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Communication

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Organocatalytic Diboration Involving "Reductive Addition" of a Boron–Boron σ-Bond to 4,4'-Bipyridine

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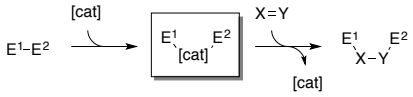
Supporting Information Placeholder

ABSTRACT: A 4,4'-bipyridine-based catalyst system for diboration of pyrazine derivatives was established. The catalyst cycle consists of the following two steps: (1) reductive addition of the boron–boron bond of bis(pinacolato)diboron to 4,4'-bipyridine to form *N*,*N'*-diboryl-4,4'-bipyridinylidene, and (2) oxidative boryl transfer from the intermediate to pyrazine to give *N*,*N'*-diboryl-1,4-dihydropyrazine with regeneration of 4,4'-bipyridine.

Transition metal catalysts have played privileged roles in the development of catalytic additions of nonpolar σ-bonds E^1–E^2 such as H–H, B–B, Si–Si, and B–Si bonds across carbon–carbon and carbon–heteroatom multiple bonds.[1,2] A key feature of transition metal catalysts is their high ability to activate nonpolar σ-bonds, mainly through oxidative addition to form E^1–[cat]–E^2 (Scheme 1, [cat] = transition metal).[3]

Scheme 1. Catalytic Addition Reaction of E^1–E^2 to X=Y via Formation of E^1–[cat]–E^2



[cat] = transition metal (common)
[cat] = **organic molecule (uncommon, This Work)**

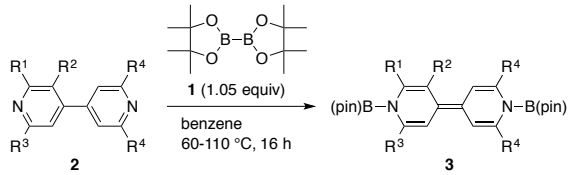
On the other hand, rapid progress in organocatalysis has also enabled activation of nonpolar σ-bonds. It has been shown that H–H bond is successfully activated by a frustrated Lewis pair (FLP) catalyst, allowing organocatalytic hydrogenation of carbon–nitrogen and carbon–carbon double bonds.[4,5] Moreover, diboration of alkenes in the presence of a catalytic amount of Lewis bases such as *t*-BuONa or Cs_2CO_3 has been demonstrated.[6,7,8] These new reactions clearly suggest further development of useful transformations through organocatalytic activation of nonpolar σ-bonds.

Is it then possible to generate an intermediate E^1–[cat]–E^2 in organocatalytic addition reactions (Scheme 1, [cat] = organic molecule)?[9,10] Because the organocatalyst is formally reduced, the elementary step to form the E^1–[cat]–E^2 species is now regarded as formal "reductive addition." Transfer of E^1 and E^2 from E^1–[cat]–E^2 species to unsaturated organic molecules results in the formation of an addition product. In the current paper, we discuss the organocatalytic addition proceeding through formation of isolable E^1–[cat]–E^2 intermediates, taking 4,4'-bipyridine-catalyzed diboration of pyrazines as an example.

We have recently reported that nitrogen-containing aromatic compounds undergo addition of boron reagents to give the dearomatized products.[11,12,13] Silaboration[11a] and hydroboration[11b] of pyridines take place at 50 °C in the presence of palladium and rhodium catalysts. Further, we established an addition of bis(pinacolato)diboron (**1**)[14] to sterically unhindered pyrazines, which proceeds efficiently at room temperature even in the absence of transition metal catalysts.[12] A possible driving force of the reactions is formation of a stable boron–nitrogen bond. We then turned our attention to diboration of bipyridines, in which aromaticity at the two aromatic rings is lost simultaneously.

