Alkene Synthesis

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Haloboration of Internal Alkynes with Boronium and Borenium Cations as a Route to Tetrasubstituted Alkenes**

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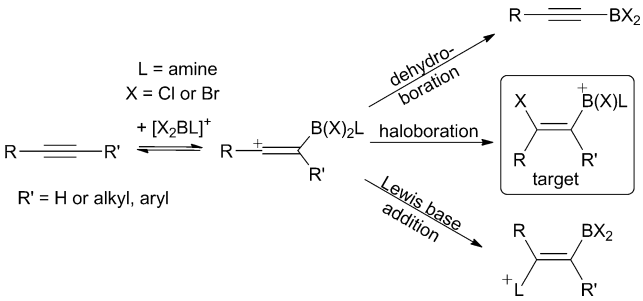
Vinyl boronates are extremely useful precursors, especially for the formation of new C–C bonds by cross-coupling and conjugate addition reactions.[1,2] Although alkyne hydroboration is a powerful synthetic route,[3,4] it is not applicable to the synthesis of trisubstituted vinyl boronates. Thus, alternative regio- and stereospecific methods are needed, particularly for subsequent use in the formation of tetrasubstituted alkenes,[5–7] as the production of these important biologically active compounds as single isomers by classical methods is challenging.[8] One simple approach to trisubstituted vinyl boronates is the functionalization of internal alkynes by metal-catalyzed 1,2-carboboration[9–13] and 1,1-carboboration.[14] The introduction of two selectively transformable moieties onto an internal alkyne should enable ready access to tetrasubstituted alkenes by successive cross-coupling reactions. Significant progress has been made in this area, particularly in the dimetalation of internal alkynes to provide two nucleophilic sites of distinct reactivity.[15–19] The haloboration of internal alkynes is an attractive alternative to dimetalation, as it generates ambivalent synthetic intermediates that contain both a nucleophilic and an electrophilic position.[20] These synthetic intermediates are ideally suited for the diversity-oriented synthesis of tetrasubstituted alkenes. To date, the application of alkyne haloboration with boron trihalides (BX_3) has been limited to terminal alkynes, and has proved an effective route to produce trisubstituted alkenes with excellent regio- and stereoselectivity.[21–25] The haloboration of internal alkynes is unsuccessful with BCl_3, and it is either slow[25] or produces isomeric mixtures susceptible to B–C bond cleavage when BBr_3 is used.[21,26] Recent calculations found that the haloboration of internal alkynes with BCl_3 is endothermic, but as the Lewis acidity of BX_3 increases (Cl < Br < I), haloboration becomes exothermic, and the energy of the key transition state is also reduced.[27] This result suggested that an increase in the electrophilicity at boron beyond that of BX_3 would facilitate the haloboration of internal alkynes.

In the boron analogue of the Friedel–Crafts reaction, three-coordinate $[X_2BL]^+$ borocations (termed borenium cations; X = halide, L = amine)[28,29] were considerably stronger electrophiles towards arene nucleophiles than BX_3.[30,31] Borenium cations were thus expected to be highly reactive towards other π nucleophiles, and a recent report on borenium-ion-catalyzed alkene hydroboration supports this premise.[32] However, when an alkyne and $[X_2BL]^+$ are combined, a range of outcomes are possible beyond the desired alkyne haloboration. By analogy to the reactivity of frustrated Lewis pairs (FLPs),[33] both dehydroboration and Lewis base addition are also feasible (Scheme 1). We envisaged that



Scheme 1. Possible outcomes of the combination of an alkyne with $[X_2BL]^+$.

systems in which the Lewis base coordinates strongly to boron throughout the reaction would favor the haloboration of alkynes, as continuous base coordination precludes the presence of a free base, which is essential for both dehydroboration and Lewis base addition.[30] Herein we report that the borocation-based haloboration of internal alkynes is indeed possible and proceeds with excellent regio- and stereoselectivity. A reaction sequence consisting of successive haloboration, esterification, and cross-coupling is demonstrated as an effective route for the construction of analogues of important tetrasubstituted-alkene drug molecules in isomerically pure form.

