{Cl}, 1_{Br}, or 1_{OTf}, respectively, owing to the formation of the corresponding borafluorene-Et₃PO adduct (Table 1 and Figure S12 in the Supporting Information). The values of acceptor number (AN), defined as $AN = (\delta_{31P} - 41.0) \times [100/$ (86.14-41.0)],^[15] were determined to be 89.7, 93.5, and 91.5 for $\mathbf{1}_{Cl'} \ \mathbf{1}_{Br'}$ and $\mathbf{1}_{OTf'}$ respectively. Based on this criterion relying on Lewis acid-base complexation in solution, $\mathbf{1}_{Br}$ is considered to be the strongest Lewis acid among the three borafluorenes. The Gutmann-Beckett analysis also showed that 1_{otf} is a stronger Lewis acid than $\mathbf{1}_{Cl'}$ whereas the theoretical calculation suggested that 1_{OTF} (LUMO level: -0.37 eV) has a lower electron-accepting ability than 1_{cl} (LUMO level: -0.62 eV).

Similar to the case of $1_{CI}^{[11]}$ when diphenylacetylene was reacted with 1_{Br} or 1_{OTf} at 80 °C in 1,2-dichloroethane (1,2-DCE),

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$\label{eq:table1} \begin{array}{l} \textbf{Table 1. Experimentally and theoretically evaluated electronic properties} \\ \text{of the borafluorenes (1}_{Cl'} \ 1_{Br'} \ \text{and} \ 1_{OTf} \text{)}. \end{array}$						
	LUMO level [eV] ^[a]	NBO charge of boron ^[a]	¹¹ B NMR [ppm] ^[b]	³¹ P NMR [ppm] ^[c]	AN ^[d]	
1 _{cl}	-0.62	+0.74	63.6	81.5	89.7	
1 _{Br}	-0.72	+0.64	65.7	83.2	93.5	
1 _{otf}	-0.37	+ 1.05	50.2	82.3	91.5	
C D				0 5 1 11		

[a] ω B97X-D/[SDD for Cl, Br, and S, 6-31G(d,p) for C, B, O, F, and H] level. [b] In CDCl₃ at 25 °C. [c] The ³¹P NMR chemical shift of Et₃PO (0.1 M) in the presence of 5 equivalents of the borafluorene in CDCl₃ at 25 °C. [d] Acceptor number (AN) is defined as AN = ($\delta_{_{31P}}$ -41.0)×[100/(86.14-41.0)].^[15]

direct 1,2-carboboration took place to give the corresponding borepin $(\mathbf{2}_{Br} \text{ or } \mathbf{2}_{OTf})$ quantitatively. The borepin products were unambiguously characterized by ¹H, ¹¹B, ¹³C, and ¹⁹F NMR spectroscopy, IR spectroscopy, and X-ray crystallography (Figures S1, S2, and S17–S23 in the Supporting Information).^[14] To evaluate the rate constant (k) of the 1,2-carboboration, a $CDCl_3$ solution containing an equimolar amount of diphenylacetylene and the borafluorene $(1_{CI}, 1_{Br'} \text{ or } 1_{OTf})$, together with an internal standard (hexamethylbenzene), was prepared in a sealed NMR tube (initial concentrations: $[1_{CI}] = 0.3 \text{ M}$, $[1_{Br}] = 0.1 \text{ M}$, and $[1_{OTf}] = 0.3 \text{ M}$). The reaction was monitored by ¹H NMR spectroscopy at a given temperature (Tables S1-S3 in the Supporting Information). In every case, the signals resulting from the corresponding borepin product $(\mathbf{2}_{CI}, \mathbf{2}_{Br'} \text{ or } \mathbf{2}_{OTf})$ monotonically increased with the decrease in those resulting from diphenylacetylene and the borafluorene, and no other detectable product was observed (Figure S13 in the Supporting Information). The 1,2-carboboration was characterized as a second-order reaction (Figure 3), and the obtained k values at 50–80 $^{\circ}$ C for 1_{cl} and at 30-60 °C for 1_{Br} and 1_{otf} are summarized in Table 2. Notably, the rate constant at 50 $^\circ C$ for the reaction with $\mathbf{1}_{Br}$ or $\mathbf{1}_{OTf}$ was approximately 20 or 6 times greater than that for the reaction with $\mathbf{1}_{cl}$ (Table 2). The k values increased $(\mathbf{1}_{Br} > \mathbf{1}_{OTf} > \mathbf{1}_{cl})$ with the increase in the AN of the borafluorenes (Table 1).

