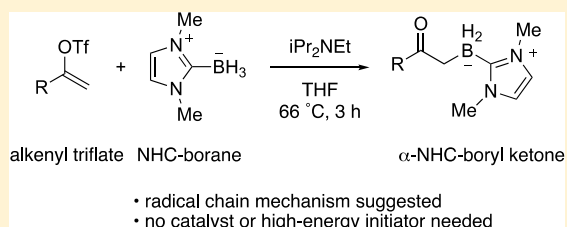


Facile Synthesis of  $\alpha$ -N-Heterocyclic Carbene-Boryl Ketones from N-Heterocyclic Carbene-Boranes and Alkenyl TriflatesWen Dai,<sup>ID</sup> Steven J. Geib,<sup>ID</sup> and Dennis P. Curran<sup>\*ID</sup>

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15208, United States

## Supporting Information

**ABSTRACT:** Reactions of readily available alkenyl triflates with N-heterocyclic carbene (NHC)-boranes in the presence of diisopropyl ethyl amine provided about three dozen stable  $\alpha$ -NHC-boryl ketones. Isolated yields were typically 40–56% for B-unsubstituted NHC-boranes (NHC-BH<sub>3</sub>), and somewhat lower for NHC-boranes with B-substituents (NHC-BH<sub>2</sub>R). The requisite alkenyl triflates can be made separately or prepared in situ from either ketones or alkynes. The experimental evidence supports a radical chain mechanism that involves the following: (1) addition of an NHC-boryl radical to the alkenyl triflate, (2) fragmentation to give the  $\alpha$ -NHC-boryl ketone, SO<sub>2</sub>, and trifluoromethyl radical, and (3) hydrogen abstraction by trifluoromethyl radical from the starting NHC-borane to return the NHC-boryl radical along with trifluoromethane. Reactions 1 and 3 are both new and evidently rather fast.



## INTRODUCTION

Boron enolates of various types are readily available and have a rich chemistry.<sup>1</sup> Until recently, their  $\alpha$ -boryl carbonyl isomers (sometimes called C-boron enolates) have been the poorer cousins of the family. However, that situation is changing.<sup>2</sup>

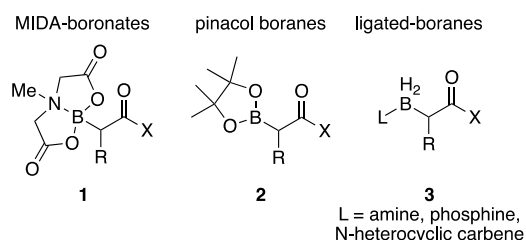
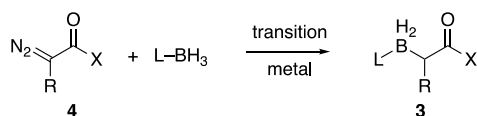
Recent work has shown that strong electron donating substituents on boron tend to favor the  $\alpha$ -boryl carbonyl form, as shown by the examples in Figure 1a. Classes of  $\alpha$ -boryl carbonyls in the boronic acid oxidation state include N-methyliminodiacetic acid (MIDA) boronates **1** and pinacol boranes **2**.<sup>4</sup> In the borane oxidation state, various classes of ligated boranes **3** are known with amine, phosphine, and N-

heterocyclic carbene (NHC) ligands.<sup>5</sup> Trivalent pinacol boranes **2** are moisture sensitive, but the tetravalent species **1** and **3** tend to be robust compounds, stable to air, water, and chromatography.

To date, most ligated  $\alpha$ -boryl carbonyl compounds **3** have been made by transition metal catalyzed B–H bond insertion reactions between  $\alpha$ -diazocarbonyl compounds **4** and ligated boranes (L–BH<sub>3</sub>), see Figure 1b.<sup>5</sup> On the plus side, these are one-step reactions that often give good yields and selectivities due to the hydridic nature of the B–H bonds in L–BH<sub>3</sub>.<sup>6</sup> On the minus side, diazocarbonyl compounds are potentially hazardous, and transition metals catalysts can be expensive.

Recently, we have described reactions between **4** (X = OR) and NHC-boranes that are catalyzed by borenium ions rather than transition metals,<sup>7</sup> and Wang and co-workers have made various benzyl-substituted  $\alpha$ -NHC-boryl esters and amides by radical hydroboration of cinnamic esters and amides.<sup>8</sup> Finally, Zhou and co-workers have introduced gold-catalyzed reactions of carbenes generated from alkynes rather than diazo compounds.<sup>9</sup> These transformations starting from alkynes are oxidative (8-isopropylquinoline-N-oxide is the oxidant) and serve well to make amine–borane analogues of **3** (X = R) but not N-heterocyclic carbene analogues.