Reaction of 4,4'-bipyridine (**2a**) with **1** (1.05 equiv) was carried out in benzene (entry 1, Table 1). Because two adjacent pyridine rings would lose aromaticity, the addition reaction of **1** into **2a** was expected to be rather unfavorable. However, we found that the reaction took place efficiently at 110 °C (bath temperature) to give *N*,*N'*-diboryl-4,4'-bipyridinylidene **3a** as a yellow solid in 94% yield after 16 h.[15] Although dearomatized **3a** was air and moisture sensitive both in a solid state and in a solution, it was thermally stable and

Table 1. Addition of **1** to 4,4'-Bipyridines **2**[a]



entry	R^1	R^2	R^3	R^4		temp (°C)	% yield[b]
1	H	H	H	H	**2a**	110	94 (**3a**)
2	Me	H	H	H	**2b**	110	50 (**3b**)
3[c]	Cl	H	H	H	**2c**	60	65 (**3c**)
4[d]	F	H	H	H	**2d**	60	60 (**3d**)
5	H	OMe	H	H	**2e**	110	62 (**3e**)
6[e]	H	Cl	H	H	**2f**	60	56 (**3f**)
7	H	F	H	H	**2g**	60	93[f] (**3g**)
8	Me	H	Me	H	**2h**	110	61 (**3h**)
9	Cl	H	Cl	H	**2i**	60	0[g] (**3i**)
10	Me	Me	Me	Me	**2j**	110	0[h] (**3j**)

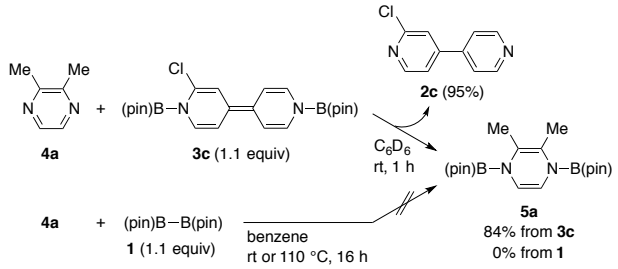
[a] **1** (0.21 mmol) and **2** (0.20 mmol) in benzene (0.4 mL) was stirred at 110 °C for 16 h. [b] Isolated yield based on **2**. [c] For 4 h with **1** (1.5 equiv). [d] For 10 h. [e] For 24 h. [f] Including $O[B(pin)]_2$ (4%) that could not be removed. [g] No desired product was obtained. [h] No reaction took place.

could be stored under inert atmosphere at room temperature for at least 3 months.

Substituted 4,4'-bipyridines **2b-2j** were subjected to reaction with **1** in benzene (entries 2-10, Table 1). 2-Methyl-4,4'-bipyridine (**2b**) underwent addition of **1** at 110 °C to afford **3b** (entry 2). The isolated yield was moderate, because of its relatively high solubility in benzene. 2-Chloro- (**2c**) and 2-fluoro-4,4'-bipyridine (**2d**) were more reactive than **2a** and **2b**: the reaction with **1** proceeded smoothly at 60 °C to give **3c** and **3d** in moderate yields (entries 3 and 4).[16] Addition of **1** to 3-methoxy-, 3-chloro-, and 3-fluoro-4,4'-bipyridines **2e-2g** also took place at 60-110 °C to give **3e-3g** (entries 5-7). 2,6-Dimethyl-4,4'-bipyridine (**2h**) afforded the corresponding product in moderate yield (entry 8), whereas no reaction took place for 2,2',6,6'-tetramethyl-4,4'-bipyridine (**2j**, entry 10). These results indicate that steric hindrance around both nitrogen atoms retards the reaction, as observed in the reaction of pyrazine.[12] 2,6-Dichloro-4,4'-bipyridine (**2i**) may undergo the addition of **1** at 60 °C, but no desired adduct **3i** was obtained probably because **3i** was unstable under these conditions (entry 9).

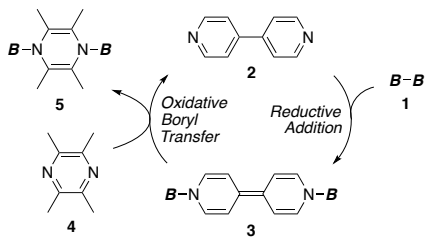
In the course of examination of the synthesis and reactivity of **3**, we found that boryl groups on **3c** migrated to 2,3-dimethylpyrazine (**4a**) within 1 h even at room temperature, giving *N,N'*-diboryl-1,4-dihydropyrazine **5a** in high yield (Scheme 2, top).[17] It is interesting to note that no borylation of **4a** took place in the attempted direct diboration with diboron **1** at room temperature or even under reflux in benzene (Scheme 2, bottom).[12] The formation of **5a** was accompanied by quantitative formation of bipyridine **2c** (Scheme 2, top). These results suggest that the diboration of sterically demanding pyrazine is enabled by using a diboration product of bipyridine **2** as an intermediate, instead of using diboron **1** directly.

