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Radical *trans*-Hydroboration of Alkynes with N-Heterocyclic Carbene BoranesMasaki Shimoi,^[a] Takashi Watanabe,^[b] Katsuhiro Maeda,^[a,c] Dennis P. Curran,^{*,[d]} and Tsuyoshi Taniguchi^{*,[a,b]}

Abstract: Hydroboration of internal alkynes with N-heterocyclic carbene boranes (NHC-boranes) occurs to provide stable NHC-(*E*)-alkenylboranes upon thermolysis in the presence of di-*tert*-butyl peroxide. The (*E*)-isomer results from an unusual *trans*-hydroboration, and the *E/Z* selectivity is typically high (90:10 or greater). Evidence suggests that this hydroboration occurs by a radical chain reaction involving addition of an NHC-boryl radical to an alkyne to give a β -NHC-borylalkenyl radical. Ensuing hydrogen abstraction from the starting NHC-borane provides the product and returns the starting NHC-boryl radical. Experiments suggest that the observed *trans*-selectivity results from kinetic control in the hydrogen transfer reaction.

Hydroboration of multiple bonds is a fundamental method for synthesis of organoboron compounds.^[1] Hydroborations of alkynes with trivalent boranes provide synthetically useful alkenyl boron compounds, but only *cis*-adducts are readily accessible. This is because typical trivalent boranes induce concerted hydroboration in a *syn*-selective manner.^[2] Direct hydroboration of alkynes in an *anti*-selective fashion is usually called *trans*-hydroboration. This is an attractive complement classical *cis*-selective hydroboration, but examples are sparse.

Several examples of transition-metal-catalyzed *trans*-hydroborations of alkynes have been reported since Miyaura and co-workers first reported rhodium- and iridium-catalyzed *trans*-hydroborations of terminal alkynes in 2000 (Figure 1a).^[3] In 2016, Wang reported that a combination of 2-alkynylpyridines and 9-borabicyclo[3.3.1]nonane (9-BBN) caused *trans*-hydroboration without a catalyst (Figure 1b).^[4a] This is an example of a directed *trans*-hydroboration. Quite recently, Ohmiya and Sawamura reported phosphine-catalyzed *trans*-hydroboration of alkynoates

and their derivatives.^[4b] Similarly, the selectivity is directed by coordination of substrates to a boron atom.

Also in 2016, Ingleson reported that reactions of N-heterocyclic carbene (NHC) complexes of 9-BBN with terminal alkynes and $B(C_6F_5)_3$ provided *trans*-hydroboration products (Figure 1c).^[5] These reactions are thought to occur by hydride abstraction by $B(C_6F_5)_3$ to give an NHC-9-BBN borenium ion. This adds electrophilically to the alkyne followed by back hydride transfer. The 9-BBN borenium ion lacks B–H bonds so the usual *syn*-hydroboration path is unavailable. Borenium ions formed from simpler N-heterocyclic carbene boranes (NHC-BH₃) also hydroborate alkynes, but by the *syn*-addition pathway.^[6]

Radical-mediated hydroboration processes are conceptually appealing because they may offer different regio- or stereoselectivities. But such processes are not practical for most kinds of boranes both because ionic hydroborations are already fast and because most kinds of B–H bonds are too strong to undergo radical hydrogen transfer reactions. In contrast, NHC-boranes do not thermally hydroborate unstrained alkynes. And they are good precursors of boryl radicals because their B–H bond dissociation energies are lower than either free boranes or typical borane complexes with ethers, amines and sulfides.^[7]