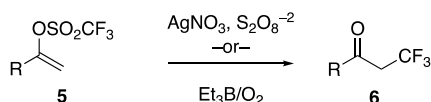
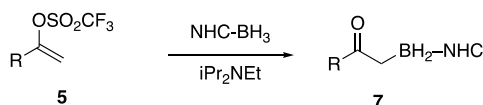
Here we describe a new route to  $\alpha$ -NHC-boryl ketones that does not start from a diazo-carbonyl compound and does not require either a catalyst or an oxidant. This method was inspired by recent independent discoveries of Li<sup>10</sup> and Kamimura<sup>11</sup> that alkenyl triflates **5** rearrange to  $\alpha$ -trifluoromethyl ketones **6** under radical conditions (Figure 2a). (Alkenyl triflates are also commonly called vinyl triflates and

(a) classes of stable  $\alpha$ -boryl carbonyl compounds(b) ligated  $\alpha$ -boryl carbonyl compounds **3** are made by metal-catalyzed B–H insertion reactions of diazocarbonyls and ligated boranesFigure 1.  $\alpha$ -Boryl carbonyl compounds.

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(a) radical rearrangements of enol triflates to  $\alpha$ -trifluoromethyl ketones (Li and Kamimura)(b) interrupting the direct enol triflate reaction with NHC-boranes provides  $\alpha$ -NHC-boryl ketones (this work)**Figure 2.** (a) Known conversion of alkenyl triflates to  $\alpha$ -trifluoromethyl ketones and (b) proposed conversion to  $\alpha$ -NHC-boryl ketones.

enol triflates.) Under Kamimura's conditions, for example, an alkenyl triflate **5** is simply treated with  $\text{Et}_3\text{B}$  and  $\text{O}_2$  to initiate chains. A trifluoromethyl radical ( $\text{CF}_3\cdot$ )<sup>12</sup> is thought to add to **5**, followed by  $\beta$ -fragmentation to give **6**,  $\text{SO}_2$ , and  $\text{CF}_3$ .<sup>13</sup>

We hypothesized that addition of an NHC-borane ( $\text{NHC-BH}_3$ ) to an alkenyl triflate would result in an interrupted reaction wherein an NHC-boryl radical would add to the alkenyl triflate rather than the trifluoromethyl radical, as shown in Figure 2b. Supporting this idea, Kim and co-workers have described interrupted reactions of alkenyl triflates with various ethers and alkanes, which result in  $\alpha$ -alkylation.<sup>14</sup> B–H bonds of NHC-boranes are weaker than most C–H bonds and therefore more prone to abstraction. Still, even if NHC-boryl radicals are formed as projected, it is unclear whether they will add rapidly to alkenyl triflates.

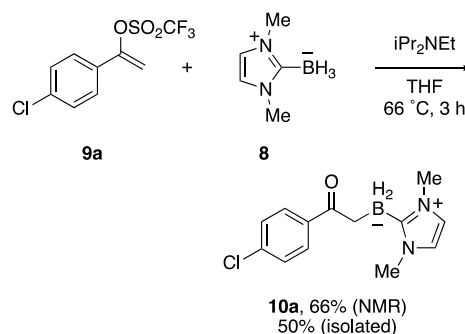
We now report that reactions of alkenyl triflates **5**, NHC-boranes, and diisopropyl ethyl amine provide various stable  $\alpha$ -NHC-boryl ketones **7** in good yields. Evidence suggests that these are radical transformations that occur without the need for a traditional radical initiator.

## RESULTS AND DISCUSSION

The results of preliminary experiments were discouraging. Reactions of NHC-borane **8** and alkenyl triflate **9a** under the conditions of Li<sup>10</sup> ( $\text{AgNO}_3$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $t\text{BuOH}/\text{H}_2\text{O}$ ) provided no target product **10a**. Further, the added NHC-borane spoiled the default reaction—the  $\alpha$ -trifluoromethyl ketone was not formed either. Under Kamimura's conditions<sup>11</sup> ( $\text{Et}_3\text{B}$ , ambient air,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ), the  $\alpha$ -NHC-boryl ketone **10a** was formed, but only in small amounts according to  $^{11}\text{B}$  NMR analysis.

However, we soon found that the target reaction proceeded rather smoothly when all the other reagents were replaced by a simple *tert*-amine (Scheme 1). For example, heating of NHC-borane **8**, alkenyl triflate **9a** (1.3 equiv), and diisopropyl ethyl amine ( $i\text{Pr}_2\text{NEt}$ , 0.8 equiv) in THF at 66 °C for 3 h provided  $\alpha$ -NHC-boryl ketone **10a** in 66% yield according to  $^{11}\text{B}$  NMR analysis of the reaction mixture. Solvent evaporation and flash chromatography provided pure **10a** in 50% yield as a stable white solid.