Scheme 2. Boryl Transfer from **3i** to **4a**

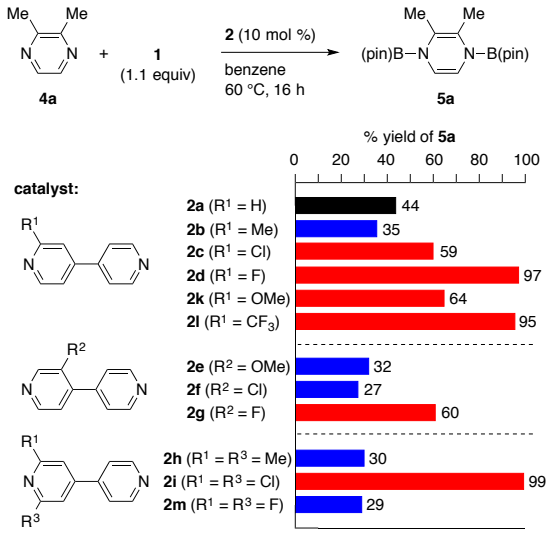


A new organocatalytic diboration of sterically hindered **4** was designed as shown in Scheme 3. The catalytic cycle consists of the following two steps: (1) reductive addition of the B–B bond of diboron **1** to bipyridine **2** to form a dearomatized intermediate **3**, and (2) oxidative boryl transfer from **3** to pyrazine **4** to give **5** with regeneration of **2**. This catalytic reaction indeed worked well as expected. A reaction of **4a** with **1** (1.1 equiv) in benzene at 60 °C in the presence of **2a** (R^1 = H, 10 mol %) afforded **5a** in 44% yield (Scheme 4). As mentioned above, no reaction took place in the absence of **2**, even at 110 °C (Scheme 2, bottom), indicating significant

Scheme 3. Possible Catalytic Cycle



Scheme 4. Screening of Catalysts for Addition of **1** to **4a**[a]

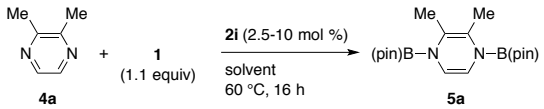


[a] **1** (0.44 mmol), **2** (0.040 mmol), and **4a** (0.40 mmol) were stirred in benzene (0.2 mL) at 60 °C for 16 h. Yields were determined by ^{1}H NMR based on **4a**.

rate acceleration was accomplished by the catalytic amount of **2a**.

The catalyst efficiency of 4,4'-bipyridines was highly dependent on the substituent at the C2 position (Scheme 4). The yields of **5a** were improved by **2c** (R^1 = Cl), **2d** (R^1 = F), **2k** (R^1 = OMe), and **2l** (R^1 = CF_3), whereas **2b** (R^1 = Me) resulted in lower yields. These results indicate that the catalyst efficiency correlates closely with inductive effect of the substituents, and that the bipyridines bearing stronger electron-withdrawing groups achieve higher catalyst efficiency (**2d**, **2l** > **2c**, **2k** > **2a** > **2b**). The substituents at the C3 positions also affected the catalyst efficiency. The product **5a** was formed in moderate yield with **2g** (R^2 = F), whereas **2e** (R^2 = OMe) and **2f** (R^2 = Cl) gave **5a** in low yields. These results indicate the effect of the dihedral angle made by the two pyridine rings. We finally found that **2i** (R^1 = R^3 = Cl) showed the highest catalyst efficiency. Unexpectedly low catalyst efficiency of **2m** (R^1 = R^3 = F) could be attributed to excessive electron deficiency on the pyridine ring because of the double substitution of the fluorine atoms.

