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Ligand-controlled regiodivergent Ni-catalyzed *trans*-hydroboration/carboboration of internal alkynes with B_2pin_2†

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Unprecedented regioselective *trans*-hydroboration and carboboration of unbiased electronically internal alkynes were realized *via* a nickel catalysis system with the aid of the directing group strategy. Furthermore, the excellent α- and β-regioselectivity could be accurately switched by the nitrogen ligand (terpy) and phosphine ligand (Xantphos). Mechanistic studies provided an insight into the rational reaction process, that underwent the *cis*-to-*trans* isomerization of alkenyl nickel species. This transformation not only expands the scope of transition-metal-catalyzed boration of internal alkynes but also, more particularly, portrays the vast prospects of the directing group strategy in the selective functionalization of unactivated alkynes.

Introduction

Organoboron compounds are versatile building blocks in the pharmaceutical industry and materials science, and could be rapidly and conveniently converted into more complicated molecules *via* cross-coupling and other well-established reactions, in which the stereochemistry of organoboron compounds are always retained.[1] Undeniably, the hydroboration reaction of easily available unsaturated hydrocarbons is still a straightforward and indispensable method to synthesize boron-containing compounds.[2]

Generally, the hydroboration of alkynes with trivalent boranes provides synthetically useful alkenyl boron compounds, including 1,2-addition[3a–c] and 1,1-addition products;[3d] however, the *cis*-addition mode is strictly complied in the transition metal-catalyzed 1,2-hydroboration reactions (Scheme 1, I). Even so, *trans*-selective hydroboration of terminal alkynes was firstly realized through the metal vinylidene intermediate two decades ago.[4] With respect to the hydroboration of internal alkynes, regio- and stereoselectivity would give mixtures of α- and β-addition, *cis*- and *trans*-addition products, due to isomerization and other related processes.[5]

Since Früstner's group reported the first real *trans*-hydroboration of internal alkynes with $[Cp^*Ru(MeCN)_3]PF_6$ and HBpin,[6] a few examples of *trans*-hydroboration reactions have been disclosed in the past decade (Scheme 1, II). However, these work particularly well with symmetrical internal alkynes,[6] activated internal alkynes,[7] 1,3-enynes[8] or 1,3-diynes.[9] For the unsymmetrical internal alkynes with unbiased electricity, few examples were reported, which were limited to a weak coordinate group (propargyl amines and ether)[10] and NHC-boryl radical process.[11] To the best of our knowledge, ubiquitous electronically unbiased internal alkynes with unobvious different steric bulks between R^1 and R^2 rarely underwent *trans*-hydroboration reactions because of unmanageable regio- and stereoselectivity. Therefore, the development of feasible, efficient methods for the hydroboration of widespread unsymmetrical internal alkynes is highly desirable. As part of our continuing studies on transition-metal catalyzed boronation reactions of multiple bonds with the hydrostable and easily handled diboron(4) compounds ($B_2(OR)_4$) as a boron source,[12] herein, we developed nickel-catalyzed *trans*-hydroboration of electronically unbiased internal alkynes. Furthermore, opposite regioselectivity in a cyclization carboboration reaction was also established depending on the regulation of the ligand (Scheme 1, III).

Results and discussion

In order to acquire high regioselectivity, we attempted to utilize the directing group strategy in the hydroboration of internal alkynes.[13] And optimization of the directing group and reaction