We chose 2-(*N*,*N*-dimethylamino)pyridine (2-DMAP) as an ideal amine, as it is inexpensive, strongly nucleophilic, and robust to C–N cleavage reactions.[34] $[X_2B(2\text{-DMAP})][EX_4]$ (X = Cl, E = Al: **1**; X = Br, E = B: **2**) and $[Ph(Cl)B(2\text{-DMAP})][AlCl_4]$ (**3**) were readily synthesized by the sequential addition of 2-DMAP and $AlCl_3$ (or BBr_3) to BX_3 or $PhBCl_2$. In solution (^{11}B NMR resonances $\delta_B = 12.1$ and 16.4 ppm for **1** and **3**, respectively; **2** is insoluble in non-coordinating halogenated solvents) and in the solid state (the

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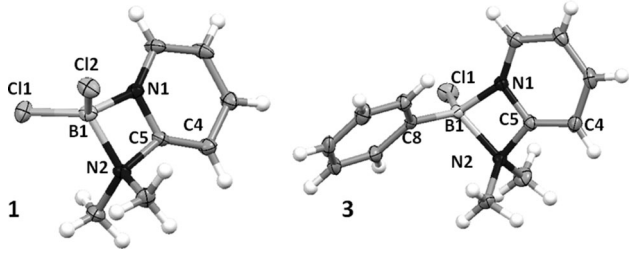


Figure 1. ORTEP representations of the cationic portions of **1** and **3** with ellipsoids drawn at the 50% probability level. Selected bond distances [Å] and angles [°] for **1**: B1–N1 1.567(4), B1–N2 1.697(4); N2-C5-N1 99.1(2), C4-C5-N2 136.5(3); for **3**: B1–N1 1.588(2), B1–N2 1.726(2); N2-C5-N1 100.37(14), C4-C5-N2 135.27(15).

structures of **1** and **3** are shown in Figure 1), the boron center in these compounds is four-coordinate, and 2-DMAP chelation to boron is observed. Coordinative saturation at boron suggested that **1**–**3** may not be viable boron Lewis acids. However, the boracycles in **1** and **3** are significantly strained and contain long Me_2N–B bond distances (1.697(4) and 1.726(2) Å, respectively) relative to those in most boronium cations (N–B ca. 1.60 Å).[28,29] The Me_2N–B distances in **1** and **3** are comparable to those in the strained boronium cation [*N*,*N*′-(9-BBN)-1,8-bis(dimethylamino)naphthalene]$^+$ (B–N 1.72–1.73 Å; 9-BBN = 9-borabicyclo[3.3.1]nonane),[35] which does react as a boron Lewis acid at 20 °C.

A low barrier to ring opening was predicted for **1** by calculations at the M06-2X/6-311G(d,p) (PCM, CH_2Cl_2) level. Experimental confirmation of facile ring opening was forthcoming from the rapid reaction of **1** with PPh_3 at 20 °C to form the boronium cation $[Cl_2B(PPh_3)(2\text{-DMAP})][AlCl_4]$, in which 2-DMAP is now a monodentate ligand. Thus, **1** can be viewed as a masked form of a borenium cation that is an intramolecular FLP, termed $\mathbf{1_{RO}}$. The ring-opened form of **1**, $\mathbf{1_{RO}}$, was calculated to be 12.3 kcal mol^{-1} higher in energy than four-coordinate **1**; thus, a relatively minor modification of the structure to increase the electron density on boron was expected to favor the open-ring isomer. Indeed, [(*o*-catecholato)B(2-DMAP)][$AlCl_4$] (**4**), in which the chloride ligands have been replaced by aryloxy ligands with higher π basicity, does exist in the ring-opened form in solution and in the solid state (Figure 2). Compound **4** has structural