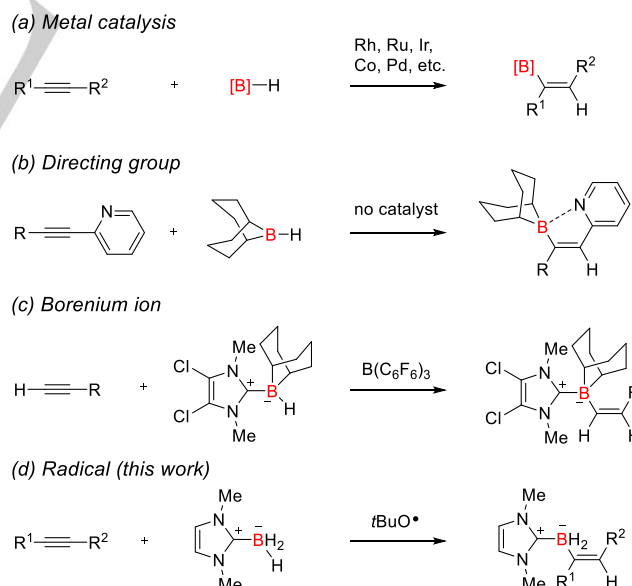


Figure 1. Methods for *trans*-hydroboration of alkynes.

Recently, we disclosed radical borylation-cyclization reactions of strained cyclic diynes with NHC-boranes.^[8] Likewise, Wang and co-workers reported radical borylation-cyclization reactions of enynes with NHC-boranes and thiols as polarity

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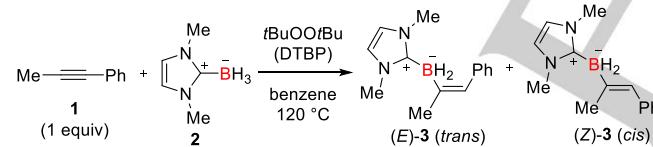
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reversal reagents.^[9] These reactions can be viewed as hydroboration reactions that are interrupted by a radical cyclization. In these cases, stereoselectivity of resultant cyclic alkenes is not of interest because only a geometry is possible in such five- or six-membered ring compounds. We set out to learn whether direct radical 1,2-hydroboration reactions of alkynes were possible, and if so, whether these reactions were stereoselective.

Here we report that radical hydroboration of alkynes with NHC-boranes is achieved by heating with di-*tert*-butyl peroxide (Figure 1d). This reaction is a new approach to *trans*-selective hydroborations of alkynes without the need for a catalyst or a directing group.

We initially studied the reaction of 1-phenyl-1-propyne (**1**) and 1,3-dimethylimidazol-2-ylidene borane (**2**) as a model. Di-*tert*-butyl peroxide (DTBP) was chosen as a radical initiator because the *tert*-butoxyl radical rapidly abstracts hydrogen atoms from NHC-boranes to form boryl radicals.^[7c,8] A benzene solution of alkyne **1** (0.2 mmol), NHC-borane **2** (2 equiv), DTBP (1 equiv) was heated at 120 °C. Alkyne **1** was mostly consumed after 16 h, and ¹H and ¹¹B NMR analyses of the crude product indicated production of two hydroborated isomers in 44% total yield and in high selectivity (94:6) (Table 1, Entry 1). The products were separated by silica gel chromatography, and they turned out to be stereoisomers (rather than regioisomers). Both products **3** are β-NHC-boryl styrenes and NOE experiments showed that the (*E*)-**3** predominates. This results from *anti*-addition of the NHC-boryl group and a hydrogen atom. In other words, *trans*-selective hydroboration occurs.

Table 1. Reactions of 1-phenyl-1-propyne (**1**) and diMe-lmd-BH₃ (**2**).^[a]



Entry	2 [equiv]	DTBP [equiv]	Time [h]	Yield [%] ^[b]	Ratio [<i>E</i> / <i>Z</i>] ^[b]
1	2	1	16	44	94:6
2	2	1.5	7	47	95:5
3	4	1	16	60	91:9
4	4	1.5	5	70 [66] ^[c]	94:6
5	5	1.5	5	73	93:7
6	4	0.5 ^[d]	1	52	94:6
7	4	1.5	24	53	48:52