The results of other optimization experiments with **8** and **9a** are summarized in Table S1 of the Supporting Information. Briefly, various other amines ( $\text{Et}_3\text{N}$ ,  $\text{Bu}_3\text{N}$ ,  $\text{MeN}(c\text{-C}_6\text{H}_{11})_2$ ) gave about the same yield as  $i\text{Pr}_2\text{NEt}$ . The amount of amine could be varied somewhat, but no reaction occurred if it was

**Scheme 1.** Preferred Reaction Conditions for Synthesis of  $\alpha$ -NHC-Boryl Ketone **10a**

omitted. THF was superior to other solvents surveyed ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ , dioxane). A reaction time of about 1–3 h was sufficient; shorter times (<1 h) gave lower yields, and longer times gave about the same yield. Finally, formation of the product **10a** was blocked by addition of the radical inhibitor TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl, 2 equiv).

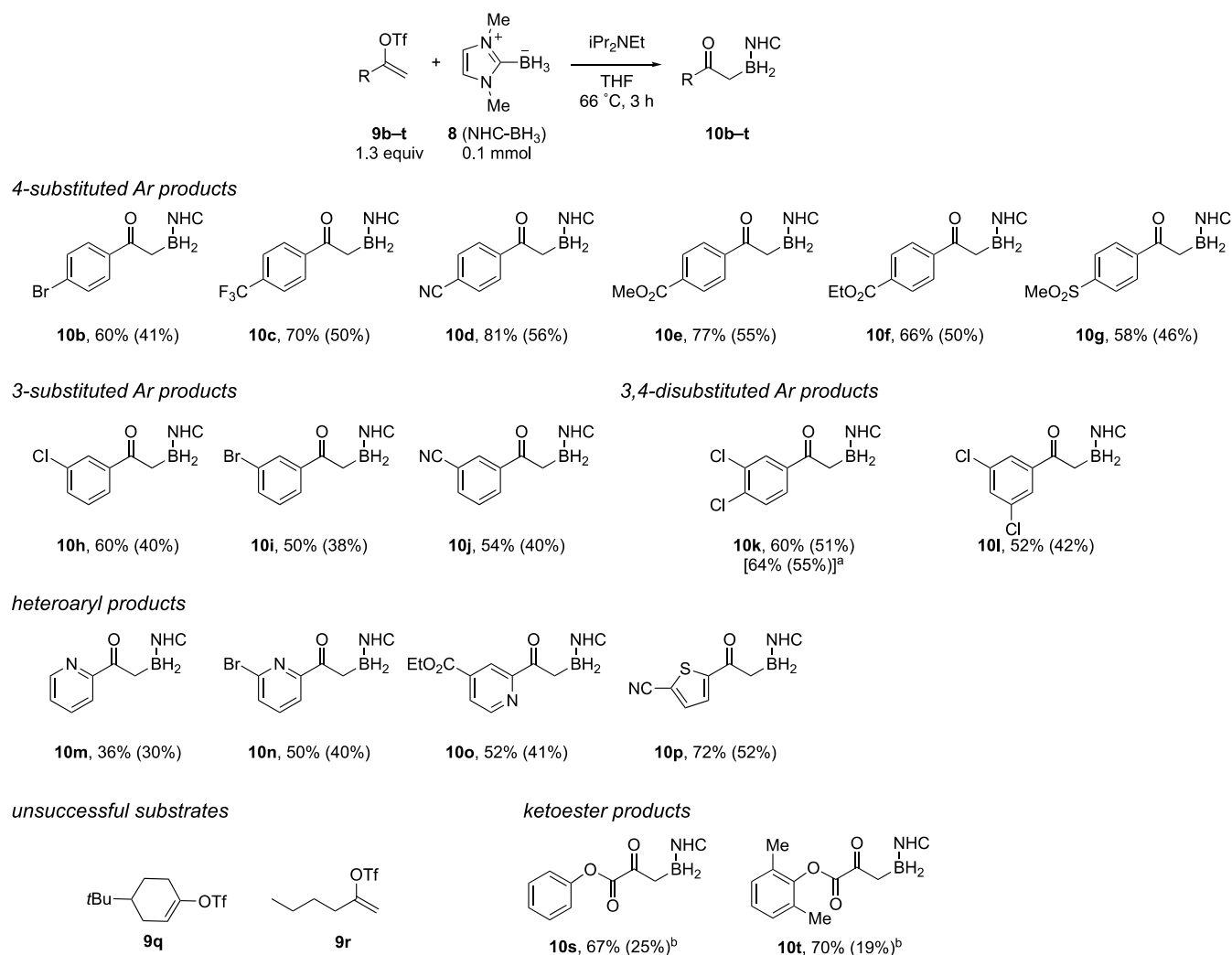
The results of a scope study with readily available alkenyl triflates are summarized in Figure 3, which shows structures of  $\alpha$ -boryl ketone products,  $^{11}\text{B}$  NMR yields, and isolated yields (in parentheses) of the various products that were prepared. The standard procedure from Scheme 1 was used in all of these experiments (0.1 mmol NHC-borane **8**; alkenyl triflate, 1.3 equiv;  $i\text{Pr}_2\text{NEt}$ , 0.8 equiv, THF, 66 °C, 3 h). A quick glance at the products in Figure 3 shows that many common functional groups are tolerated in the reaction.