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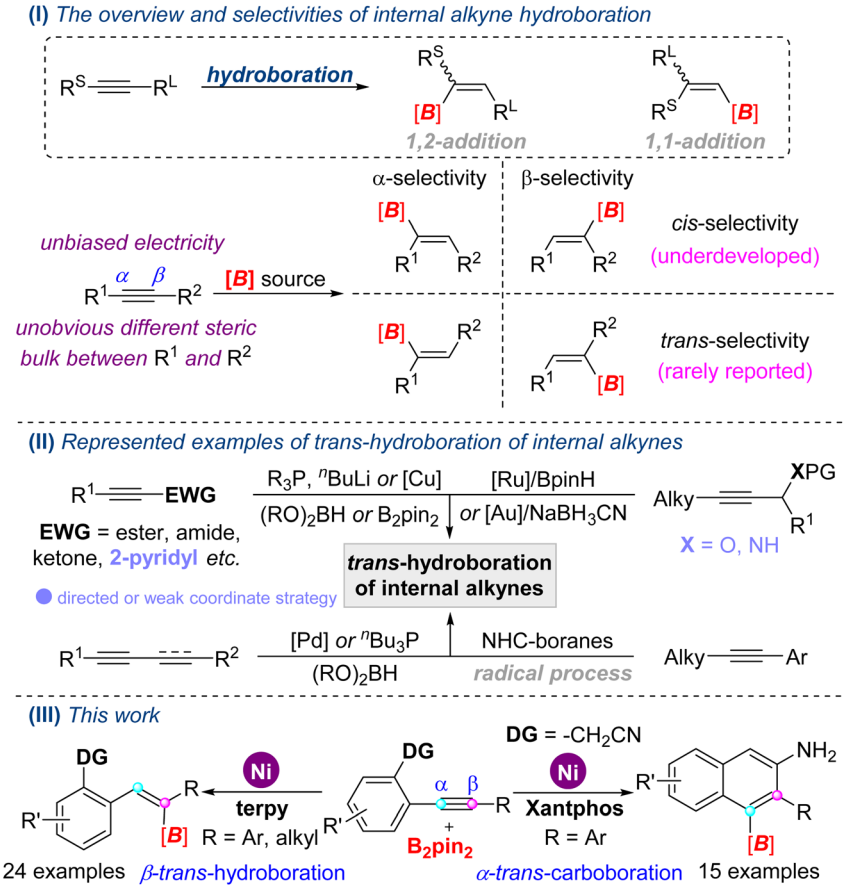
‡ Equal contribution.

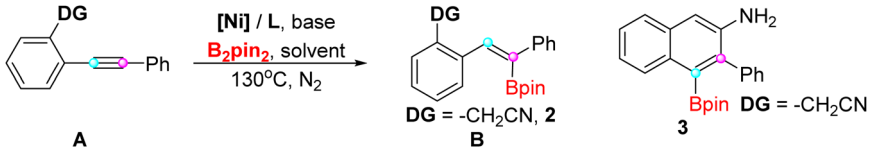


Scheme 1 Background and project synopsis.

conditions was carried out in parallel (Table 1). Firstly, due to the good coordinating function of cyano-containing groups, the cyano group (–CN) and cyanomethyl (–CH_2CN) were installed next to the triple bond and showcased disparate outcomes (entries 1 and 2). Furthermore, the electron-deficient sulfamide with lower pK_a values of N–H bonds was unreactive (entry 3). An oxygen atom as a coordinating site was considered and diaryl alkynes with methyl ketone (–$COCH_3$) among oxygen-containing directing groups (entries 4–6) afford the *trans*-hydroboration product with 47% yield. Obviously, diphenyl acetylene only generated unassigned geometry alkenylborate **B** in very low yield without the aid of an auxiliary group (entry 7). Taken together, after initial screening revealed that a cyanomethyl (–CH_2CN) directing group (as in **1**) provided the highest yield and selectivity, reaction conditions were optimized with this substrate as a model substrate (**1**). From the reaction conditions (entry 1) as a reference, this transformation could also work by other nickel salts catalysis, albeit with lower yields of 50–73% (entries 8–12). However, changing the ligands has an effect on the reaction so that quite a few other products are formed. The carboboration product 1-boryl naphthylamine **3** was generated while xantphos acted as a ligand.[14] Next, various kinds of base were screened, and phosphate salts were still the optimized choice (entries 19–21). Lastly, a single solvent system was beneficial for the production of **2** and **3**, respectively (entries 22–23). Noticeably, *trans*-hydroboration product **2** could not be obtained without the limited detection amount under anhydrous conditions (entry 24). Lastly, quantitative water was added in the anhydrous solvent for better reproducibility (entry 25).

Having ascertained the optimized conditions with 2-(2-(phenylethynyl)phenyl)acetonitrile **1** as the standard substrate, we conducted *trans*-hydroboration reaction of a series of *ortho*-acetonitrile internal aryl alkynes with B_2pin_2 as the integrated partner (Table 2). In terms of the electronic properties, biaryl internal alkynes ranging with substitutions in *para*- and *meta*-positions including electron-donating and electron-withdrawing groups were well-tolerated and afforded the corresponding alkenyl boronates in moderate to excellent yields (**10–16**). Significantly, highly regioselective *trans*-alkenylborates transforming from biaryl alkynes with *ortho*-position substituents in moderate yields suggested that steric-hindrance couldn't influence regioselectivity under the present system (**17–19**). Furthermore, heteroaromatic aryl alkyne and conjugated enyne could be tolerated and converted into desired products (**20**). Of particular interest is that the reaction with high *trans*-addition selectivity was compatible with aryl–alkyl alkynes, that could give the moderate yields, that was compatible with 1-cyclohexenyl (**21**), cyclohexyl (**22**), phenethyl (**23**), *n*-butyl (**24**), methyl (**25**), siloxane (**26**) and carbamate (**27**).