^[a]Conditions: **1** (0.2 mmol), **2** (0.4–1.0 mmol), DTBP (0.2–0.3 mmol) in benzene (0.4 mL) at 120 °C in a sealed tube. ^[b]Total yield and ratio of (*E*)- and (*Z*)-**3** estimated by ¹H and ¹¹B NMR analysis of the crude product (internal standard for ¹H NMR: dimethyl sulfone). ^[c]Yield of (*E*)-**3** isolated by silica gel chromatography (0.2 and 1.0 mmol scales). ^[d]Di-*tert*-butyl hyponitrite (TBHN) was used instead of DTBP at 80 °C.

The use of an increased amount of DTBP (1.5 equiv) accelerated the reaction, and the use of an increased amount of DTBP NHC-borane **2** improved the yield of **3** (Entries 2–4). The pure *trans*-hydroboration product (*E*)-**3** was isolated in 66% yield in the reaction using 4 equiv of **2** and 1.5 equiv of DTBP (Entry 4). Similar results were obtained in larger scale experiments (see the Supporting Information). Further increase in the amount of NHC-borane **2** did not improve the results (Entry 5). In all cases, the high *E*-selectivity was observed.

When di-*tert*-butyl hyponitrite (*t*BuON=NO*t*Bu, TBHN) was used as an initiator in place of DTBP, the reaction was complete with lower loading of the initiator (0.5 equiv) and at lower temperature (80 °C) (Entry 6). However, DTBP is an inexpensive commercial reagent so we used it in the preparative experiments going forward unless otherwise noted.

The hydroboration reaction of **1** affords surprisingly high *trans*-selectivity given the high reaction temperature (120 °C). We conducted three experiments to shed light on the origin of this selectivity. First, a reaction similar to that in entry 4 was assessed by ¹¹B NMR after 30 min and showed an *E/Z* selectivity of 95:5 (see the Supporting Information). Thus, there is little selectivity change between 30 min (95:5) and 5 h (94:6). Second, a similar reaction was continued for about 19 h after the starting alkyne **1** was consumed (24 h total time, Entry 7). This resulted in a decreased total yield of **3** (from 70% to 53%) and a decreased *E/Z* ratio (from 94:6 to 48:52). The decreased yield must result from slow decomposition, but the change in *E/Z* ratio cannot be accounted for by selective decomposition of the *E*-isomer. This means that some isomerization has occurred upon extended reaction and accordingly that initial 95:5 ratio is not the thermodynamic product ratio. Finally, third, no isomerization was observed when a benzene solution of isolated (*E*)-**3** and NHC-borane **2** was heated for 24 h at 120 °C in the absence of DTBP. This indicates that (*E*)-**3** is thermally stable, and therefore that radicals are involved in the isomerization process (see the Supporting Information for a proposed mechanism).

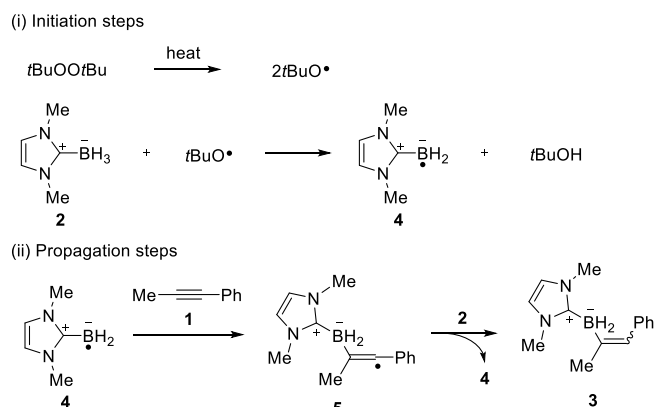
Taken together, these results suggest that the predominate formation of the *E*-isomer is a kinetically controlled result. Radical isomerization to the *Z*-isomer can occur at long reaction times but is inefficient.