Products **10b–g** with assorted 4-substituents (Br,  $\text{CF}_3$ , CN, esters, sulfone) on the aromatic ring were isolated in yields ranging from 41 to 56%. Products with 3-substituents were isolated in somewhat lower yields. For example, 3-chloro product **10h** was isolated in 40% whereas the 4-isomer **10a** was isolated in 50% yield. Likewise, the yields of 3-bromo and 3-cyano products **10i** and **10j** (38% and 40%) were somewhat lower than the corresponding 4-isomers **10b** and **10d** (41% and 56%). The 3,4- and 3,5-dichlorophenyl products **10k** and **10l** were isolated in 51% and 42% yield, respectively. Again the 4-Cl isomer was formed in somewhat higher yield. The reaction with **9k** was also conducted on a 1 mmol scale and gave marginally improved results; the NMR yield of **10k** was 64%, and the isolated yield was 55%.

Alkenyl triflates bearing heteroaryl groups were also viable substrates.  $\alpha$ -NHC-boryl ketones bearing pyridine (**10m**) and substituted pyridine (**10n**, **10o**) rings were isolated in yields of 30%, 40%, and 41%, respectively, and a 2-cyanothiophene analogue (**10p**) was isolated in 52% yield.

In contrast, alkenyl triflates with two or three alkyl substituents (**9q** and **9r**) were inert and did not provide  $\alpha$ -NHC-boryl ketones. This shows that some kind of activating group is needed on the triflate. However, the formation of  $\alpha$ -NHC-boryl keto ester **10s** in 25% isolated yield shows that the activating group does not have to be aryl. Related ketoester **10t** was isolated in 19% yield.

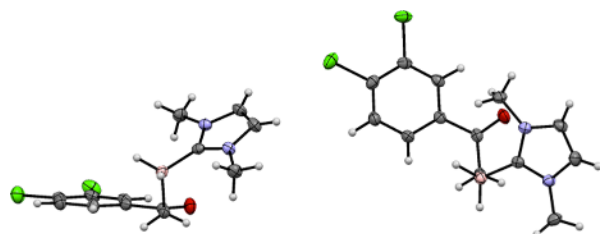
For most of the products in Figure 3, the  $^{11}\text{B}$  NMR yield exceeds the isolated yield by about 10–20%, suggesting that there may be some decomposition during flash chromatography. This problem is most acute with  $\alpha$ -ketoesters **10s** (NMR yield, 67%) and **10t** (NMR yield, 70%), where the NMR yield exceeds the isolated yield by 40–50%. Once



**Figure 3.** Results of scope study with NHC-borane **8** with about 20 additional alkenyl triflates under standard conditions (0.1 mmol **8**, 1.3 equiv alkenyl triflate, 0.8 equiv  $i\text{Pr}_2\text{NEt}$ , THF, 66 °C, 3 h). (a) Results of a 1 mmol scale experiment, 2 equiv  $i\text{Pr}_2\text{NEt}$ , THF, 66 °C, 8 h; (b) at 40 °C for 1 h.

isolated, however, the pure products are stable to storage and handling under ambient lab conditions.

The 3,4-dichlorophenyl  $\alpha$ -NHC-boryl ketone **10k** was nicely crystalline. Its X-ray structure was solved, and two views of the structure are shown in Figure 4. The left view approximates a Newman projection looking down the  $\text{CH}_2\text{--C(O)Ar}$  bond. Notice that the  $\text{CH}_2\text{--B}$  bond is roughly orthogonal to the carbonyl group (the  $\text{B--C--C=O}$  torsion angle is 93°). NHC-boryl groups are among the strongest known  $\sigma$ -electron