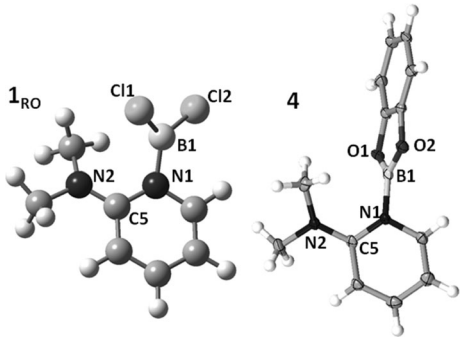
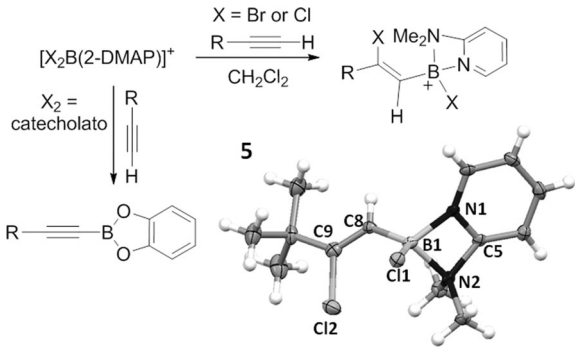


Figure 2. Left: Calculated structure for $\mathbf{1_{RO}}$. Right: ORTEP representation of the cationic portion of **4** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances [Å] for $\mathbf{1_{RO}}$: N1–B1 1.49, N2–C5 1.33; for **4**: N1–B1 1.472(5), N2–C5 1.340(4).

dimensions very similar to those calculated for $\mathbf{1_{RO}}$. In particular, the bond distances are consistent with a significant degree of Me_2N=C and B=N multiple-bond character.

Studies on the reactivity of **1** towards alkynes started with the more reactive terminal alkynes as substrates. Haloboration, dehydroboration, and Lewis base addition were all feasible. The addition of *tert*-butylacetylene (1 equiv) to **1** resulted in the formation of a single product containing a vinylic C–H moiety and a four-coordinate boron center (as determined by ^{1}H and ^{11}B NMR spectroscopy). Confirmation of *syn* haloboration and the expected regiochemical outcome on the basis of electronic and steric factors was provided by single-crystal X-ray diffraction analysis of the product derived from the haloboration of *tert*-butylacetylene, [*cis*-Cl(*t*Bu)C=C(H)(BCl(2-DMAP))][$AlCl_4$] (**5**; Scheme 2). Compound **5** is

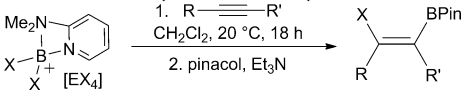


Scheme 2. Haloboration and dehydroboration of terminal alkynes, as determined by the nature of the ligand X. Bottom right: ORTEP representation of the cationic portion of **5** with ellipsoids drawn at the 50% probability level.

stable in solution: after 6 days in dichloromethane, no other haloboration isomers were observed. Compound **1** could be used for the haloboration of two equivalents of a terminal alkyne, and the addition of a further equivalent of *tert*-butylacetylene to **5** also gave the double-haloboration product, [(*cis*-Cl(*t*Bu)C=C(H))$_2$B(2-DMAP)][$AlCl_4$]. The reaction of **3** with alkynes is potentially more complex, since both haloboration and carboboration are feasible through Cl^- or Ph^- migration, respectively.[21,36] In this case, the haloboration of terminal alkynes with **3** occurred exclusively; no carboboration was observed. Compound **3** reacts with only one equivalent of a terminal alkyne, thus precluding a subsequent carboboration step upon the addition of more of the alkyne. The reactivity of **1** and **3** stands in contrast to that of FLPs containing neutral borane Lewis acids. Such FLPs undergo addition of the Lewis base/Lewis acid across the alkyne or dehydroboration.[33,37] As the chelating catechol moiety in **4** precludes anion migration, compound **4** does display FLP-type reactivity. With **4**, exclusive dehydroborylation of alkynes was observed (72 h at 60 °C; Scheme 2, left), with no Lewis base addition products formed.[38]

To probe the scope of the haloboration, we treated a range of terminal alkynes with **1**. In each case, a single *syn*-haloboration isomer was produced (Table 1, entries 1–5). Subsequent esterification to give the corresponding pinacol boronate esters proceeded in good yield with no loss in stereo-/regioisomeric purity. Attempts to expand the reac-

Table 1: Haloboration of alkynes and subsequent esterification.