Scheme 1 shows a radical chain mechanism that is consistent with these results. To initiate the chain, DTBP thermolyzes to *tert*-butoxyl radical (*t*BuO•), which in turn abstracts a hydrogen atom from NHC-borane **2** to form NHC-boryl radical **4** [step (i)].^[7d] In the first propagation step, the boryl radical **4** adds to alkyne **1** to form an alkenyl radical **5** stabilized by the phenyl ring [step (ii)]. This step dictates the regioselectivity. In the second propagation step, a hydrogen transfer reaction between alkenyl radical **5** and NHC-borane **2** gives (*E*)- and (*Z*)-**3** and the starting NHC-boryl radical **4**.^[8] This step is kinetically controlled and dictates the stereoselectivity.^[10] The fact that stoichiometric amounts of the initiator are helpful suggests that chain lengths in these reactions are rather short.

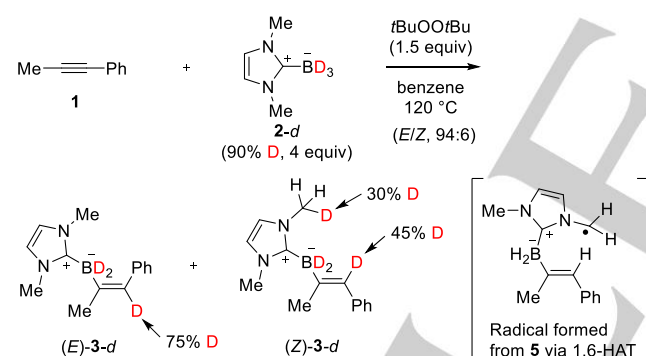
When the reaction of alkyne **1** with NHC-BD₃ **2-d** (90% D) was conducted under the standard conditions, a deuterium atom was incorporated on the alkene of both isomers of hydroboration

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product **3** (Scheme 2). This supports the step (ii) shown in Scheme 1. The 75% D incorporation of (*E*)-**3-d** can be rationalized by a kinetic isotope effect due to 90% D purity of the deuterated NHC-borane. On the other hand, 45% D incorporation on the olefin of (*Z*)-**3-d** was observed, and a hydrogen atom of an NHC-methyl group was partially replaced with a deuterium atom (30% D). This suggests that the (*Z*)-isomer is partially formed via 1,6-hydrogen atom transfer (HAT) of radical **5** onto an NHC-methyl group.^[11] Overall, these results are consistent with the radical mechanism shown in Scheme 1.



Scheme 1. Proposed reaction mechanism.



Scheme 2. Reaction of **1** with NHC-BD₃.

Compare the reaction of **1** and NHC-borane **2** with standard hydroborations of **1**. For example, hydroboration of **1** with 9-BBN (at room temperature in THF) provides the α -boryl styrene isomer as the major product, though the α/β regioselectivity is modest (65/35).^[12] Of course both products are *Z*-isomers resulting from *cis*-hydroboration. Borane itself gives more α -isomer than 9-BBN, whereas some bulky boranes give more β -isomer. Such boranes are air-sensitive and must be converted in situ to other products. In contrast, radical hydroboration of **1** with NHC-borane **2** needs high temperature but gives almost only the β -NHC-boryl styrene regioisomer with good *E*-selectivity.^[13] This *trans*-hydroboration product is not air- or moisture sensitive.

Preparative experiments with other representative NHC-borane reagents were conducted under the standard conditions (Table 1, Entry 4), and Figure 2 shows the products and isolated yields. All products were separable and stable, and the isolated yields are for the pure *E*-isomers. Small amounts of *Z*-isomers were formed, and the *E/Z* ratios taken from the ¹H and ¹¹B NMR spectra of the crude products are also reported.