Table 1 Optimization of the reaction conditions and directing group[a]



Entry	DG	[Ni]	L	Base	Solvent	**B** (%)	**3** (%)
1	$-CH_2CN$ (**1**)	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh/Tol	78	ND
2	–CN (**4**)	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh/Tol	<10	—
3	$-CH_2NHTs$ (**5**)	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh/Tol	ND	—
4	$-COCH_3$ (**6**)	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh/Tol	47	—
5	–CHO (**7**)	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh/Tol	<10	—
6	$-CH_2OH$ (**8**)	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh/Tol	ND	—
7	None (**9**)	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh/Tol	<10	—
8	**1**	$Ni(OAc)_2$	Terpy	K_3PO_4	Cyh/Tol	58	ND
9	**1**	$Ni(dppe)Cl_2$	Terpy	K_3PO_4	Cyh/Tol	50	ND
10	**1**	$Ni(dppp)Cl_2$	Terpy	K_3PO_4	Cyh/Tol	53	ND
11	**1**	$Ni(acac)_2$	Terpy	K_3PO_4	Cyh/Tol	55	ND
12	**1**	$Ni(cod)_2$	Terpy	K_3PO_4	Cyh/Tol	73	ND
13	**1**	$Ni(PPh_3)_2Cl_2$	Bpy	K_3PO_4	Cyh/Tol	<10	ND
14	**1**	$Ni(PPh_3)_2Cl_2$	^{t}Bu-terpy	K_3PO_4	Cyh/Tol	23	ND
15	**1**	$Ni(PPh_3)_2Cl_2$	DAF	K_3PO_4	Cyh/Tol	65	ND
16	**1**	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	Cyh/Tol	ND	76
17	**1**	$Ni(PPh_3)_2Cl_2$	DPEPhos	K_3PO_4	Cyh/Tol	<10	57
18	**1**	$Ni(PPh_3)_2Cl_2$	None	K_3PO_4	Cyh/Tol	<5	21
19	**1**	$Ni(PPh_3)_2Cl_2$	Terpy	Na_3PO_4	Cyh/Tol	<10	ND
20	**1**	$Ni(PPh_3)_2Cl_2$	Terpy	K_2CO_3	Cyh/Tol	34	ND
21	**1**	$Ni(PPh_3)_2Cl_2$	Terpy	MeOK	Cyh/Tol	15	ND
22	**1**	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh	**88** (**85**)	ND
23	**1**	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	Tol	ND	**79** (**74**)
24[b]	**1**	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh	ND	ND
25[c]	**1**	$Ni(PPh_3)_2Cl_2$	Terpy	K_3PO_4	Cyh	89	ND
26[d]	**1**	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	Tol	ND	78

[a] Conditions: substrate **A** (0.2 mmol), nickel catalyst (5 mol%), ligand (10 mol%), B_2pin_2 (1.5 equiv.), base (1.5 equiv.), cyclohexane (Cyh)/toluene (Tol) (v/v = 1 : 1, 2.0 mL) under an N_2 atmosphere at 130 °C for 24 h in a sealed tube; yields were determined by ^{1}H NMR with CH_2Br_2 as an internal standard, isolated yield is in parentheses; ND = not detected. [b] Absolute dry cyclohexane. [c] Absolute dry cyclohexane, H_2O (5 equiv.). [d] Absolute dry toluene, H_2O (5 equiv.).

However, a secondary nitrile as a directing group was less beneficial for the reaction than a primary nitrile due to weaker coordination ability, which further supported the directing role of the $-CH_2CN$ group (**28**). On the other hand, the variation of substitutions on the acetonitrilyl phenyl ring was acceptable with slightly deceasing yields (**29–31**). Besides, the structures of alkenyl boronates **10** (CCDC: 2265346) and **24** (CCDC: 2265348)† in the solid state identified the constitution and assignment of the double bond geometry, and elaborative NMR analysis confirmed that either regio-isomer incorporated an E-olefin moiety. According to our knowledge, high stereoselectivity values (>20 : 1) have not previously been developed for any *trans*-addition hydroboration reactions of diaryl internal alkynes. Moreover, the trisubstituted alkenylborates obtained through the hydroboration of diaryl alkynes are difficult to obtain by known methods.