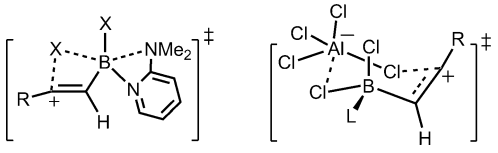


Entry	X/E	R	R′	Yield [%][a,b]
1	Cl/Al	*t*Bu	H	63
2	Cl/Al	Ph	H	88
3	Cl/Al	Pr	H	73
4	Cl/Al	4-BrC_6H_4	H	68
5	Cl/Al	4-MeC_6H_4	H	65
6	Br/B	Pr	H	78
7	Br/B	Et	Et	62
8	Br/B	Me	*i*Pr	52

[a] Yield of the isolated product. [b] The isomeric purity was above 99% in all cases; the alkene geometry was determined by ^{1}H NMR spectroscopy through NOE measurements. Pin = 2,3-dimethyl-2,3-butanedioxy.

tivity of **1** to the haloboration of internal alkynes were unsuccessful. However, the ring-opened form of the bromine analogue, $\mathbf{2_{RO}}$, was expected to be more electrophilic than $\mathbf{1_{RO}}$ and concomitantly more reactive towards alkynes as a result of diminished X→B π bonding. Compound **2** was effective for the haloboration of terminal alkynes (e.g., 1-pentyne; Table 1, entry 6) and also internal dialkyl-substituted alkynes (Table 1, entries 7 and 8). Again, esterification provided the vinyl pinacol boronate esters in good yield. The haloboration of an unsymmetrical dialkyl alkyne (Table 1, entry 8) proceeded with excellent regioselectivity to form a single isomer as a result of synergic steric and electronic control. However, less nucleophilic alkynes, including diaryl and aryl/alkyl-substituted alkynes, did not react with **2**.

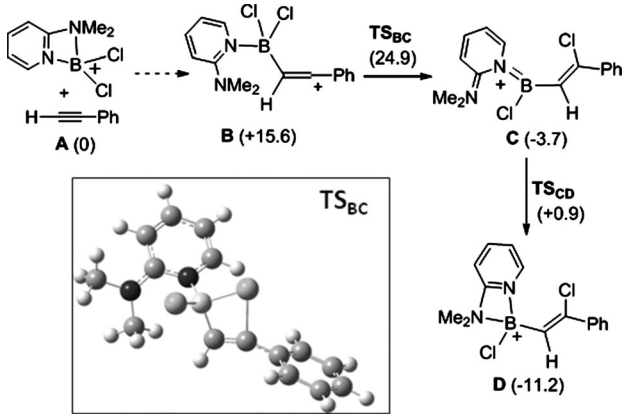
The significant B=$N_{pyridyl}$ character observed in **4** and calculated in the ring-opened borenium-cation forms of **1** and **2** (Figure 2) attenuates the electrophilicity at boron and thus limits the scope of the reaction with respect to the alkyne substrate. The replacement of 2-DMAP with a less nucleophilic amine can be expected to enhance the electrophilicity at boron and thus broaden the scope of the reaction, provided that: 1) halide migration is faster than amine dissociation and subsequent deprotonation or Lewis base addition, and 2) 2-DMAP is not mechanistically crucial. Conceivably, 2-DMAP is only essential if the pendant NMe_2 group facilitates the transfer of a halide to a carbon atom of the alkyne by concomitant chelation to boron (as in Scheme 3, left). The mechanism of haloboration with **1** was therefore probed at the M06-2X/6-311G(d,p) (PCM CH_2Cl_2) level. Calculations were limited to the cationic component and a reaction pathway involving the direct transfer of a chloride from boron to carbon. Chloride transfer mediated by $[AlCl_4]^-$



Scheme 3. Proposed transition states for concerted and anion-mediated haloboration mechanisms.