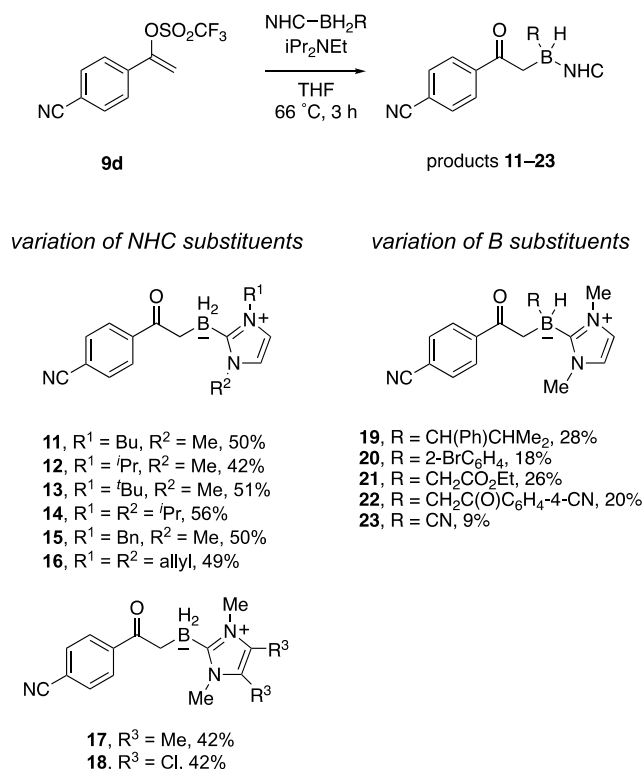


**Figure 4.** Two views of the X-ray crystal structure of **10k** (ORTEP at 50% probability level): right, approximate Newman projection of the  $\text{CH}_2\text{--C(O)Ar}$  bond; left, approximate Newman projection of the  $\text{BH}_2\text{--CH}_2$  bond.

donors, with  $\sigma_p^+$  for 1,3-dimethylimidazol-2-ylidene boryl estimated at +0.48.<sup>15</sup> So this orientation might result due to hyperconjugation of the  $\text{CH}_2\text{--BH}_2\text{NHC}$  group with the carbonyl group.

The right view of the crystal structure in Figure 4 is an approximate Newman projection looking down the  $\text{BH}_2\text{--CH}_2$  bond of **10k**. This bond is approximately staggered, but the ketone on the carbon atom and the NHC ring on the boron atom are oriented gauche rather than anti. The  $\text{NHC--B--C--C(O)Ar}$  torsion angle is 69°. This is somewhat larger than a perfect gauche angle (60°), doubtless due to some steric repulsion between the two gauche substituents.

We next surveyed variation of the NHC-borane component with alkenyl triflate partner fixed as **9d**. Reactions were conducted under the standard conditions, and Figure 5 shows product structures and isolated yields. Products **11–16** with various N-substituents ( $\text{R}^1, \text{R}^2 = \text{Me}, i\text{Pr}, \text{Bu}, t\text{Bu}, \text{Bn}, \text{allyl}$ ) were isolated in yields ranging from 42 to 56%. Products **17** and **18** with two additional substituents on the NHC ring (Me and Cl, respectively) were both isolated in 42% yield. Many of these products have C–H bonds that are susceptible to abstraction by trifluoromethyl radicals,<sup>13a–c,14</sup> and the tight



**Figure 5.** Variation of substituents on the NHC ring and the boron; products and isolated yields (0.1 mmol NHC-borane, 1.3 equiv **9d**, 0.8 equiv iPr<sub>2</sub>NEt, THF, 66 °C, 3 h).

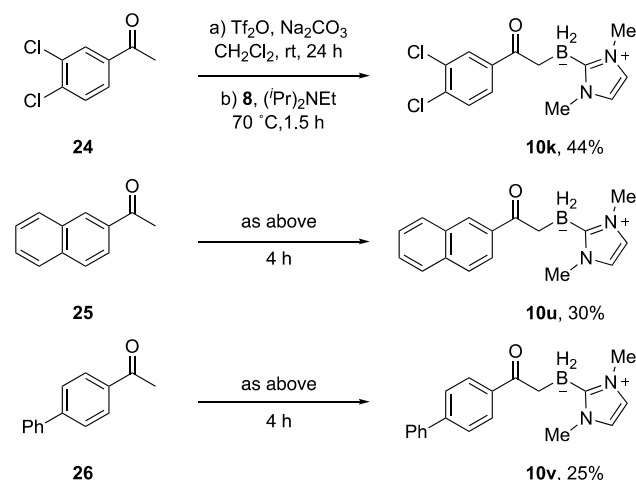
range of yields indicates that B–H bond abstraction is preferred in all cases.

Adding a substituent on boron dented the isolated yields, but products were still isolated in all five of the reactions studied. The hindered B-alkyl borane **19** was isolated in 28% yield, while the B-aryl borane **20** was produced in 18% yield. An  $\alpha$ -boryl ester and ketone produced the corresponding products **21** and **22** in 26% and 20% yields. Finally, a B-cyanoborane produced product **23** in only 9% yield. This poor result could be because the cyano group retards the B–H abstraction reaction due to a polarity mismatch or because the resulting radical (NHC–B(•)HCN) is too stable.