Next, we turned to evaluate the scope of *ortho*-acetonitrile internal aryl alkynes for the α-selective cyclization carboboration in the presence of xantphos ligand (Table 3), in which the $-CH_2CN$ group participated in the formation of naphthylamine derivatives and acted as a directing group and reaction partner. Generally, a wide range of diaryl alkynes, bearing electron-donating or withdrawing substituents on the *para*-, *meta*-, or *ortho*-positions of aromatic rings (**32–41**), all *ortho*-acetonitrile internal aryl alkynes, underwent efficient cyclization to furnish 1-boryl-2-aryl-3-naphthylamines with excellent regioselectivity. Even the hindrance effect of the *ortho*-position substituent group didn't influence reaction results (**40–41**), including 2-naphthyl-phenyl alkyne (**42**). Additionally, the electron-donating or withdrawing substitutions on the acetonitrilyl phenyl ring was compatible under standard conditions (**43–45**). Furthermore, the structure of 1-boryl-2-aryl-3-naphthylamine **36** was confirmed by X-ray analysis (CCDC: 2265345†); interestingly, single-crystal analysis of **36** showed phenyl and dioxaborolane rings are all vertical with naphthyl planes, and a formal dihedral angle existed between the adjacent two groups. Regretfully, aryl–alkyl alkynes failed in the cyclizative carboboration reaction for a special electronic effect.

To exhibit the practicality of this strategy, a gram-scale synthesis was performed under β-selective *trans*-hydroboration