(through a six-membered transition state; Scheme 3, right) was discounted, as the observed similarity of the reaction profile for the haloboration of terminal alkynes with $[Cl_2B(2\text{-DMAP})][B(3,5\text{-}C_6H_3Cl_2)_4]$ to that with **1** indicated anion independence.

The haloboration of alkynes with BX_3 has been calculated to proceed via a weak van der Waals complex and concerted C–B/C–X bond formation.[27] In contrast, the sequence of elementary steps calculated for haloboration with $[\mathbf{1}]^+$ proceeds via a strongly bonded vinyl-cation intermediate, **B** (Scheme 4). Intermediate **B** was calculated to contain a B–C



Scheme 4. Relative energies (kcal mol^{-1}) in CH_2Cl_2 of intermediates in the haloboration of phenylacetylene with $[\mathbf{1}]^+$. The structure of the transition state $\mathbf{TS_{BC}}$ is also shown.

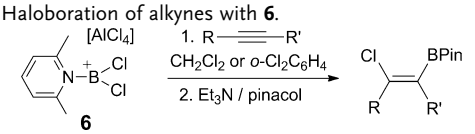
bond and two B–Cl bonds with lengths consistent with single bonds to four-coordinate boron (1.66 and 1.83–1.88 Å, respectively). Importantly, the key transition state for haloboration, $\mathbf{TS_{BC}}$, indicated that the chloride transfer occurs in a separate exothermic step prior to the rechelation of 2-DMAP to boron. These calculations therefore suggest that a pendant base is not essential for chloride transfer; thus, more reactive (than $\mathbf{1_{RO}}$ and $\mathbf{2_{RO}}$) borenium cations containing less nucleophilic amines were explored for haloboration.

The use of our most reactive arene borylating agent, formed from stoichiometric *N*,*N*,4-trimethylaniline (Me_2NTol), BCl_3, and $AlCl_3$,[39] only led to intractable mixtures when combined with terminal alkynes. The combination of Me_2NTol, BCl_3, and $AlCl_3$ produces a complex equilibrium mixture containing both boron and aluminum Lewis acids, and we postulate that the latter lead to undesired reactivity, such as alkyne polymerization. The use of 2,6-lutidine as a bulkier and more nucleophilic amine (as compared to Me_2NTol) ensures that the equilibrium position lies significantly towards the borenium ion $[Cl_2B(2,6\text{-lutidine})][AlCl_4]$ (**6**). Initial reactions between **6** and phenylacetylene confirmed rapid *syn* haloboration and the formation of a single isomer, *cis*-[Cl(Ph)C=C(H)(B(Cl)(2,6-lutidine))]$^+$. The lack of evidence for dehydroboration to form $PhC{\equiv}CBCl_2$ suggests that 2,6-lutidine does not dissociate rapidly from the vinyl-cation intermediate relative to the rate of halide migration. The vinyl chloroborenium cation [Cl(Ph)C=C(H)(B(Cl)(2,6-lutidine))]$^+$ is, to the best of our

knowledge, the first example of a boron analogue of an allyl cation.