As shown in Figure 4a, the plot of $\ln k$ versus 1/T [K⁻¹] for each 1,2-carboboration showed a linear relationship, from which the values of activation energy (E_a) and frequency factor (A) were obtained (Table 3). In E_{a} , only small differences (<1 kcalmol⁻¹) were seen among the reactions with $\mathbf{1}_{Cl'}$, $\mathbf{1}_{Br'}$ and $\mathbf{1}_{\text{OTf.}}$. However, there were significant differences in A, and the reaction with $\mathbf{1}_{Br}$ showed the highest A value (2.19× $10^6 \,\mathrm{m^{-1} \, s^{-1}}$), which may account for the greatest k value for $\mathbf{1}_{Br}$ Note that the magnitude of the A values correlates with that of the AN of the borafluorenes (Table 1). From the plot of $\ln(k/$ T) versus T^{-1} [K⁻¹] (Figure 4b), we also determined the thermodynamic parameters (ΔG^{*} , ΔH^{*} , and ΔS^{*}) for the 1,2-carboboration (Table 3).^[16] Clearly, the entropy term largely affects the reaction rates, rather than the enthalpy term. A notable difference can be seen for the 1,2-carboboration reactions with 1_{cl} and $\mathbf{1}_{\mathbf{Br}}$ which provide ΔS^{\pm} values of -39.1 ± 2.4 and $-31.6 \pm$ 3.3 cal K⁻¹ mol⁻¹, respectively. As the $T\Delta S^{+}$ value for $\mathbf{1}_{Br}$ (e.g., at $50 \degree C$, $-10.2 \pm 1.0 \text{ kcal mol}^{-1}$) is negatively much smaller than that for $\mathbf{1}_{Cl}$ (-12.6 \pm 0.8 kcal mol⁻¹), the difference in the en-



Figure 3. Plot of 1/[borafluorene] $[M^{-1}]$ versus reaction time *t* [s] for the reaction of an equimolar mixture of diphenylacetylene and (a) $\mathbf{1}_{cl'}$ (b) $\mathbf{1}_{Br'}$ or (c) $\mathbf{1}_{OTf}$ in CDCl₃. Initial concentration: $[\mathbf{1}_{cl}] = [\mathbf{1}_{OTf}] = 0.3 \text{ M}$, $[\mathbf{1}_{Br}] = 0.1 \text{ M}$. See also Tables S1–S3 in the Supporting Information.

Table 2. Second-order rate constants (*k*) for the 1,2-carboboration between diphenylacetylene and the borafluorenes $(1_{Cl'}, 1_{Br'}, and 1_{OTf})$ in $CDCl_3$.^(a)



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Figure 4. (a) Arrhenius plot and (b) Eyring plot^[16] for the reaction of an equimolar mixture of diphenylacetylene and $1_{Cl'}$ $1_{Br'}$ or 1_{OTf} in CDCl₃. Initial concentration: $[1_{Cl}] = [1_{OTf}] = 0.3 \text{ M}$, and $[1_{Br}] = 0.1 \text{ M}$.

Table 3. Experimentally obtained thermodynamic parameters for the 1,2-carboboration between diphenylacetylene and the borafluorenes $(1_{Cl'}, 1_{Brr}$ or $1_{OTf})$ in CDCl ₃ .								
	E _a ^[a] [kcal mol ⁻¹]	ln A ^[a]	$\Delta H^{\pm[b]}$ [kcal mol $^{-1}$]	$\Delta S^{\pm[b]}$ [cal K ⁻¹ mol ⁻¹]	$\Delta G^{+}_{323.15 \text{ K}}^{[b]}$ [kcal mol ⁻¹]			
1 _{сі} 1 _{вг} 1 _{отf}	$\begin{array}{c} 12.3 \pm 0.8 \\ 12.7 \pm 1.1 \\ 13.1 \pm 1.3 \end{array}$	$\begin{array}{c} 10.9 \pm 1.2 \\ 14.6 \pm 1.7 \\ 13.8 \pm 1.9 \end{array}$	$\begin{array}{c} 11.7 \pm 0.8 \\ 12.1 \pm 1.1 \\ 12.5 \pm 1.3 \end{array}$	$-39.1 \pm 2.4 \\ -31.6 \pm 3.3 \\ -33.2 \pm 4.0$	$\begin{array}{c} 24.9 \pm 1.8 \\ 22.3 \pm 2.1 \\ 23.2 \pm 2.6 \end{array}$			
[a] Obtained from the Arrhenius plot by using k values in Table 2. [b] Obtained from the Eyring plot ^[16] by using k values in Table 2.								

thalpy terms between 1_{Br} and 1_{CI} is compensated, resulting in a positively smaller ΔG^{\dagger} value for 1_{Br} than 1_{CI} .