The reactions of alkyne **1** with 1,4-dimethyl-1,2,4-triazolium-5-ylidene borane and 1,3,4,5-tetramethylimidazol-2-ylidene borane were faster than those of **2** and gave the corresponding hydroboration products **6** and **7** in similar yields (63% and 67%) and *E/Z* ratios (90:10 and 96:4). When 4,5-dichloro-1,3-dimethylimidazol-2-ylidene borane was used, alkyne **1** was gradually consumed over 9 h, but a complex mixture resulted. ¹H and ¹¹B NMR analyses of the crude product suggested decomposition of the starting borane or products, and hydroboration product **8** was hardly detected. The reaction with 1,3-diisopropylimidazol-2-ylidene borane was extremely sluggish and afforded only a trace amount of the corresponding hydroboration product **9**. Accordingly, the hydroboration reaction might be sensitive to sterics and small N-substituents are preferred on the NHC ring. On the other hand, we cannot rule out promotion of 1,6-hydrogen atom transfer on an N-isopropyl (Scheme 2), which breaks the radical chain reaction by formation of a stable tertiary radical. Tetra-*n*-butylammonium cyanoborohydride (*n*Bu₄NBH₃CN) can mediate radical reactions such as reductive dehalogenation,^[14] but little hydroboration product **10** was detected in a reaction between *n*Bu₄NBH₃CN and **1**.

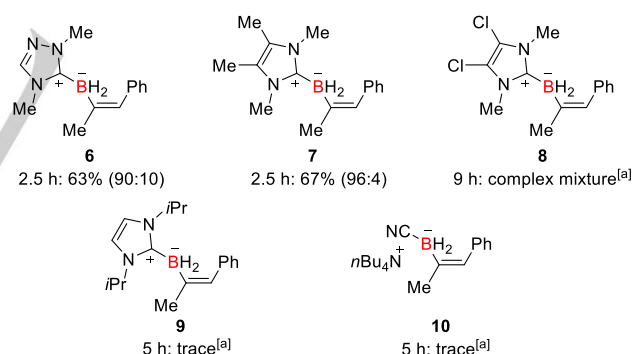


Figure 2. Results of reactions of 1-phenyl-1-propyne (**1**) and several boranes. Reaction conditions: **1** (0.2 mmol), borane (0.8 mmol), DTBP (0.3 mmol) in benzene (0.4 mL) at 120 °C in a sealed tube. Yields of the isolated (*E*)-isomer are shown unless otherwise noted. Ratios of *E/Z* estimated by ¹H and ¹¹B NMR analysis of the crude product are shown in parentheses. ^[a]Results from ¹H and ¹¹B NMR analysis of the crude product.

Figure 3 shows additional examples of radical hydroboration products from reactions of various alkynylarene derivatives with NHC-borane **2**. The standard conditions were used, and reaction times typically ranged from 5–11 h. The *E/Z* ratios are of the crude products, whereas the percentage yields are of the *E*-isomers only. Few α -isomers were detected in most cases.^[13] All the products are bench-stable compounds. NHC-borane **2** is

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readily available, but it can be easily recovered during flash chromatography if desired.

The reactions of representative 1-aryl-1-propyne derivatives provided the corresponding *trans*-hydroboration products **11–18** in yields ranging from 50 to 75% with selectivities typically ranging from 90:10 to 98:2.

