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ARTICLE TYPE

Diboron as Reductant for Nickel-Catalyzed Reductive Coupling: Rational Design and Mechanistic Studies

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Diboron (B₂pin₂) has been identified as an efficient and environmentally benign reducing reagent for reductive coupling reactions for the first time, which enables the nickel-catalyzed reductive tetramerization of alkynes to be performed with high efficiency. Mechanistic and kinetic studies indicate that the facile reductive elimination to form B-B bond from the dinuclear Ni-Ni complexes is responsible ¹⁰ for the high efficiency. The activation enthalpy ($\Delta H^{\dagger} = 56.5$ kJ/mol), entropy ($\Delta S^{\dagger} = -128$ J/mol/K) and

the substituent effect ($\rho = 1.43$) on this reaction were gained.

Introduction

Transition-metal-catalyzed reductive coupling reactions have long been recognized as a versatile and powerful synthetic tool ¹⁵ for assembly of functionalized organic compounds and fine chemicals from simple raw materials.¹ Essential to the catalytic nature of such a process, however, is that requires stoichiometric reducing reagents. Although enormous efforts have been devoted to the expanding the substrate scope for C-C bond cross-coupling ²⁰ and other transformations,² few effort has been devoted to developing new and efficient reductants for sustaining the catalytic cycle. Currently, the reductants employed in these procedures are largely limited to super-stoichiometric metals (such as Zn, Mn and Cr),³ air and moisture sensitive ²⁵ organometallics (such R₂Zn, RMgX, Et₃SiH and BR₃),⁴ and other

organic reducing agents,⁵ which indisputably suffer from some fatal drawbacks such as generation of a large amount of undesired waste, catalyst poisoning and lower atom-efficiency.

Bis(pinacolato)diboron (B₂pin₂) has been extensively utilized as storable and easy to handle reagent for a series of transition metal-catalyzed reactions.⁶ Nonetheless, to the best of our knowledge, the B₂pin₂ has never been used as a reductant for transition metal catalyzed reductive coupling reactions. The B-B bond of B₂pin₂ could be facilely cleaved by active metal complex as via ovidative addition or transmetalation. On the contrary, the P

- ³⁵ via oxidative addition or transmetalation. On the contrary, the B-B bond could also be constructed via the reductive elimination from a suitable boron-containing metal complex (Scheme 1, Top).⁷ Inspired by this unique feature and prior success in metalcatalyzed reductive coupling with organometallics as reductants,⁴
- $_{\rm 40}$ we envisioned the possibility to establish a reductive coupling reaction by using $B_2 pin_2$ as an environmentally benign reductant

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Scheme 1. Proposed reductive coupling with $B_2 pin_2$ as reductant.

with sequential transmetalation as the key steps (Scheme 1). Taking into account the reversibility of the cleavage of B-B bond, one possible catalytic cycle shown in Scheme 1 is assumed to 55 furnish a reductive coupling reaction with $B_2 pin_2$ as reducing reagent. The oxidative addition of M(0) with R-X would directly afford R-M-X, which reacts with B₂pin₂ to generate R-M-Bpin via transmetalation. The self-transmetalation between two molecules of R-M-Bpin to produce one molecule of R-M-R 60 together with one molecule of M(Bpin)₂. Subsequent reductive elimination would take place in these two species to liberate the coupling product and revive the chain carrier M(0) as well as 0.5 molecules of B₂pin₂ for next catalytic cycle. On the basis of this mechanistic assumption, we recognized that consuming one 65 molecule of B₂pin₂ would give rise to at least two molecules of product in this reductive coupling reaction. To realize this concept, the successful formation of the boron-containing metal complex species via transmetalation is essential.

Ni-catalyzed reductive coupling reactions have recently ⁷⁰ emerged as direct methods for carbon-carbon bond formation between two organic electrophiles.⁸ As active electrophiles, alkynes have been used as coupling partners for the Ni-catalyzed reductive coupling reactions.⁹ One such method for synthesis of octatetraenes was reported by Wu and co-workers with Ni as ⁷⁵ catalyst in the presence of super-stoichiometric amount of Zn.^{9g} Although the detailed mechanism is not clear, one possibility is

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that the catalytic cycle involves the protonation of the nickelacycle with H₂O. If this protonation is realized by alcohol, the corresponding Ni-B bond would be formed via transmetalation of Ni-OR species with B₂pin₂, and then the ⁵ corresponding reductive self-coupling of alkynes might be realized with B₂pin₂ as terminal reducing reagent. Herein, we describe the first nickel-catalyzed reductive coupling of alkynes

- that employs formal substoichiometric amount of B₂pin₂ as a clean and environmentally benign reductant. Mechanistic studies to disclosed how the substoichiometric amount of B₂pin₂ to sustain the catelytic auda and provide avidences to support that the
- the catalytic cycle and provide evidences to support that the diboron could facilely promote this nickel-catalyzed reductive coupling.