For further understanding of the direct 1,2-carboborations, we performed DFT calculations on the 1,2-carboboration of diphenylacetylene with $\mathbf{1}_{cl}$ or $\mathbf{1}_{Br}$ in vacuum at the $\omega b97X\text{-}D/$ [SDD for Cl and Br, 6-31G(d,p) for C, B, and H] level (Figure 5 and Tables S4–S13 in the Supporting Information).^[14] These two reactions not only showed the maximum and minimum rate constants but also allowed us to unequivocally determine the computational geometry in each reaction step. Gibbs free energy was calculated by taking into account the zero-point energy and intramolecular entropy term at 298.15 K. As illustrated in Figure 5a, the borafluorene and diphenylacetylene (reactants; RTs) molecules approach each other to form a complex (CP), which is transformed into a borepin product (2) through the formation of a transition state (TS) with a B-C_{ipso}-Calkyne-Calkyne quasi-four-membered ring structure. In CP_{CI}, distances between the boron and the two alkyne carbon atoms are nearly the same (3.308 and 3.338 Å, Figures 5 and S7 in the Supporting Information), and the two B-Cipso bond lengths in



Figure 5. (a) Schematic illustration and (b) energy diagrams of the 1,2-carboboration reactions of diphenylacetylene with 1_{c1} (black) and 1_{Br} (red) to form borepin 2, calculated at the ω B97X-D/[SDD for Cl and Br, 6-31G(d,p) for C, B, and H] level. BSSE correction was applied to the energies of CP_{Cl} and CP_{Br}.

the borafluorene moiety (1.553 Å) scarcely change from those in the RTs (Figure S3 in the Supporting Information). In TS_{CI}, a B–C bond is newly formed between the boron atom and one of the two alkyne carbons (B–C_{alkyne}: 1.651 Å), which is accompanied by the elongation of the C_{alkyne} bond by 0.062 Å and one of the B–C_{ipso} bonds of the borafluorene moiety by approximately 0.1 Å compared with those in CP_{CI} (Figures S7 and S8 in the Supporting Information). Accordingly, C_{ipso} of borafluorene and C_{alkyne} that is non-bonded to boron become close to each other (interatomic distance: 2.155 Å, Figure S8 in the Supporting Information), leading to an alkyne insertion to the B–C_{ipso} bond to form a borepin structure (**2**). Molecular geometries of CP_{Br} and TS_{Br} are virtually identical to CP_{CI} and TS_{CI}, respectively, with the exception of the boron–halogen bonds (Figures S9 and S10 in the Supporting Information).

When looking at the total free energies of each reaction step, the formations of CP_{CI} and CP_{Br} are slightly endothermic $(\Delta G = +2.9 \text{ and } +4.6 \text{ kcal mol}^{-1}, \text{ respectively; Figure 5 b)}$. The ΔG^{\dagger} value for the 1,2-carboboration to form **2**_{cl} was calculated to be + 17.2 kcal mol⁻¹, which was greater than that for the reaction to form $\mathbf{2}_{Br}$ (+ 11.9 kcal mol⁻¹). This trend is consistent with that of ΔG^{\dagger} obtained experimentally (Table 3). The ΔS^{\dagger} values were also calculated based on translational, rotational, and vibrational modes for the computed geometries (Table S14 in the Supporting Information), where the calculated $T\Delta S^{\dagger}$ value at 298.15 K for 1_{Cl} was negative (-3.0 kcal mol⁻¹), whereas that for $\mathbf{1}_{Br}$ is positive (+0.8 kcal mol⁻¹). Although the difference in the ΔS^{\pm} values (3.8 kcal mol⁻¹) between the reactions with 1_{cl} and 1_{Br} seems not so large at this calculation level, the computational results may support the experimental observation that the 1,2-carboboration with $\mathbf{1}_{Br}$ is more entropically favored than that with 1_{CI} .