Table 2 Substrates scope of the β-*trans*-hydroboration reaction

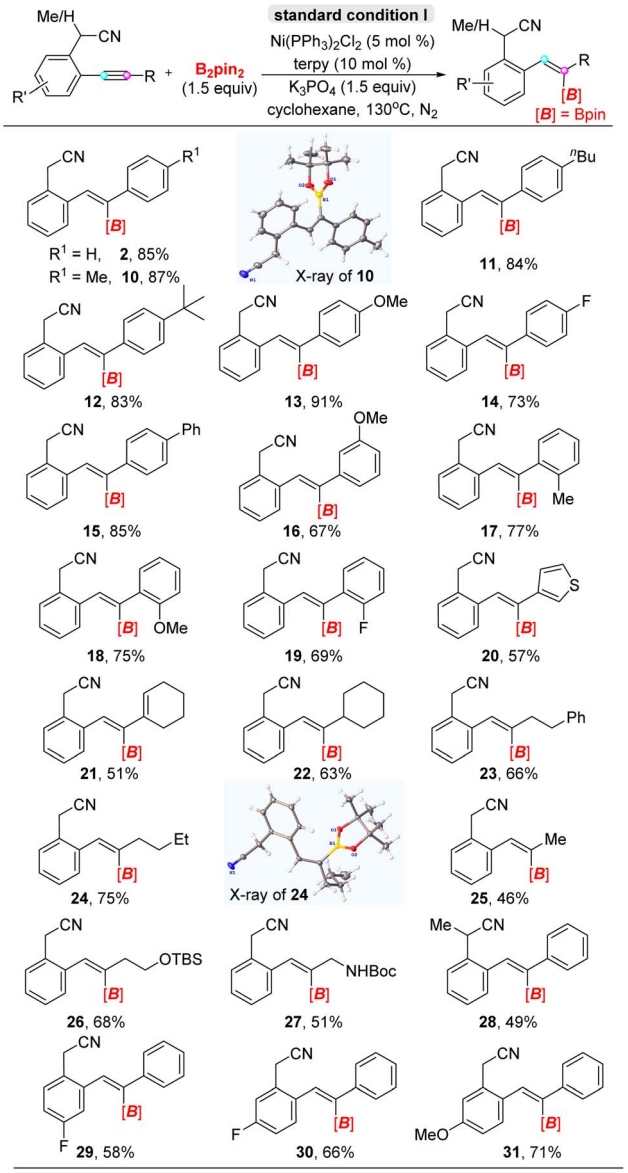
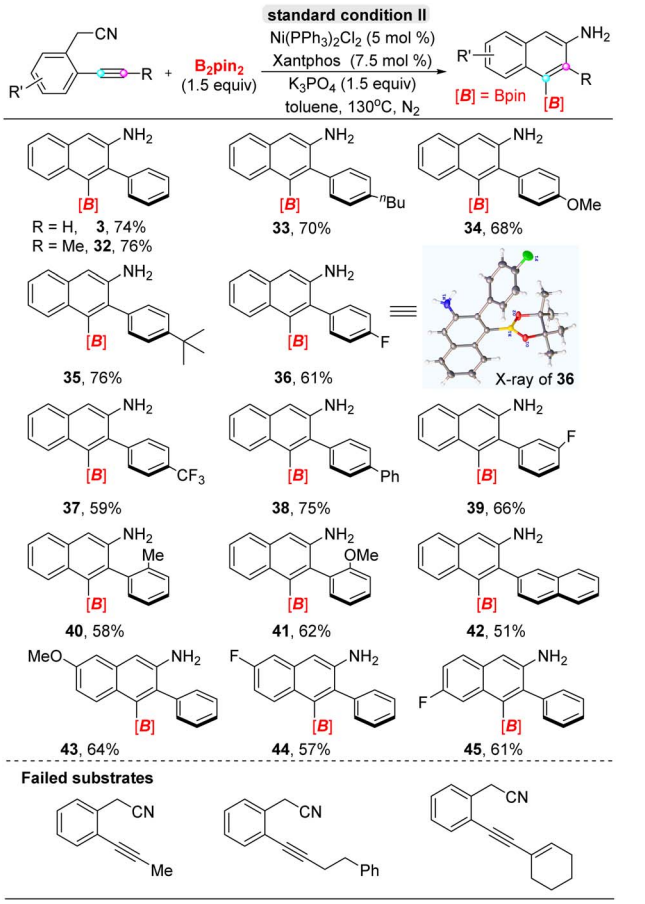
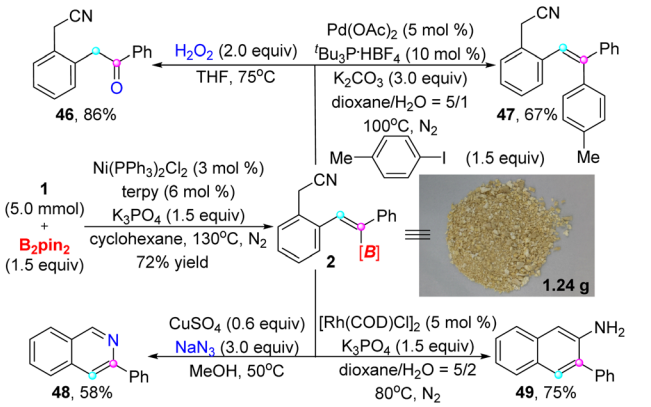


Table 3 Substrates scope of the α-*trans*-carboboration reaction

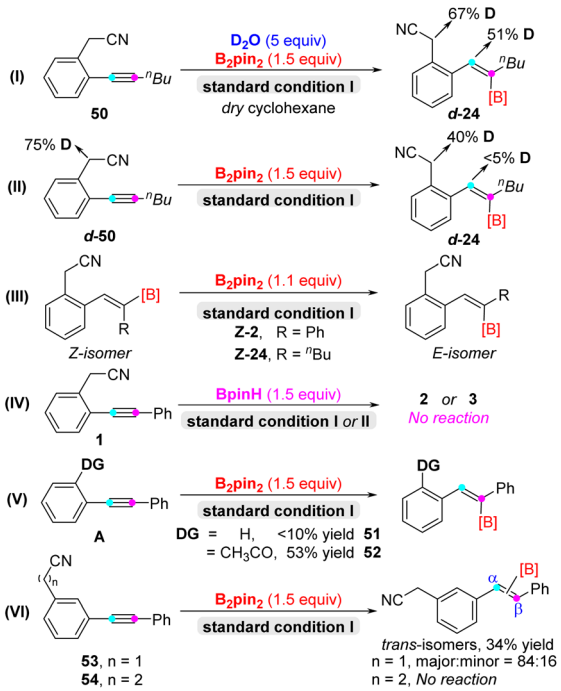




Scheme 2 Gram-scale reaction and the transformation of alkenyl boronate product **2**.

standard conditions with lower amounts of catalyst (3 mol%) and ligand (6 mol%) (Scheme 2). In view of the importance of alkenyl boronate in organic synthesis, we conducted some further transformations on the target product. As the examples show, **2** could be smoothly converted to a ketone (**46**) and polysubstituted alkene (**47**) *via* oxidation and cross-coupling processes. Intriguingly, 3-phenyl isoquinoline (**48**) instead of alkenyl azide was generated under the reaction of alkenyl boronate **2** with NaN_3.[15] Moreover, 2-amino-3-phenylnaphthalene (**49**) was acquired through an approach of rhodium catalysis.