Resluts and Discussion

15 To probe the validity of our hypothesis, we examined the possibility of tetramerization reaction of diphenylethyne 1a with B₂pin₂ as a reductant. When the reaction was catalyzed with $Ni(PPh_3)_2Cl_2$ in the presence of stoichiometric B_2pin_2 in MeOH at 120 °C, the desired product 2a was isolated in 87% yield (Table 1, 20 entry 1). The structure of 2a was confirmed by single-crystal Xray analysis and revealed that the reaction conducted with high regioselectivity.¹⁰ Several other nickel catalysts, such as NiBr₂(PPh₃)₂, NiI₂(PPh₃)₂ NiCl₂(dppe) showed much less catalytic activity (Table 1, entries 2-4) under the same reaction 25 conditions. The reaction performed smoothly with Ni(COD)₂ as nickel source in the presence of PPh₃, suggesting that Ni(0) was involved in the present reaction (Table 1, entry 5). However, the reaction virtually stopped with stoichiometric BEt₃, HBpin or HSiEt₃ as reducing reagents (Table 1, entries 6-8). As expected, 30 high yield was still obtained when the loading of B2pin2 decreased to 0.2 equivalents, which indicated that the reductive coupling reaction was most likely sustained by B-B bond cleavage (Table 1, entries 9-12). The reaction could be conducted Table 1. Optimization of the reaction conditions ^a

		[Ni] (5 mol %)	H	Ph Ph	Ph
Ph 5		120 °C, 18 h	► Ph´ Ţ F	h Ph Ph 2a	Ť
Entry	[Ni]	A	dditive	Solvent	Yield (%)
1	NiCl ₂ (PPh ₃) ₂	B	2pin2 (1.0)	MeOH	87
2	NiBr ₂ (PPh ₃) ₂	B	2pin2 (1.0)	MeOH	69
3	NiI ₂ (PPh ₃) ₂	B	2pin2 (1.0)	MeOH	35
4	NiCl ₂ (dppe)	B	2pin2 (1.0)	MeOH	37
5	Ni(COD) ₂ /PF	$^{2}h_{3}(1:2)$ B_{2}	2pin2 (1.0)	MeOH	79
6	NiCl ₂ (PPh ₃) ₂	Bl	Et ₃ (1.0)	MeOH	0
7	NiCl ₂ (PPh ₃) ₂	H	Bpin (1.0)	MeOH	<5
8	NiCl ₂ (PPh ₃) ₂	H	SiEt ₃ (1.0)	MeOH	<5
9	NiCl ₂ (PPh ₃) ₂	B	2pin2 (0.6)	MeOH	86
10	NiCl ₂ (PPh ₃) ₂	B	pin ₂ (0.3)	MeOH	89
11	NiCl ₂ (PPh ₃) ₂	B	2pin2 (0.2)	MeOH	80
12	NiCl ₂ (PPh ₃) ₂	B	2pin2 (0.1)	MeOH	23
13	NiCl ₂ (PPh ₃) ₂	B	2pin ₂ (0.3)	EtOH	76
14	NiCl ₂ (PPh ₃) ₂	B	2pin ₂ (0.3)	n-PrOH	83
15	NiCl ₂ (PPh ₃) ₂	B	2pin2 (0.3)	i-PrOH	<5
4.9			EN 113 (0.05		(1.0 - 1)

^a General conditions: **1a** (1.0 mmol), [Ni] (0.05 mmol), solvent (1.0 mL), N₂, 120 °C for 18 h, isolated yield, unless otherwise noted.

perfectly in alcohol solvents, and MeOH was the best for this

reaction (Table 1, entries 13-15).

Table 2. Sub	strate scope	of alkynes a
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_1	NiCl ₂ (PPh ₃) ₂ (5 m	(1%) $(1%)$ $(1%)$ $(1%)$	R^1 R^2
R'		R^{2} R^{2} Γ	\hat{R}^2 \hat{H}
	Meon, 120 C,	2 Z	
Entry	\mathbf{R}^1	\mathbf{R}^2	Yield (%)
1	C ₆ H ₅	C ₆ H ₅	2a , 88
2	$4-CH_3C_6H_4$	4-CH ₃ C ₆ H ₄	2b , 82
3	3-CH ₃ C ₆ H ₄	3-CH ₃ C ₆ H ₄	2c , 68
4	3,5-(CH ₃) ₂ C ₆ H ₄	3,5-(CH ₃) ₂ C ₆ H ₄	2d , 77
5	3-CH ₃ OC ₆ H ₄	3-CH ₃ OC ₆ H ₄	2e , 75
6	4-CF ₃ OC ₆ H ₄	4-CF ₃ OC ₆ H ₄	2f , 81
7	$4-FC_6H_4$	$4-FC_6H_4$	2g , 83
8	4-ClC ₆ H ₄	$4-ClC_6H_4$	2h , 64
9	3-ClC ₆ H ₄	3-ClC ₆ H ₄	2i , 80
10	3-BrC ₆ H ₄	3-BrC ₆ H ₄	2j , 45
11	C ₆ H ₅	$4-CH_3C_6H_4$	2k , 85 ^b

^{*a*} General conditions: **1** (1.0 mmol), NiCl₂(PPh₃)₂ (0.05 mmol), B₂pin₂ (0.3 mmol), MeOH (1.0 mL), N₂, 120 °C for 18 h. ^{*b*} **2k** was the regioisomers mixture.