We compared the reaction efficiency of 1,2-carboborations of several diarylacetylenes using borafluorenes 1_{Cl} , 1_{Br} and 1_{OTf} (Table 4) under identical conditions. When 1_{Br} or 1_{OTf} (0.25 M)

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was reacted with diphenylacetylene (1.0 equiv) in 1,2-DCE at 25 °C for 6 h, 1,2-carboboration proceeded quite efficiently to give the corresponding borepin, whereas the reaction with 1_{CI} was sluggish at 25 °C (entry 1). Similarly, 1_{Br} and 1_{OTF} also served as a very efficient reagent for a diarylacetylene with electron-donating *p*-methyl (entry 2) or *p*-methoxy groups (entry 3), as well as a diarylacetylene with electron-withdrawing *p*-Br (entry 4), *p*-CF₃ (entry 5), or *p*-methoxycarbonyl groups (entry 6). All the reactions with 1_{Br} smoothly proceeded at 25 °C, except for entry 6, which required a higher temperature (80 °C). Although 1_{OTF} afforded excellent-to-moderate results, it was inferior to 1_{Br} in functional-group tolerance, given the fact that the reaction between 1_{OTF} and a *p*-Br- or *p*-CF₃-substituted diarylacetylene resulted in the formation of a complex mixture (entries 5 and 6).

Finally, we confirmed that borepin derivatives 2_{Br} and 2_{oTf} successfully undergo deborylation/C–C coupling upon oneelectron oxidation to form 9,10-diarylphenanthrene derivatives. For example, when 2_{Br} or 2_{OTf} was oxidized with FeCl₃ (1 equiv) in a mixture of 1,2-DCE and MeNO₂ at 25 °C, 9,10-diphenylphenanthrene was obtained quantitatively (Figure 6a). Oxidation of substituted borepin derivatives obtained from 1_{Br} (Table 4) by using FeCl₃ (1 equiv) also afforded the corresponding 9,10diarylphenanthrene in good yields, comparable to the case of the oxidation of borepins obtained from 1_{CL} .^[11] The 1,2-carboboration of *p*-bis(phenylethynyl)benzene with two equivalents of 1_{Br} in 1,2-DCE at 25 °C completed within 24 h, and the sub-



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Figure 6. (a) Oxidative deborylation/C–C coupling of 2_{Br} and 2_{oTF} (b) Sequential 1,2-carboboration and oxidative deborylation/C–C coupling reactions of *p*-bis(phenylethynyl)benzene with 1_{Br} or $1_{Cl}^{(11a)}$ to give phenylene-bridged phenanthrene dimer **3**.

sequent treatment of the reaction mixture with FeCl₃ (2 equiv) led to the formation of a phenylene-bridged phenanthrene dimer in 81% yield (over two steps in a one-pot manner, Figure 6b). In contrast, as previously reported, a higher reaction temperature (e.g., 80 °C) is required for completing the 1,2-carboboration between *p*-bis(phenylethynyl)benzene and 1_{cl} within 24 h under otherwise identical conditions (Figure 6b).^[11a]

Conclusion

(a)

(b)

We have described the catalyst-free 1,2-carboboration of diarylacetylenes by using three 9-borafluorene derivatives 1_{Cl} , 1_{Br} and $\mathbf{1}_{\text{OTf}}$. In the present system, alkyne insertion into the boron-halogen bonds has not been observed, despite the fact that 1,2-haloboration is more common than 1,2-carboboration in related systems.^[5a] The experimental and computational results revealed the kinetic and thermodynamic aspects of this rare class of direct 1,2-carboboration. The order of reaction efficiency (i.e., reaction rate) of the 1,2-carboboration $(\mathbf{1}_{Br} > \mathbf{1}_{OTf} >$ 1_{cl}) was not consistent with those expected from the energy level of LUMOs and the NBO charges of boron but correlated with the acceptor number (AN) of the borafluorenes (1_{Br}) $\mathbf{1}_{OTF} > \mathbf{1}_{CI}$). AN, a reliable indicator to evaluate Lewis acidity in solution, should reflect the balance between the steric factor and electronic structure of the borafluorenes and may also be related to the frequency factor for the coordination of the boron functionality to the alkyne triple bond. Importantly, the kinetic analysis and DFT calculations strongly suggested that the entropy term is more important than the enthalpy term in determining the reaction rate. Overall, 1_{Br} causes the most efficient 1,2-carboboration to give borepin derivatives in excellent yields even under very mild conditions. The fact that borepins 2_{Br} and 2_{OTfr} similar to borepin 2_{Cl} , underwent deborylation/ C-C coupling upon one-electron oxidation to form 9,10-diary-Iphenanthrene derivatives, demonstrates the synthetic utility