Pleasingly, **6** displayed significantly broader reactivity than that of **1** and **2**. A range of internal alkynes underwent haloboration with **6**, and subsequent in situ esterification provided the trisubstituted vinyl boronate esters with excellent regio- and stereoselectivity. Substrates suitable for haloboration with **6** included dialkyl- (Table 2, entries 2 and 3), alkyl/aryl- (entries 4–6), and diaryl-substituted internal alkynes (entry 7). Isolated products were all derived from *syn* haloboration and are consistent with electronic effects maximizing the stability of the intermediate vinyl cation (e.g., π delocalisation > hyperconjugation). There was also a significant degree of steric control observed: the haloboration of 1-isopropyl-2-methylacetylene with **6** provided only one regioisomer derived from *syn* addition, with the boron atom at the least-hindered position (Table 2, entry 3). The borenium cation **6** can be prepared in situ from BCl_3/2,6-lutidine/$AlCl_3$ without using a glove box (provided 2,6-lutidine is slowly added to BCl_3, to prevent *ortho*-Me activation);[40] under these conditions, the yields remained respectable (Table 2, entries 5 and 6). Internal haloalkynes are also amenable to haloboration: 1-bromo-2-phenylacetylene underwent haloboration with **6** to provide a functionality-rich alkene (Table 2, entry 8). 2-Methylhexen-3-yne and allylphenylacetylene both underwent *syn*-1,2-haloboration selectively at the alkyne position to form a single product (Table 2, entries 9 and 10). No haloboration of the alkene moiety was observed, in agreement with the relative energetics calculated for haloboration, according to which alkynes are favored over alkenes.[27] The addition of **6** to 1-(2-thienyl)acetylene demonstrated that haloboration of the alkyne occurs in preference to direct borylation of the thiophene α position (Table 2, entry 11). Finally, haloboration with **6** tolerates methoxy groups (Table 2, entry 12), but it is not compatible with carbonyl moieties, as previously observed in direct electrophilic arene borylation.

Table 2: Haloboration of alkynes with **6**.

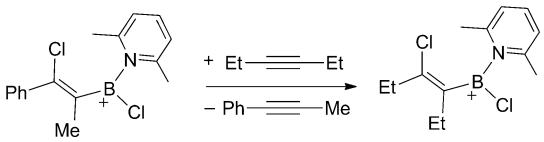


6

Entry	R	R′	*t* [h][a]	Yield [%][b,c]
1	Ph	H	4	71
2	Et	Et	24	81
3	*i*Pr	Me	48	83
4	Ph	Me	8	62
5	Ph	Et	24	72
6[d]	Ph	Et	18	69
7	Ph	Ph	48	43
8	Ph	Br	48	71
9	Et	$C(Me)=CH_2$	48	61
10	Ph	$CH_2CH=CH_2$	4	53
11	2-thienyl	H	48	65
12	4-$MeOC_6H_4$	H	4	52

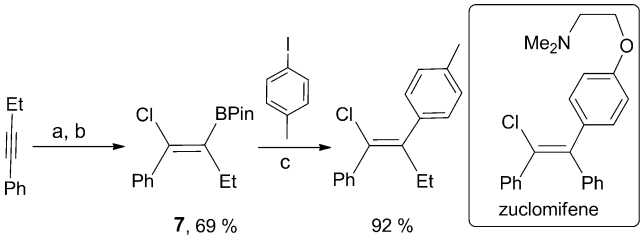
[a] Reaction time before the addition of Et_3N/pinacol. [b] Yield of the isolated product. [c] The isomeric purity was above 99% in all cases; the alkene geometry was determined by ^1H NMR spectroscopy through NOE measurements. [d] Compound **6** was prepared in situ without using a glove box.

Haloboration with **6** appears to be reversible at 20 °C. The addition of a more nucleophilic internal alkyne led to complete displacement (within 6 h at 20 °C) of the less nucleophilic alkyne in a formal retrohaloboration/haloboration process [Eq. (1)]. The vinyl chloroborenium cation formed by the chloroboration of phenylacetylene with **6** was heated to determine whether retrohaloboration and any subsequent dehydroboration occurred to form an alkynyl dichloroborane. However, no dehydroboration, and more remarkably, minimal isomerization (< 5%), occurred at reflux in dichloromethane (for 3 days). The stability to isomerization of the vinyl chloroborenium cations is remarkable and contrasts starkly with the stereoconversion that occurs during haloboration with BX_3 (particularly on heating).[26] Stereoisomerism in alkyne haloboration with BX_3 was calculated to proceed through a second haloboration of the halo boraalkene, followed by retrohaloboration to give mixtures of *cis*- and *trans*-haloborated alkenes.[27] In contrast to haloboration with BX_3, the further haloboration of vinyl chloroborenium cations by **6** will be disfavored owing to Coulombic repulsion between the two cations.