⁴⁵ Under the optimized conditions, the scope of diaryl-substituted alkynes was investigated. As shown in Table 2, diarylalkynes containing various electron-rich and electron-deficient functional groups reacted smoothly to give the corresponding tetramerization products in high yields. Typical functional groups ⁵⁰ such as methyl, methoxyl, and trifluoromethoxyl groups were compatible with the present Ni/B₂pin₂ catalytic system (**2b-2f**), which indicated that the present reductive coupling reaction had a good functional-group tolerance. The aryl halide substituent remain intact during this reductive coupling reaction (**2g-2j**), ⁵⁵ providing a useful handle for further elaboration. Meanwhile, the hindrance on the phenyl ring of diarylalkynes had a slight effect on the efficiency (**2b** *vs* **2c** and **2h** *vs* **2i**). The unsymmetrical diarylalkyne **1k** gave the desired product **2k** in high yield with lower regioselectivity.

	NiCl ₂ (PPh ₃) ₂ (5 mol %)	H/D Ph Ph Ph
Ph———Pr 1a	$B_2 pin_2 (30 \text{ mol }\%)$	Ph T T T Ph Ph Ph H/D
Solvent: 1	CD ₃ OD (1.0 mL)	2a', 86 % (> 95% D)
2 CD ₃ OH (1.0 mL)		2a , 88%
3	3 CH ₃ OD (1.0 mL)	2a', 87 % (> 95% D)

Scheme 2. Tetramerization with different proton sources.

To gain understanding into the origin of the proton in the product, we carried out labeling experiments under the standard conditions. As depicted in Scheme 2, the transformation of **1a** to **2a** was firstly conducted with deuterium-labeled CD₃OD as solvent, almost complete deuterium (>95% D) was incorporated into the product **2a**', strongly indicating that methanol serves as the proton source (entry 1). In addition, when the reaction was carried out in the presence of CD₃OH, however, the D-labeled ⁷⁰ product **2a**' was not detected, indicating that the proton was not from methyl moiety of methanol and methanol might not act as a reducing reagent in the present reaction. Further investigation with CH₃OD as the solvent resulted in good yield and nearly complete deuterated **2a**' was obtained, suggesting that the proton ⁷⁵ source was supplied from the hydroxyl of methanol.

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Figure 1. (A) Standard IR spectra of *n*-PrOBpin and B_2pin_2 . (B) Standard IR spectra of **1a** and **2a**. (C) Depletion of B_2pin_2 and formation of *n*-PrOBpin. (D) Depletion of **1a** and formation of **2a**.



Figure 2. (A) Plot of initial rates with respect to 1a showing zeroth-order dependence. (B) Plot of initial rates with respect to B_2pin_2 showing zeroth-order dependence.



10 Figure 3. Plot of initial rates with respect [Ni]² showing second-order dependence.

After confirming the origin of H atom of product, we proceeded to execute a set of experiments for elucidating how the B_2pin_2 to promote the present reaction. When the standard 15 reaction was performed in *n*-PrOH, the *n*-PrOBpin was detected by GC/MS. Furthermore, the *in situ* IR was used to monitor the standard reaction conducted in *n*-PrOH, we delighted to see that the kinetic profiles clearly revealed not only the consumption of **1a** and B_2pin_2 as well as the formation **2a** (Figure 1D) but also a

- ²⁰ new species increasing at peak 1149 cm⁻¹ (Figure 1C) which was unambiguously assigned as *n*-PrOBpin by comparison with an authentic sample of *n*-PrOBpin (Figure 1A). More detailed mechanistic studies were conducted by examining the kinetics for the reaction of **1a** with B_2pin_2 in *n*-PrOH by *in situ* IR and gas
- ²⁵ chromatography. Initial rates for the reductive coupling of **1a** were then measured by varying the concentrations of **1a**, B_2pin_2 and nickel catalyst (see Supporting Information). The kinetic profiles showed that the initial rates are independent of **[1a]** and **[B₂pin₂]**, which revealed a zeroth-order dependence of the rate on
- $_{30}$ both alkyne **1a** and B_2pin_2 concentrations (Figure 2). More intriguing is the observed second-order rate dependence on catalyst concentration (Figure 3), which suggests the involvement

of two nickel species in the turnover-limiting step.