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of the borafluorene-mediated benzannulation reaction and should eventually accelerate the development of extended π -conjugated systems featuring 9,10-diarylphenanthrene and/or dibenzo[*g*,*p*]chrysene skeletons.

Experimental Section

Materials

Handling of air- and/or moisture-sensitive compounds was performed in a glovebox under argon. *n*-Hexane was dried by passage through an activated alumina column and a Q-5 column (Nikko Hansen & Co., Ltd.). 1,2-Dichloroethane (1,2-DCE), CDCl₃, and MeNO₂ were dried over CaH₂ and freshly distilled prior to use. 9-Chloro-9-borafluorene (1_{cl}),^[10] 9-bromo-9-borafluorene (1_{Br}),^[12] bis(4-methoxyphenyl)acetylene,^[17] bis(4-methoxyphenyl)acetylene,^[17] bis(4-trifluoromethylphenyl)acetylene,^[17] and bis(4-methyoxycarbonylphenyl)acetylene^[17] were prepared according to previously reported procedures.

Methods

Melting points (m.p.) and decomposition points (d.p.) were recorded with a Yanaco model MP-500D melting-point apparatus. Fourier transform infrared (FTIR) spectra were recorded at 25 °C with a JASCO model FT/IR-4100 Fourier transform infrared spectrometer with an attenuated total reflection (ATR) equipment (ATR PRO450-S). Nuclear magnetic resonance (NMR) spectroscopy measurements were carried out with a Bruker model AVANCE-400 spectrometer (400.0 MHz for ¹H, 128.3 MHz for ¹¹B, 100.6 MHz for ¹³C, 376.4 MHz for ¹⁹F, 162 MHz for ³¹P), where chemical shifts (δ) were determined with respect to residual solvent peaks for ¹H (residual non-deuterated solvent in CDCl₃: ${}^{1}H(\delta) = 7.26 \text{ ppm}$), external BF₃OEt₂ in CDCl₃ for ¹¹B (¹¹B(δ) = 0.0 ppm), residual solvent peaks for ¹³C (CDCl₃: 13 C(δ) = 78.0 ppm), external CF₃CO₂H in CDCI₃ for 19 F (19 F(δ) = -76.6 ppm), and external H_3PO_4 in D_2O for ³¹P (³¹P(δ)=0.0 ppm). The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), multiplet (m), and broad (br). Mass spectrometry measurements were carried out with a Bruker micrOTOF II mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) probe.

Synthesis of borafluorene 1_{OTf}

Under argon at 25 °C, trimethylsilyl trifluoromethanesulfonate (16.7 g, 75.1 mmol) was added to a dry 1,2-DCE solution (20 mL) of 1_{c1} (2.98 g, 15.0 mmol). The resulting mixture was stirred at 25 °C for 12 h and then evaporated to dryness under reduced pressure. The residue was recrystallized from dry hexane at -30 °C to give 1_{orff} as yellow needles (3.47 g, 11.1 mmol) in 74% yield. m.p. (in a sealed tube under argon): 91.2 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ =7.62 (d, *J*=7.3 Hz, 2H), 7.43–7.37 (m, 4H), 7.15 ppm (ddd, *J*=7.3, 7.9, 1.9 Hz, 2H); ¹¹B NMR (128 MHz, CDCl₃, 25 °C): δ =50.2 ppm; ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ =154.0, 136.1, 134.1, 132.3 (B-C_{ipso}), 128.9, 120.4, 118.6 ppm (CF₃, q, *J*_{CF}=317 Hz); ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): δ =-75.6 ppm. ¹H, ¹¹B, ¹³C, and ¹⁹F NMR spectra of 1_{orff} are shown in Figures S14, S11, S15, and S16 in the Supporting Information, respectively.