Table 2. Reaction Conditions for **2i**-Catalyzed Addition of **1** to **4a**[a]



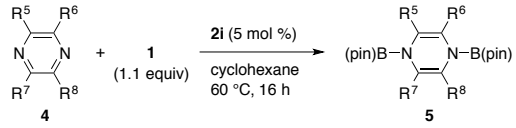
entry	catalyst loading (mol %)	solvent	% yield[b]
1	10	benzene	99
2	5	benzene	66
3	5	THF	91
4	5	cyclohexane	99 (84)[c]
5[d]	2.5	cyclohexane	71

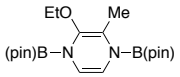
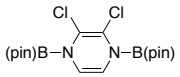
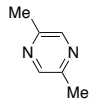
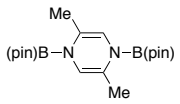
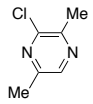
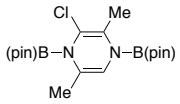
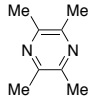
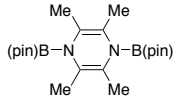
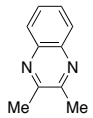
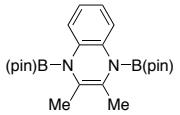
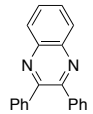
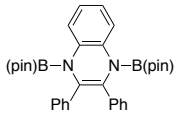
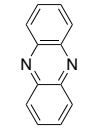
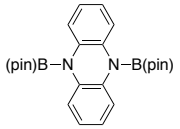
[a] **1** (0.44 mmol), **2i** (0.010-0.040 mmol), and **4a** (0.40 mmol) were stirred in a solvent (0.2 mL) at 60 °C for 16 h unless otherwise noted. [b] ^{1}H NMR yield based on **4a**. [c] Isolated yield based on **4a**. [d] At 80 °C.

The catalyst efficiency was improved further by changing the solvent from benzene to THF or cyclohexane (Table 2). The **2i**-catalyzed reaction in cyclohexane resulted in high yield formation of **5a** with lower catalyst loading (5 mol %, entry 4).[18] Dearomatized **5a** was thermally stable and could be purified by distillation. The catalyst loading could be reduced to 2.5 mol %, although elevated reaction temperature (80 °C) was required (entry 5).

To examine the scope of the catalytic B–B bond cleavage by 4,4'-bipyridine, pyrazine derivatives **4b**-**4i** were subjected to diboration with **1** using **2i** as a catalyst (Table 3).[19,20] In the presence of **2i** (5 mol %), 2-ethoxy-3-methylpyrazine (**4b**) underwent addition of **1** in cyclohexane at 60 °C to give **5b** in good yield (entry 1). In diboration of 2,3-dichloropyrazine (**4c**), **2c** gave better catalyst efficiency than **2i** (entry 2). Although 2,5-dimethylpyrazine (**4d**) reacted with **1** slowly in the absence of the catalyst to afford **5d** (23% yield at 110 °C), the reaction was accelerated in the presence of **2i**, resulting in the formation of **5d** in 88% yield at 60 °C (entry 3). Diboration of trisubstituted 3-chloro-2,5-dimethylpyrazine (**4e**) also took place efficiently to give **5e** in high yield (entry 4). 2,3,5,6-Tetramethylpyrazine (**4f**) did not undergo diboration at all under these conditions, probably because of its steric hindrance. However, we found that **4f** underwent diboration by increasing the catalyst loading (10 mol %) at an elevated reaction temperature (110 °C) (entry 5). Also diborylated efficiently were sterically demanding 2,3-disubstituted quinoxalines **4g** and **4h** and phenazine (**4i**), in which the loss of aromaticity is reduced because of the polycyclic aromatic structure (entries 6-8).[21] It should again be noted that, without catalyst **2i**, no or only inefficient reactions took place (Table 3, yields in parentheses).