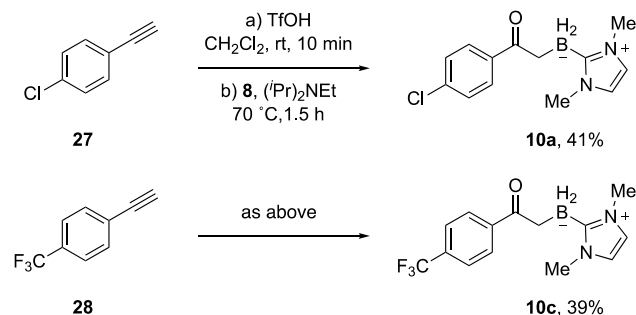
Alkenyl triflates are reactive molecules that can be inconvenient to handle (depending on substituents). So we next studied several one-pot reactions where the alkenyl triflate was generated in situ and then directly converted to an  $\alpha$ -NHC-boryl ketone. Two convenient ways to make alkenyl triflates are base-promoted triflation of ketones<sup>16</sup> and addition of triflic acid to alkynes,<sup>17</sup> so one-pot variants of each were studied.

In the standard ketone triflation procedure (Figure 6a),<sup>18</sup> ketone **24** (0.25 mmol), triflic anhydride (1.4 equiv), and Na<sub>2</sub>CO<sub>3</sub> (1.3 equiv) were stirred in CH<sub>2</sub>Cl<sub>2</sub> at rt for 24 h to make the alkenyl triflate. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated, and then THF, NHC-borane **8** (0.1 mmol), and iPr<sub>2</sub>NEt (0.1 mmol) were added. The resulting mixture was heated at 70 °C for 1.5 h and then cooled and concentrated again. Purification by flash chromatography gave existing product **10k** in 44% yield. Two new products were also made; naphthyl ketone **25** gave **10u** in 30% yield, and biphenyl ketone **26** gave **10v** in 25% yield. These one-pot yields are about the same as the two-step yields, but the procedure is more convenient.

(a) one-pot examples from ketone precursors



(b) one-pot examples from alkyne precursors



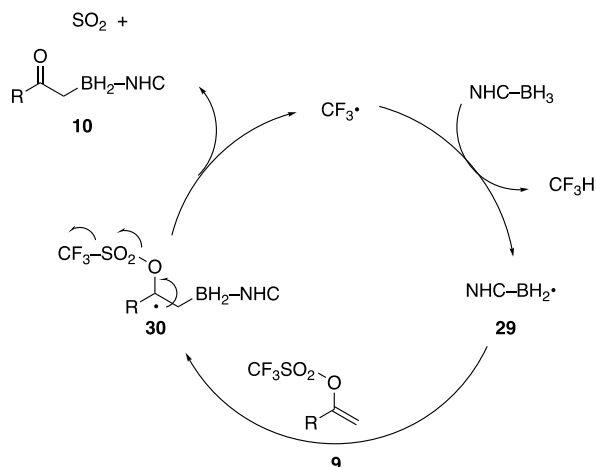
**Figure 6.** One-pot synthesis of  $\alpha$ -NHC-boryl ketones from (a) ketones and (b) alkynes.

The one-pot procedure starting from alkynes is even more convenient (Figure 6b). Trifluoromethanesulfonic acid (1.4 equiv) was added to 4-chlorophenylethyne **27** (1.3 equiv) in CH<sub>2</sub>Cl<sub>2</sub>.<sup>17</sup> After 10 min at rt, the solvent was removed and THF, NHC-borane **8** (0.1 mmol), and iPr<sub>2</sub>NEt (0.1 mmol) were added. Heating at 70 °C for 1 h, followed by cooling, concentration, and chromatography, provided **10a** in 41% yield. Likewise, 4-trifluoromethyl analogue **10c** was prepared in one pot starting from 4-trifluoromethylphenylethyne **28** in 39% yield.

To close the scope aspects of the study, we conducted reactions of alkenyl triflate **9k** (3,4-diClC<sub>6</sub>H<sub>3</sub>C(OTf)=CH<sub>2</sub>) with four different ligated boranes under the standard conditions (**9k**, 1.3 equiv; ligated borane, 1 equiv, iPr<sub>2</sub>NEt, 0.8 equiv, THF, 70 °C, 3 h). Reactions were conducted with the following ligated boranes: Et<sub>3</sub>N–BH<sub>3</sub>, Ph<sub>3</sub>P–BH<sub>3</sub>, DMAP–BH<sub>3</sub> (DMAP is 4-dimethylaminopyridine),<sup>19</sup> and DBU–BH<sub>3</sub> (DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene).<sup>20</sup> Reaction progress was followed by <sup>11</sup>B NMR spectroscopy, but in each case the resonance of the starting borane remained and no new resonances appeared. So typical amine- and phosphine- and amidine-boranes are not viable partners, at least under these conditions.