(1)

Vinyl haloboronate esters are potentially versatile precursors for the regio- and stereoselective synthesis of a range of tetrasubstituted alkenes. To confirm their utility, we explored cross-coupling with the vinyl boronate **7**. Pleasingly, Suzuki–Miyaura cross-coupling of **7** with 4-iodotoluene proceeded efficiently in excellent yield to produce only a single isomer of the desired tetrasubstituted alkene (Scheme 5). In this way, an internal alkyne could be converted into a single isomer of a clomifene analogue through a simple and high-yielding two-step route. We also investigated successive Suzuki–Miyaura cross-coupling reactions by first combining **7** with 4-iodotoluene and subsequently coupling the initial product with 4-fluorophenylboronic acid (without the purification of intermediates). Under these nonoptimized conditions, the second cross-coupling step proceeded efficiently, although a minor quantity of a second isomer was produced. The two readily separable isomers of (Ph)(4-



Scheme 5. Synthesis of a tetrasubstituted alkene: a) **6**, CH_2Cl_2, 18 h; b) Et_3N, pinacol, c) $[Pd_2(dba)_3]$ (5 mol%), $PtBu_3$ (20 mol%), KOH (300 mol%), THF/H_2O. dba = dibenzylideneacetone.

FC_6H_4)C=C(Ph)(4-MeC_6H_4) were produced in a 6:1 ratio, presumably the steric demand of P*t*Bu_3 induced *cis–trans* isomerization during cross-coupling, as previously reported.[9b,c]

In conclusion, we have synthesized highly strained 2-DMAP-ligated boronium cations that react as functional boron Lewis acids owing to a low barrier to ring opening. The ring-opened isomers possess sufficient electrophilicity for the selective haloboration of terminal alkynes and bromoboration of dialkyl-substituted internal alkynes. More reactive dichloroborenium cations, readily synthesized from inexpensive reagents, enable the chloroboration of a range of internal alkynes. The regio- and stereoselectivity of haloboration is excellent as a result of synergic steric and electronic control and the absence of stereoisomerization. Overall, this first successful haloboration/esterification of internal alkynes is an inexpensive one-pot method for the production of trisubstituted vinyl pinacol boronate esters. These products are useful precursors for the synthesis of biologically active tetrasubstituted alkenes through sequential cross-coupling reactions.

Experimental Section

Haloboration procedure: Under an inert atmosphere, a solution of 2,6-lutidine (1 equiv) in hexane was added dropwise to a Schlenk tube containing a 1M solution of boron trichloride in heptanes (1.2 equiv) at 0°C, whereupon the (2,6-lutidine)BCl_3 adduct precipitated as a pale yellow-white solid. After 20 min, the solvent was removed under reduced pressure, and (2,6-lutidine)BCl_3 was suspended in *o*-dichlorobenzene or dichloromethane. Aluminum trichloride was added as a solid to this suspension to generate the borocation **6**, and the resulting mixture was stirred for 20 min. The desired alkyne (1 equiv) was then added dropwise, and the reaction mixture was stirred for 18–48 h (see Table 2). On completion of the haloboration reaction, a solution of pinacol (2.1 equiv) in excess triethylamine was added to the reaction mixture. (**Caution**! This reaction is strongly exothermic.) Volatiles were removed under vacuum, and the product was extracted with pentane. Subsequent filtration through a short plug of silica gel removed impurities and provided the vinyl pinacol boronate ester.

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Keywords: borenium ions · boronate esters · haloboration · synthetic methods · tetrasubstituted alkenes

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