Table 3. Organocatalytic Diboration of Pyrazine Derivatives **4**[a]



entry	substrate	product	% yield[b]
1	 **4b**	 **5b**	78 (0)
2[c]	 **4c**	 **5c**	57 (0)
3	 **4d**	 **5d**	88 (23)
4	 **4e**	 **5e**	82 (0)
5[d,e]	 **4f**	 **5f**	58 (0)
6[f]	 **4g**	 **5g**	83 (<1)
7	 **4h**	 **5h**	96 (0)
8	 **4i**	 **5i**	99 (0)

[a] **1** (0.44 mmol), **2i** (0.020 mmol, 5 mol %), and **4** (0.40 mmol) were stirred in cyclohexane (0.2 mL) at 60 °C for 16 h unless otherwise noted. [b] Isolated yield based on **4**. In parenthesis, ^{1}H NMR yield of the reaction at 110 °C for 16 h in the absence of the bipyridine catalyst. [c] **2c** (9 mol %) was used instead of **2i**. [d] **2i** (10 mol %). [e] At 110 °C. [f] A gram scale reaction of **4g** (3 mmol) in THF using **2i** (8 mol %), giving **5g** (1.0 g).

In conclusion, we have established a conceptually new organocatalytic addition reaction of nonpolar E^1–E^2 bond to unsaturated substrates with formation of E^1–[cat]–E^2 as a key catalyst intermediate via reductive addition of E^1–E^2 bond to 4,4'-bipyridines used as an organocatalyst. Remarkable catalyst efficiency of 4,4'-bipyridines has been demonstrated in diboration of sterically hindered pyrazines. The mechanism involving organocatalytic σ-bond activation would be a new tool for organic transformations as an alternative to transition-metal-catalyzed reactions. The development of catalytic reactions based on this concept to enable C–B bond formation is being undertaken in this laboratory.

ASSOCIATED CONTENT

Supporting Information. Experimental details and characterization data of the products. This material is available free of charge via Internet at http://pubs.acs.org.

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(16) The adducts **3c** and **3d** were relatively unstable under the reaction conditions, thus the reaction at 110 °C resulted in significant degrease of the yields because of product decomposition.

(17) For precedents of *N,N'*-diboryl-1,4-dihydropyrazines, see refs. 12 and 15.

(18) We separately found that the stoichiometric reaction of **1** with **2a** was faster in cyclohexane than in benzene. Indeed, at 110 °C after 6 h, the reaction in cyclohexane provided 78% yield of product **3a**, while that in benzene gave 66% yield. This result may indicate that improvement of catalyst efficiency by using cyclohexane as a solvent can be attributed at least to the acceleration of the reductive addition step.

(19) Although dearomatized **5** were air and moisture sensitive, they were thermally stable and could be purified by distillation.

(20) There has been much interest in the chemistry of 1,4-dihydropyrazines, including their synthetic utilities and structural features as exemplified below. Applications in inorganic synthesis: (a) Saito, T.; Nishiyama, H.; Tanahashi, H.; Kawakita, K.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2014**, *136*, 5161. Studies focused on the antiaromatic character arising from their conjugated cyclic 8π-electron structure: (b) Kaim, W. *Angew. Chem. Int. Ed.* **1981**, *20*, 599. (c) Kaim, W. *J. Am. Chem. Soc.* **1983**, *105*, 707. (d) Lichtblau, A.; Ehlend, A.; Hausen, H.-D.; Kaim, W. *Chem. Ber.* **1995**, *128*, 745. See also ref. 15. Studies focused on their electron-rich ring systems: (e) Kaim, W. *Angew. Chem. Int. Ed.* **1981**, *20*, 600. (f) Brook, D. J. R.; Haltiwanger, R. C.; Koch, T. H. *J. Am. Chem. Soc.* **1991**, *113*, 5910. (g) Brook, D. J. R.; Haltiwanger, R. C.; Koch, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 6017. Studies on their key role in the structure of redox-active biological molecules: (h) Goto, T.; Kishi, Y. *Angew. Chem. Int. Ed.* **1968**, *7*, 407. (i) Walsh, C. *Acc. Chem. Res.* **1980**, *13*, 148.

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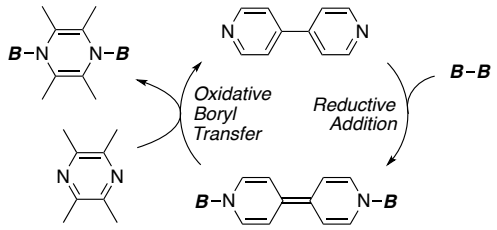
B–N
N–B
N
N
B–B
Oxidative
Boryl
Transfer
Reductive
Addition
N
N
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N–B