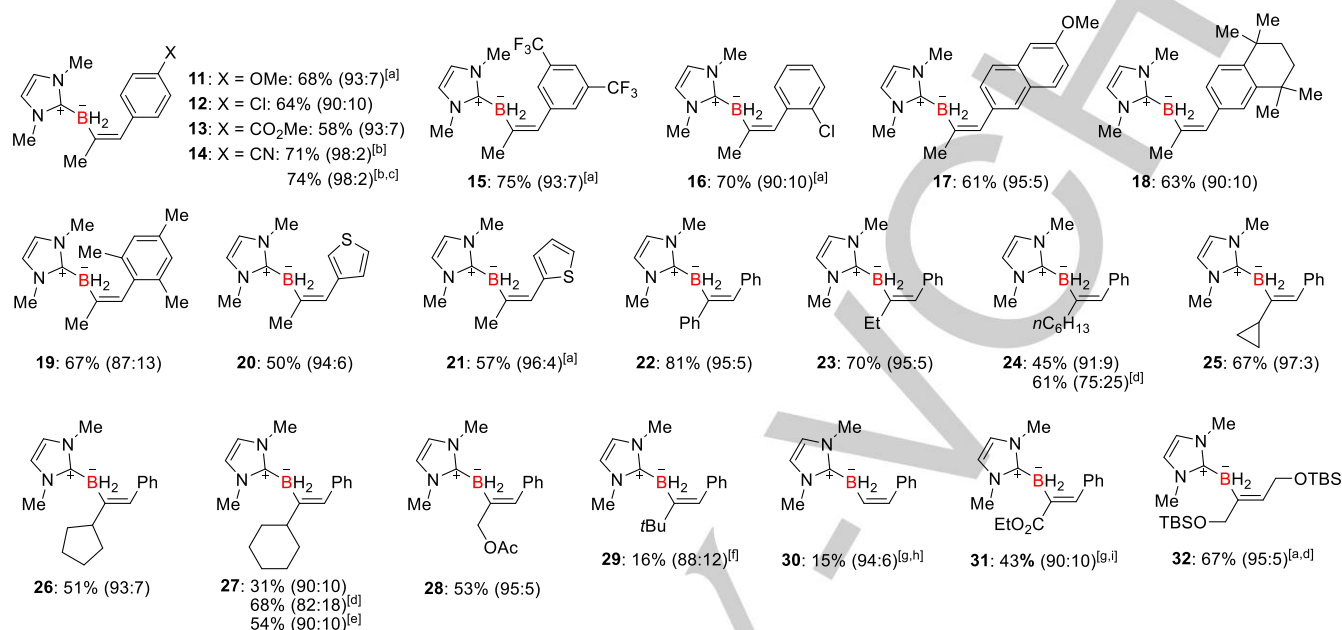


Figure 3. Reactions of various alkynes and diMe-lmd-BH₃ (**2**). Reaction conditions: Alkyne (0.2 mmol), **2** (0.8 mmol), DTBP (0.3 mmol) in benzene (0.4 mL) for 2–24 h at 120 °C in a sealed tube. Yields of the isolated (*E*)-isomer are shown unless otherwise noted. Ratios of *E/Z* estimated by ¹H and ¹¹B NMR analysis of the crude product are shown in parentheses. ^[a]Shown (*E*)-isomers were inseparable from small amounts of (*Z*)-isomers by silica gel chromatography, so yields of the (*E*)-isomers estimated from ¹H and ¹¹B NMR spectra of the isolated mixture are shown (combined yields of inseparable isomeric mixtures: **11**: 72%; **15**: 80%; **16**: 78%; **21**: 59%, **32**: 71%). ^[b]TBHN (0.2 equiv) was used instead of DTBP at 80 °C. ^[c]The reaction was carried out in a flask on a 2.0 mmol scale. ^[d]*tert*-Dodecanethiol (20 mol%) was used as an additive. ^[e]8 equiv of **2** (1.6 mmol) was used. ^[f]Regioisomers were produced in 15% yield. ^[g]Yield was estimated by ¹H NMR analysis of the crude product (internal standard: dimethyl sulfone). ^[h]2,4-diphenylbuta-1,3-dien-1-ylborane derivatives were detected in ¹H NMR spectra of the crude product. ^[i]TBHN (0.5 equiv) was used instead of DTBP at 80 °C. TBS = *tert*-butyldimethylsilyl.