Figure 7 shows a suggested radical chain mechanism for this transformation, starting from the trifluoromethyl radical (CF<sub>3</sub>•). In the transformations of Li<sup>9</sup> and Kamimura<sup>10</sup> (Figure 1a), this radical adds to the alkenyl triflate to ultimately





**Figure 7.** Propagation steps of a proposed radical chain mechanism: H-transfer, addition, and fragmentation.

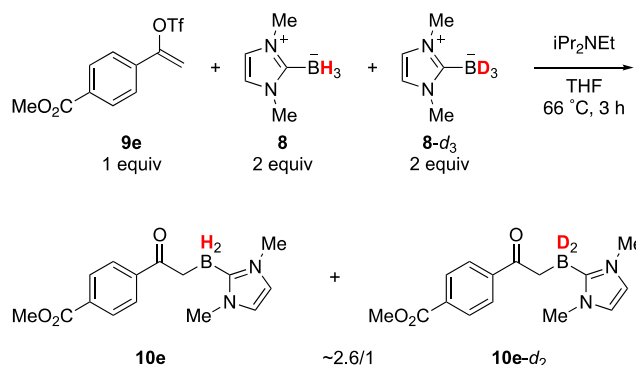
provide an  $\alpha$ -trifluoromethyl ketone. However, this reaction is interrupted by the addition of the NHC-borane **8** to the medium. Now the faster reaction of trifluoromethyl radical is abstraction of a hydrogen atom from a B–H bond of **8** to provide trifluoromethane ( $\text{CF}_3\text{H}$ ) and NHC-boryl radical **29**. This is an unknown reaction that we projected would be fast because it is exothermic by roughly 25 kcal/mol (the C–H bond dissociation energy<sup>12b</sup> of  $\text{CF}_3\text{—H}$  is about 107 kcal mol<sup>−1</sup> while the B–H bond dissociation energy<sup>21</sup> of NHC–BH<sub>2</sub>–H is about 80–82 kcal mol<sup>−1</sup>.) In addition, it is polarity matched; NHC-boranes are electron rich and trifluoromethyl radicals are electrophilic.<sup>12</sup> Reactions of NHC-boranes with alkoxy radicals have similar features (highly exothermic, polarity matched), and indeed these reactions have high rate constants ( $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>22</sup>

In turn, the NHC-boryl radical **29** then adds to the alkenyl triflate **9** to give **30**, which undergoes  $\beta$ -fragmentation to give the NHC-boryl ketone **10**,  $\text{SO}_2$ , and trifluoromethyl radical. The addition step is also a previously unknown reaction, but NHC-boryl radicals are known to add to electron-poor alkenes (such as acrylates<sup>22b,23</sup>) and to phenyl-substituted alkenes and alkynes.<sup>8,24</sup> The final fragmentation step is expected based on prior radical additions to alkenyl triflates.<sup>10–12</sup>

The function of the amine is somewhat speculative at this point, but two roles seem sensible. First, no reaction occurs if the amine is omitted, so it may function in the initiation step (for example, electron transfer to an alkenyl triflate could make an amine radical cation and trifluoromethyl radical). In addition, it likely functions as an acid scavenger. Standard (undried) THF is used in this reaction, and the residual water is expected to add to  $\text{SO}_2$  to make  $\text{H}_2\text{SO}_3$  (sulfurous acid). This is a strong acid ( $\text{p}K_{\text{a}1} = 1.8$ ) that will be neutralized by the amine.

The features of the reaction are broadly consistent with the chain mechanism in Figure 7. First, the reaction needs an initiator (the amine) and is shut down by an inhibitor (TEMPO). Second, the scope is also broadly consistent with the reaction being limited by the step of addition of the NHC-boryl radical to the alkenyl triflate. Specifically, an additional activating group on C2 of the alkene is needed besides OTf (either aryl or carbonyl), and terminal alkenes are preferred substrates.

In addition, the mechanism in Figure 7 was further supported by an isotope effect experiment, the results of which are shown in Figure 8. Alkenyl triflate **9e** was reacted



**Figure 8.** Results of an isotope effect experiment with D-labeled NHC-borane.

with an excess of NHC-borane **9** and its labeled analogue **9-d<sub>3</sub>** (2 equiv each) under the standard conditions. The isolated product was a mixture of **10e** and **10e-d<sub>2</sub>** in a ratio of about 2.6/1 according to MS analysis. This result indicates a significant primary isotope effect caused by the hydrogen atom abstraction reaction, and the value is reasonable given that this reaction is exothermic and therefore has an early transition state.