Synthesis of borepin 2_{Br}

Under argon at 25°C, diphenylacetylene (36.7 mg, 206 µmol) was added to a dry 1,2-DCE solution (1.0 mL) of 1_{Br} (50 mg, 206 μ mol). The reaction mixture was stirred at 80 °C for 12 h and then evaporated to dryness under reduced pressure. The residue was recrystallized from dry hexane at -30 °C to give $\mathbf{2}_{Br}$ as pale-yellow crystals (65.9 mg, 156 µmol) in 76% yield. d.p.: 135.2 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.93 (d, J = 7.6 Hz, 1 H), 7.88 (d, J = 7.6 Hz, 1 H), 7.73–7.69 (m, 2 H), 7.52 (t, J=7.5 Hz, 1 H), 7.39 (m, 1 H), 7.25-7.20 (m, 2H), 7.13-7.05 (m, 8H), 6.99-6.92 ppm (m, 2H); ^{11}B NMR (128 MHz, CDCl₃, 25 °C): $\delta\!=\!65.0$ ppm; ^{13}C NMR (100 MHz, $CDCl_{3}$, 25 °C): $\delta = 150.6$, 143.1, 142.9, 140.0, 139.2, 138.2, 132.3, 132.1, 132.0 (two peaks), 130.6, 130.4, 129.2, 127.6, 127.5 (two peaks), 127.2, 126.8, 126.6, 126.0 ppm; FTIR (ATR): v=3087, 2921, 2852, 1577, 1466, 1437, 1366, 1296, 1275, 1250, 1209, 1168, 1127, 1075, 1028, 929, 908, 872, 764, 751, 735, 703, 691, 660, 629, 611, 590, 569, 555, 526, 510 cm⁻¹. ¹H, ¹¹B, and ¹³C NMR spectra of $\mathbf{2}_{Br}$ are shown in Figures S17, S18, and S19 in the Supporting Information, respectively.

Synthesis of Borepin 2_{otf}

Under argon at 25 °C, diphenylacetylene (57.1 mg, 320 µmol) was added to a dry 1,2-DCE solution (1.3 mL) of 1_{oTf} (100 mg, 320 $\mu mol).$ The reaction mixture was stirred at 80 $^\circ C$ for 12 h and then evaporated to dryness under reduced pressure. The residue was recrystallized from dry hexane at $-30\,^\circ\text{C}$ to give $\mathbf{2}_{\text{OTF}}$ as paleyellow crystals (115.3 mg, 235 μ mol) in 73% yield. d.p.: 135.2 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta = 7.96$ (d, J = 7.8 Hz, 1 H), 7.89 (d, J=7.6 Hz, 1 H), 7.83-7.74 (m, 2 H), 7.55 (t, J=7.6 Hz, 1 H), 7.44 (m, 1 H), 7.31-7.20 (m, 2 H), 7.18-7.06 (m, 6 H), 6.99-6.85 ppm (m, 4 H); ^{11}B NMR (128 MHz, CDCl₃, 25 °C): $\delta\!=\!48.0$ ppm; ^{13}C NMR (100 MHz, $CDCI_3$, 25 °C): $\delta = 155.6$, 145.2, 142.4, 139.0, 137.8, 132.9, 132.3, 132.2, 130.4, 130.2 (two peaks), 129.7, 128.0 (two peaks), 127.6, 127.3, 127.1, 127.0, 126.5, 118.4 ppm (CF₃, q, J_{CF}=316 Hz); ¹⁹F NMR (376 MHz, CDCl₃, 25 °C): $\delta = -76.3$ ppm; FTIR (ATR): $\tilde{v} = 2952$, 2923, 2855, 1592, 1486, 1433, 1409, 1323, 1208, 1186, 1141, 1103, 1073, 1053, 1032, 1015, 930, 911, 878, 796, 768, 741, 728, 698, 672, 650, 615 cm⁻¹. ¹H, ¹¹B, ¹³C, and ¹⁹F NMR spectra of 2_{otf} are shown in Figures S20, S21, S22, and S23 in the Supporting Information, respectively.