The reaction of an alkynylarene with a cyano group was complicated at high temperature, but the reaction at 80 °C in the presence of TBHN (0.2 equiv) gave radical hydroboration product **14** in high *trans*-selectivity on 0.2 and 2.0 mmol scales.^[15] The analogue having a bulky mesityl group gave slightly lower selectivity (87:13), but the starting alkyne was fully consumed in 5 h to give hydroboration product (*E*)-**19** in 67% yield.

Substrates having a thiophene ring worked well and afforded alkenylboranes **20** and **21**. The reactions of representative 2-substituted phenylacetylenes gave the corresponding *trans*-hydroboration products **22–28** in high selectivity (90:10–97:3). These results indicate that *trans*-selectivity is independent of 2-substituted groups of alkynes. The cyclopropyl ring in product **25** remains intact. The yield of alkenyl borane **27** having a cyclohexyl group was moderate (31%), but an increase of NHC-borane **2** to 8 equiv improved the yield to 54%.

The high regioselectivity finally broke down with 2-*tert*-butyl-1-phenylacetylene. This reaction was sluggish (24 h) and gave the usual β-NHC-boryl styrene **29** in 16% yield along with its α-NHC-boryl regioisomer (not shown) in 15% yield. The *trans*-selectivity, however, was still good (88:12). We also observed moderate regioselectivity in the reactions non-symmetric diaryl and dialkyl alkynes (see the Supporting Information).

The reaction of phenylacetylene was complete in 2 h and afforded a rather complex mixture from which alkenylborane **30** was obtained in 15% yield. Alkene **30** again results from *trans*-hydroboration but is a *Z*-isomer due to a CIP priority change. Side products were tentatively identified as stereoisomers of 2,4-diphenylbuta-1,3-dien-1-ylborane [NHC-BH₂(CH=CPh)₂H] by ¹H NMR analysis of the crude product. These are double adducts to phenylacetylene, which in turn suggests that radical oligomerization competes with this terminal alkyne.^[16]

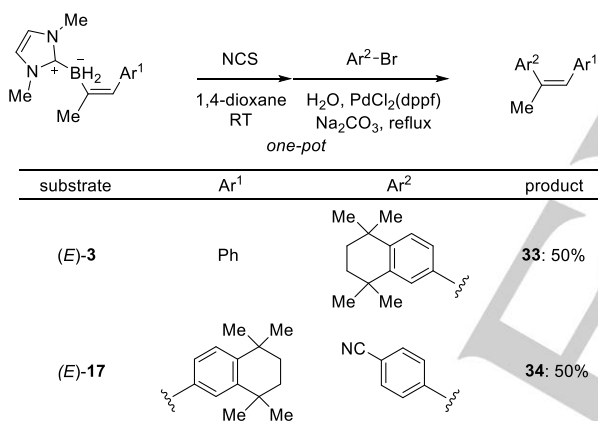
When ethyl 3-phenylpropionate was subjected to the standard conditions, the ionic hydroboration induced 1,4-hydride addition to the alkyne competes with radical hydroboration (see the Supporting Information).^[17] Since the ionic path could be suppressed by lowering the temperature (80 °C), using TBHN as an initiator at lower temperature (80 °C) again gave mainly **31** (90:10) in moderate yield (Figure 3). Yield was estimated by ¹H NMR analysis of the crude product because small amounts of regioisomers were detected (<5% yield) and because products and unreacted **2** were inseparable.

TBS-protected but-2-yne-1,4-diol was less reactive and was not consumed in 24 h. The *trans*-hydroboration product **32** was formed in low yield (<10%). However, we found that addition of 20 mol% of *tert*-dodecanethiol (TDT) as a polarity reversal catalyst