Next, in order to gain insight into the detailed reaction mechanism, a series of control experiments were conducted (Scheme 3). Firstly, there was 51% proportion of deuterium detected at the double bond of **d-24** and 67% proportion of deuterium detected in the activated methylene of **d-24**, indicating that water was the hydrogen source in the deuterium labeling experiments (eqn (I)). Meanwhile, deuterated starting materials **d-50** locating in the position of activated methylene delivered the desired product **d-24** without deuterium labeling in the double-bond position (eqn (II)). Furthermore, the *Z*-isomer of diaryl alkenyl boronate ***Z*-2** and ***Z*-24** couldn't transform into the corresponding *E*-isomer under the standard conditions I (eqn (III)).[16] Additionally, BpinH was not suitable



Scheme 3 Control experiments.

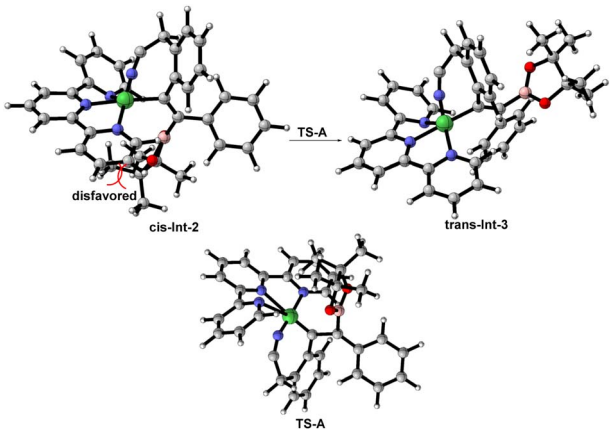
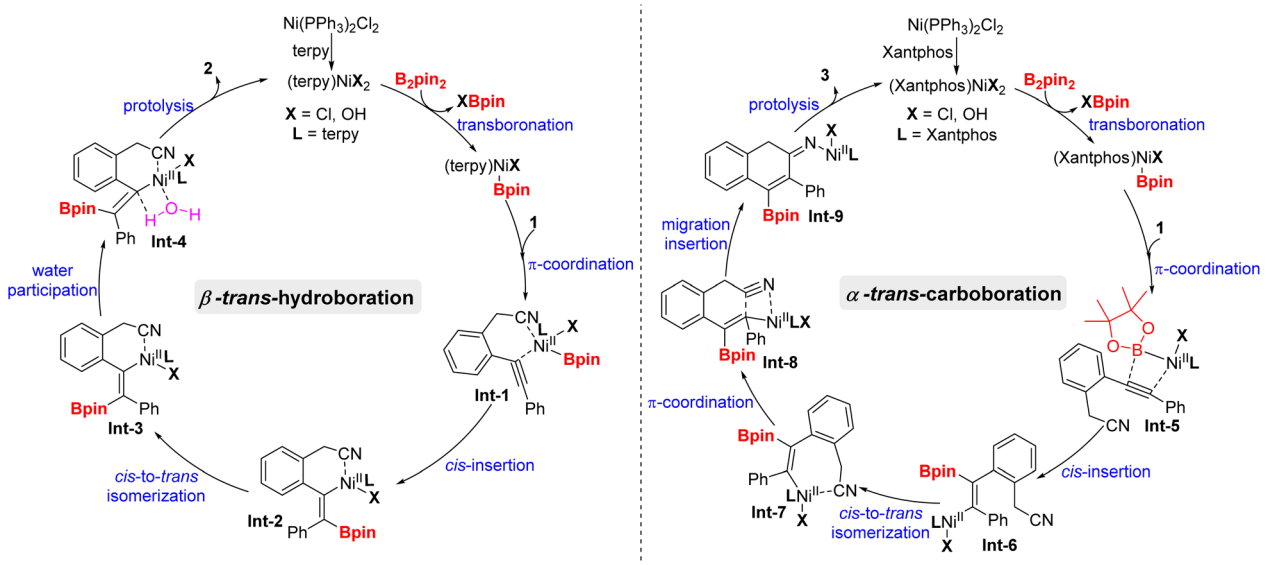