Synthesis of 9,10-diphenylphenanthrene by the oxidation of 2_{Br} with FeCl₃

Under argon at 25°C, a dry MeNO₂ solution (2.0 mL) of FeCl₃ (81 mg, 0.50 mmol) was added to a dry 1,2-DCE solution (2.0 mL) of 2_{Br} (211 mg, 0.50 mmol). After stirring for 1 h at 25 °C, the resulting mixture was poured into MeOH (100 mL), diluted with water, and extracted with CH₂Cl₂. The organic layer was washed with water, dried over anhydrous Na2SO4, and evaporated to dryness under reduced pressure. The obtained residue was dissolved in CH₂Cl₂, and the solution was passed through a plug of Florisil, to allow isolation of 9,10-diphenylphenanthrene as colorless crystals (162 mg, 0.49 mmol) in 98% yield. m.p. (in a sealed tube under argon): 242 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.81$ (d, J = 8.2 Hz, 2 H), 7.67 (ddd, J=8.3, 7.7, 1.3 Hz, 2 H), 7.56 (dd, J=8.3, 1.2 Hz, 2 H), 7.48 (ddd, J=8.3, 7.7, 1.1 Hz, 2 H), 7.28-7.12 ppm (m, 10 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 139.7$, 137.3, 132.0, 131.1, 130.1, 128.0, 127.7, 126.8, 126.6, 126.5, 122.6 ppm; FTIR (ATR): v=3100, 3056, 3048, 3027, 1606, 1584, 1575, 1527, 1487, 1441, 1419, 1321, 1139, 1073, 1047, 1028, 999, 885, 760, 750, 727, 701, 630 $\mbox{cm}^{-1}.$ APCI-TOF MS: calcd for C₂₆H₁₈ [*M*]⁺: *m*/*z*=330.14; found: 330.14.

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Synthesis of 9,10-diphenylphenanthrene by the oxidation of 2_{OTf} with FeCl_3

Using a procedure similar to that for the oxidation of $\mathbf{2}_{Brr}$ 9,10-diphenylphenanthrene was obtained in 96% yield from $\mathbf{2}_{OTf}$ (245 mg, 0.50 mmol) and FeCl₃ (81 mg, 0.50 mmol).

Synthesis of 3 from 1_{Br}

A dry 1,2-DCE solution (1.5 mL) of a mixture of 1_{Br} (100 mg, 0.41 mmol) and 1,4-bis(phenylethynyl)benzene (57 mg, 0.21 mmol) was stirred for 24 h at 25 °C under argon. A dry MeNO₂ solution (1.0 mL) of FeCl₃ (67 mg, 0.41 mmol) was added to the reaction mixture. The resulting mixture was stirred for 1 h at 25 °C and poured into MeOH (80 mL), and the precipitate thus formed was collected by filtration. The residue was dissolved in CH₂Cl₂, and the solution was passed through a plug of Florisil, to allow isolation of 3 (95 mg, 163 µmol) as a colorless powder in 81% yield. d.p.: 371 °C; ¹H NMR (500 MHz, CDCl₃): δ = 8.83–8.80 (m, 4H), 7.70–7.57 (m, 7H), 7.53-7.46 (m, 4H), 7.35-7.29 (m, 4H), 7.24-7.20 (m, 5H), 7.09-7.07 (m, 3 H), 7.02-7.00 ppm (m, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ = 139.7, 137.7, 137.2, 131.3, 130.8, 130.4, 130.3, 130.0 (two peaks), 127.9, 127.8, 126.8, 127.6, 126.7, 126.6 (two peaks), 126.3 (two peaks), 122.5, 122.4 ppm; FTIR (KBr): $\tilde{v} = 3062$, 3024, 2880, 1609, 1588, 1528, 1511, 1487, 1446, 1418, 1401, 1352, 1321, 1308, 1286, 1237, 1167, 1141, 1103, 1000, 972, 948, 916, 884, 858, 807, 794, 760, 741, 726, 700, 672, 639, 605 cm⁻¹; APCI-TOF MS: calcd for C₄₆H₃₀ [*M*]⁺: *m/z*=582.23; found: 582.23.