On the basis of the kinetic studies, two tentative reaction 35 pathways for this reductive tetramerization reaction were proposed. The in situ formed Ni(0) could undergo oxidative cycloaddition with alkyne to furnish the five-membered nickelacycle A. Path I including the protonation of fivemembered nickelacycle A to generate intermediate E, the 40 consequent transmetalation of E with B₂pin₂ to form the intermediate F, the rate-limiting self-transmetalation between two Ni-species to generate the intermediate G and the final reductive elimination to obtain the desired product 2a, are illustrated in Scheme 3. Path II involving the formation of dinuclear Ni-Ni 45 complexes was also proposed.¹¹ The key step of this pathway is the dimerization of intermediate A to produce the dinuclear Ni-Ni intermediate **B**, which would produce the desired tetramerization product by protonation with alcohol and reacting with two molecules of B₂pin₂ to give the Ni-B complex **D** and MeOBpin. 50 Reductive elimination of intermediate D could regenerate the Ni(0) species and one molecule of $B_2 pin_2$ for the next catalytic cycle.



As described in Scheme 3, if the reaction proceeded along path 55 I, the desired product could not be formed in the absence of B₂pin₂ even the reaction was conducted with stoichiometric amount of Ni(0)-catalyst. If the reaction performed along path II, the dimerization of five-membered nickelacycle A would be the 60 rate-determining step and the desired coupling product 2a was produced prior to B₂pin₂ involved in the catalytic reaction. Thus, the desired product 2a would be produced with Ni(0)-catalyst even if the reaction was conducted in the absence of B₂pin₂. To distinguish the two reaction pathways, we studied a reaction with 65 stoichiometric amount of Ni(COD)₂/PPh₃ in the absence of B₂pin₂ under the other identical reaction conditions (see Supporting Information). The good yield was obtained clearly revealed that the reaction proceeds along path II. Further strong evidences for supporting the path II was stemmed from the ESI-70 MS studies (see Supporting Information). In the catalytic reaction, we are delighted that two signals at m/z 895.2460 and 633.1544, assigned $[(NiBpinPPh_3)_2+H]^+$ which are to and

which are assigned to $[(NiBpinPPn_3)_2+H]$ and $[(NiBpin)_2PPh_3+H]^+$, were observed. This result indicated that a dinuclear-Ni intermediate **D** was indeed involved in the present ⁷⁵ reaction.

After confirmed that the reaction proceeds along path II and the dimerization of nickelacycle A to B is the rate-limiting step, we quantitatively measured the activation parameters by carrying out the reaction at different temperatures. As shown in Figure 4, plotting of $\ln(k/T)$ versus 1/T give a smooth linear relationship (Figure 4), allowing us to calculate the activation enthalpy ($\Delta H^{\ddagger} = 56.5 \text{ kJ/mol}$) and activation entropy ($\Delta S^{\ddagger} = -128 \text{ J/mol/K}$). We further investigated the reductive coupling reactions using 5 different diarylethynes. Plotting $\log(k/k_H)$ versus σ_p for these substrates indeed gave a rather linear relation (see Supporting

Information), and the positive slope ($\rho = 1.43$) can be associated with a developing negative charge in the transition state.



10 Figure 4. Eyring plot for rate constants.

The usefulness of this new protocol was demonstrated via the gram scale reaction in the presence of 0.01 mol% of catalyst with substoichiometric amount of (30 mol%) B₂pin₂. High yield (70%) together with long-lived catalysts (12 days) was observed in this ¹⁵ gram scale reaction (see Supporting Information), showing that the clean reaction created by B₂pin₂ can improve the catalytic efficiency via suppressing the formation of intractable black Nisolid which was usually observed with Zn or Mn as reducing reagents.

20 Conclusions

In summary, B₂pin₂ has been identified, for the first time, as a novel, efficient, and environmentally benign reductant thanks to rational design, which enables the nickel-catalyzed reductive coupling of alkynes to proceed efficiently with very low catalyst ²⁵ loading (0.01 mol%) in the presence of formal substoichiometric

- amount of (0.3 equiv) B_2pin_2 . Our mechanistic studies are consistent with a catalytic cycle in which the formation of dinuclear Ni-Ni complex is the rate-limiting step and the facile nature of reductive elimination of pinB-Ni-Ni-Bpin to regenerate
- ³⁰ Ni(0) is responsible to the high efficiency of this catalytic reaction. This result gives a clue that B₂pin₂ has promise as a valuable reducing reagent for a variety of reductive C-C bondforming manifolds. Further investigations on application of the B₂pin₂ as environmentally benign reductant in other reductive ³⁵ coupling reactions are currently underway in our laboratory.

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