Fig. 1 DFT calculation to investigate *cis*-to-*trans* isomerization.

for the hydroboration and carboboration reactions instead of B_2pin_2 (eqn (IV)). Based on the above results, nickel hydride species could be ruled out in the hydroboration/carboboration process.[17] In order to assess the importance of the directing group, diphenyl acetylene afforded the target product **51** with very low efficiency. And 2-acetyl diphenyl acetylene could convert into alkenyl boronate product **52** with 53% yield, since ketone may act as the directing group (eqn (V)). Last but not least, *meta*-CH_2CN diphenyl acetylene **53** could convert into α/β-*trans*-isomers with the ratio of 84 : 16 in major/minor (see details in the ESI†),[18] and *meta*-propionitrile diphenyl acetylene **54** was unreactive under the standard conditions II, and exhibited poor regioselectivity and reactivity, respectively (eqn (VI)).

On the basis of the experimental results as well as previous reports,[19] a plausible mechanistic pathway for the *trans*-hydroboration is tentatively proposed in Scheme 4 (left). Initially, $Ni(PPh_3)_2Cl_2$ exchanges the phosphorus ligand with terpy to afford new nickel species (Bpin)Ni(terpy)Cl, that undergoes transmetalation with B_2pin_2 to generate (Bpin)Ni(terpy)Cl. Then, **Int-1** is obtained through the coordination of (Bpin)Ni(terpy)Cl with the alkyne and cyano group of substrate **1** and experiences a *cis*-insertion process to deliver alkenylnickel species **Int-2**. Noticeably, reversible *cis*-to-*trans* isomerization between **Int-2** and **Int-3** is essential for the formation of *trans*-hydroboration. Finally, water-participation protolysis reaction of **Int-3** gives the target **2** and releases the active nickel species $(terpy)NiCl_2$. Furthermore, the mechanism of *cis*-to-*trans*



Scheme 4 Plausible mechanistic pathways.

isomerization may involve the intermediacy of zwitterionic carbene-type species **TS-A** according to primary DFT calculation (Fig. 1). Meanwhile, ***trans*-Int-3** is more stable than ***cis*-Int-2** due to removal of the huge steric-hindrance between the Bpin and tpy ligand, that may be the inherent driving force for selective formation of the *trans*-isomer (see details in the ESI†).[20]

On the other hand (Scheme 4, right), when the nitrogen ligand terpy was replaced with phosphine ligand xantphos, the similar nickel complex (Bpin)Ni(Xantphos)Cl coordinates with substrate **1** without the aid of the cyano group due to the stronger coordination and steric hindrance effect of xantphos. Next, *cis*-nickelboration of **Int-5** produces α-alkenyl borate **Int-6**, that undergoes *cis*-to-*trans* isomerization with the induction of the cyano group. Spontaneously, migration insertion of alkenyl nickel to the carbon–nitrogen triple bond in **Int-7** of the cyano group generates cyclizative intermediate **Int-9**. Lastly, the successive protolysis and imine isomerization process of **Int-9** produce the 1-boryl-2-aryl-3-naphthylamine product **3**.

Conclusions

In conclusion, we have successfully developed a facile and efficient approach for the synthesis of high-value alkenyl and 1-naphthyl boronates with high stereo- and regioselectivity *via* ligand-controlled Ni-catalyzed *trans*-hydroboration/carboboration of unactivated internal alkynes. In the case of carboboration of alkynes, the cyano group played dual roles of directing group and reaction partner, delivering synthetically useful 1-boryl-2-aryl-3-naphthylamines. The detailed mechanism suggested that Ni-Bpin species should be the key intermediate and *cis*-to-*trans* isomerization of the alkenyl nickel intermediate was a crucial procedure for the unusual stereoselectivity. This system provides a potentially powerful strategy to access the *trans*-boration reaction of alkynes that may find applications in other *trans*-functionalization processes of internal alkynes.

Data availability

General information, detailed experimental procedures, characterization data for all new compounds, NMR spectra, and X-ray crystallographic data are provided in the ESI.†

Author contributions

J. Huang and C. Li conceived the idea. J. Huang and X. Li directed the project. Z. Chen, T. Liu and B. Nie performed the experiments. J. Huang and B. Nie wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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