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improved yield (67%) with good *trans*-selectivity (95:5) in 5 h (Figure 3).^[7e] Turning back to conjugated alkynes, the reactions of substrates that gave **24** and **27** in moderate yields (45% and 31%) under the standard conditions gave improved yields of **24** and **27** (61% and 68%) in the presence of 20 mol% of TDT (Figure 3). However, *E/Z* ratios estimated from NMR spectra of crude products were somewhat lower (75:25 and 82:18) probably because an isomerization process was also promoted by TDT in these reactions. The total yields of *E*- and *Z*-isomers were more than 80%. Promotion of reactions by a polarity reversal catalyst suggests that the hydrogen transfer step (to **3** from **5** in Scheme 1) is slow in this reaction like radical dehalogenation with NHCboranes.^[7d]

Examples of preparation of (*E*)-phenylalkenyl boron compounds such as (*E*)-**3** are limited,^[18] and such compounds can be useful for synthesis of 1,2-bisaryl alkenes having a *Z* configuration. To illustrate, we targeted two retinoid mimics having a *Z* configuration. Mimics bearing a 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene ring act on retinoic acid receptors (RARs) and retinoid X receptors (RXRs) and are potential anti-cancer agents.^[19]



Scheme 3. Representative examples of synthesis of trisubstituted alkenes using Suzuki-Miyaura reaction. Conditions (0.1 mmol scale): NCS (2 equiv), 1,4-dioxane (1 mL) for 15 min at room temperature, then H₂O (0.2 mL), aryl bromide (1.3 equiv), PdCl₂(dppf) (5 mol %), Na₂CO₃ (5 equiv) for 3 h at reflux. NCS = *N*-chlorosuccinimide.

(Z)-Retinoid derivative **33**^[18] was synthesized by a one-pot procedure involving treatment of NHC-alkenylborane (*E*-**3** with *N*-chlorosuccinimide (NCS) in 1,4-dioxane (Scheme 3). Water was then added (to form a boronic acid) along with 6-bromo-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene, PdCl₂(dppf) and Na₂CO₃. A Suzuki-Miyaura reaction ensued,^[20,21] and **33** was isolated in 50% yield. The strategy was reversed in the synthesis of cyano analog **34**.^[19] Here the 1,1,4,4-tetramethyl-1,2,3,4-tetrahydro-naphthalene is present in the starting alkenylborane (*E*-**18**. Reaction of this with NCS followed by direct Suzuki-Miyaura coupling with 4-bromobenzonitrile provided **34** is 50% yield. Since NMR spectra of (Z)-1,2-bisaryl alkenes **33** and **34** accorded with those of literature, *trans*-hydroboration of alkyne **1** was synthetically confirmed.

In summary, we have discovered that radical hydroboration of internal alkynes with NHC-boranes is *trans*-selective. Experimental results suggest that this selectivity is due to kinetic control in the hydrogen atom transfer step. The reaction works best with conjugated internal alkynes, which provide good yields of stable (*E*)-NHC-boryl alkenes. From a standpoint of organoboron chemistry, this reaction is a method for synthesis of new boron-containing π -systems. From a standpoint of radical chemistry, this reaction suggests expanded potential for preparative reactions with boron-centered radicals.

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Keywords: Alkynes • Boranes • Hydroboration • Radical reactions • Synthetic methods

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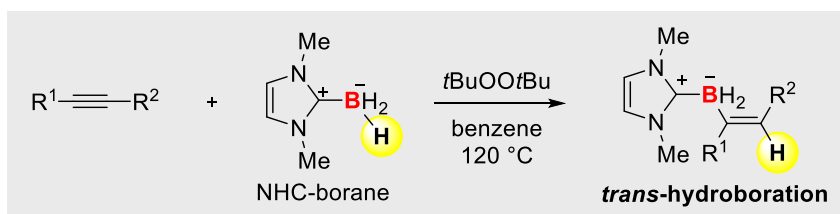
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Radical hydroboration of alkynes with N-heterocyclic carbene boranes (NHC-boranes) has been developed. The reaction occurs in a highly *trans*-selective manner to provide bench-stable NHC-(*E*)-alkenylboranes from internal alkynes.

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Katsuhiro Maeda, Dennis P. Curran,*
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Boranes