Single-crystal X-ray analysis

Single crystals of $\mathbf{2}_{Br}$ (pale-yellow blocks) and $\mathbf{2}_{OTf}$ (pale-yellow blocks) were obtained from CH₂Cl₂/hexane and toluene, respectively. A single-crystal sample of each compound was coated with immersion oil (type B: Code 1248, Cargille Laboratories, Inc.) and mounted on a micromount. Diffraction data were collected at 90 K under a cold nitrogen gas stream with a Bruker APEX2 platform-CCD X-ray diffractometer system, using graphite-monochromated $Mo_{\kappa\alpha}$ radiation ($\lambda = 0.71073$ Å). Intensity data were collected by an ω -scan with 0.5° oscillations for each frame. Bragg spots were integrated by using the ApexII program package, $\ensuremath{^{[18]}}$ and the empirical absorption correction (multi-scan) was applied by using the SADABS program.^[19] Structures were solved by a direct method (SHELXT Version 2014/4)^[20] and refined by full-matrix least-squares (SHELXL Version 2014/7).^[21] Hydrogen atoms were placed at calculated positions and refined by applying riding models. CCDC 1836231 ($\mathbf{2}_{Br}$) and 1836232 ($\mathbf{2}_{OTf}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Crystal data for $C_{26}H_{18}BBr$ (2_{Br}): pale-yellow blocks, 0.48×0.35× 0.28 mm³, orthorhombic, *Pbca*, a = 8.716(7) Å, b = 11.267(9) Å, c =39.28(3) Å, V = 3857(5) Å³, Z = 8, density_{calcd} = 1.450 g cm⁻³, T = 90 K, $2\theta_{max} = 47.0^{\circ}$, Mo_{Ka} radiation, $\lambda = 0.71073$ Å, $\mu = 2.140$ mm⁻¹, 14050 reflections measured, 2813 unique reflections, 253 parameters, $R_{int} = 0.0156$, GOF = 1.065, R1 = 0.0249 ($l > 2\sigma(l)$), wR2 = 0.0605 (all data), $\Delta \rho_{\mathrm{min,max}} \!=\! -$ 0.380, 0.263 e Å⁻³.

Crystal data for C₂₇**H**₁₈**BF**₃**O**₃**S (2**_{0Tf}): pale-yellow blocks, 0.48× 0.44×0.39 mm³, triclinic, *P*Ī, *a*=13.165(2) Å, *b*=17.473(3) Å, *c*= 21.534(4) Å, *α*=94.293(2)°, *β*=105.089(2)°, *γ*=96.680(2)°, *V*= 4721.7(14) Å³, *Z*=8, density_{calcd}=1.379 g cm⁻³, *T*=90 K, 2θ_{max}= 57.7°, Mo_{Kα} radiation, *λ*=0.71073 Å, *μ*=0.188 mm⁻¹, 39876 reflections measured, 15392 unique reflections, 1261 parameters, *R*_{int}= 0.0202, GOF=1.046, *R*1=0.0481 (*I*>2σ(*I*)), *wR*2=0.1380 (all data), $\Delta\rho_{min, max}$ =-0.407, 0.764 e Å⁻³.

Electronic structure calculations

Density functional theory (DFT) calculations were performed by using the Gaussian 09 program package.^[22] All geometry optimizations including the transitions states were performed by using the ω B97X-D functional. The SDD effective core potential and its basis set were used for Cl, Br, and S, whereas the 6-31G(d,p) basis set was used for H, C, B, O, and F. The normal coordinate analysis was carried out for all stationary points to characterize the optimized structures on the energy hypersurface and to evaluate the zeropoint energy at each stationary point. The free energy changes along the reaction path were evaluated by taking into account the intramolecular entropy terms at 298.15 K. For CP_{CL} and CP_{Br} the basis-set superposition error (BSSE) was evaluated by using the counterpoise method, where BSSE in CP_{CI} and CP_{Br} were 4.0 and 4.1 kcal mol⁻¹, respectively. The charge distributions were calculated with the natural bond orbital (NBO) 5.9 program package.^[23-25] The Cartesian coordinates and energies of the computed structures are listed in Tables S4–S13 in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: borafluorene · boranes · borepin · carboboration · Lewis acid

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FULL PAPER

Catalyst-free 1,2-carboborations between diarylacetylenes and 9-borafluorenes $(1_{CI}, 1_{Br'} \text{ or } 1_{OTf})$ are described. Among the borafluorenes, 1_{Br} exhibited the highest reactivity, which agrees with the trend of the acceptor number of the borafluorenes evaluated by the Gutmann–Beckett method. Experimental and computational results indicated that the activation entropy term, rather than activation enthalpy term, largely contributes to the reaction rate.





Direct 1,2-Carboboration

Y. Shoji, N. Shigeno, K. Takenouchi, M. Sugimoto, T. Fukushima*



Mechanistic Study of Highly Efficient Direct 1,2-Carboboration of Alkynes with 9-Borafluorenes