## CONCLUSIONS

We have described a fundamentally new approach to making  $\alpha$ -NHC-boryl ketones. Most previous approaches are based on carbene B–H insertion reactions and require both a diazocarbonyl precursor and a transition metal catalyst.

In a complementary approach, we reacted readily available alkenyl triflates with NHC-boranes in the presence of diisopropyl ethyl amine in refluxing THF for several hours. Solvent evaporation and flash chromatography provided about three dozen stable  $\alpha$ -NHC-boryl ketones. Isolated yields were typically 40–56% for B-unsubstituted NHC-boranes (NHC–BH<sub>3</sub>), and somewhat lower for NHC-boranes with B-substituents (NHC–BH<sub>2</sub>R). No catalyst is needed for this reaction, and a traditional high-energy initiator (for example  $\text{Et}_3\text{B}$ , AIBN, or  $t\text{BuOO}^t\text{Bu}$ ) is not needed either.

The requisite alkenyl triflates can be made separately or, more conveniently, prepared in situ either from ketones (by triflation with triflic anhydride) or from alkynes (by ionic addition of triflic acid). Following the triflate-forming reaction, the NHC-borane and amine are added directly, and the products are isolated as usual. The yields for the one-pot, two-step reactions are about the same as when the two steps are conducted separately with purification of the alkenyl triflate in between.

The substrate scope and the results of mechanistic experiments support a radical chain mechanism in which the propagation steps are (1) addition of an NHC-boryl radical to the alkenyl triflate, (2) fragmentation of the resulting  $\alpha$ -triflyloxy radical to give the  $\alpha$ -NHC-boryl ketone,  $\text{SO}_2$ , and trifluoromethyl radical, and (3) hydrogen abstraction by trifluoromethyl radical from the starting NHC-borane to return the NHC-boryl radical along with trifluoromethane.

The mild conditions and broad substituent tolerance suggest that the new method will be useful for making various types of

$\alpha$ -NHC-boryl ketones. In addition, the results show for the first time that trifluoroalkyl radicals rapidly abstract hydrogen atoms from NHC-boranes and therefore suggest that other new chain reactions can be designed with this reaction as a key step.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b05547.

Full experimental and compound characterization details; copies of NMR spectra ( $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$ ) of all new compounds (PDF)

Details of X-ray structure (CIF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*curran@pitt.edu

### ORCID

Wen Dai: 0000-0002-9098-5215

Steven J. Geib: 0000-0002-9160-7857

Dennis P. Curran: 0000-0001-9644-7728

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Abiko, A. Boron enolate chemistry. In *Boron Reagents in Synthesis*; American Chemical Society: Washington, DC, 2016; Vol. 1236, pp 123–171.
- (2) He, Z.; Zajdlik, A.; Yudin, A. K.  $[\alpha]$ -Borylcarbonyl compounds: From transient intermediates to robust building blocks. *Dalton Trans* **2014**, 43, 11434–11451.
- (3) (a) He, Z.; Yudin, A. K. Amphoteric  $\alpha$ -boryl aldehydes. *J. Am. Chem. Soc.* **2011**, 133, 13770–13773. (b) Li, J.; Burke, M. D. Pinene-derived iminodiacetic acid (PIDA): A powerful ligand for stereoselective synthesis and iterative cross-coupling of  $\text{C}(\text{sp}^3)$  boronate building blocks. *J. Am. Chem. Soc.* **2011**, 133, 13774–13777. (c) Corless, V. B.; Holownia, A.; Foy, H.; Mendoza-Sanchez, R.; Adachi, S.; Dudding, T.; Yudin, A. K. Synthesis of  $\alpha$ -borylated ketones by regioselective Wacker oxidation of alkenylboronates. *Org. Lett.* **2018**, 20, 5300. (d) Trinchera, P.; Corless, V. B.; Yudin, A. K. Synthesis of previously inaccessible borylated heterocycle motifs using novel boron-containing amphoteric molecules. *Angew. Chem., Int. Ed.* **2015**, 54, 9038–9041.
- (4) Ng, E. W. H.; Low, K. H.; Chiu, P. Synthesis and applications of unquaternized C-bound boron enolates. *J. Am. Chem. Soc.* **2018**, 140, 3537–3541.
- (5) (a) Li, X.; Curran, D. P. Insertion of reactive rhodium carbenes into boron-hydrogen bonds of stable N-heterocyclic carbene boranes. *J. Am. Chem. Soc.* **2013**, 135, 12076–12081. (b) Cheng, Q. Q.; Zhu, S. F.; Zhang, Y. Z.; Xie, X. L.; Zhou, Q. L. Copper-catalyzed B-H bond insertion reaction: A highly efficient and enantioselective C-B bond-forming reaction with amine-borane and phosphine-borane adducts. *J. Am. Chem. Soc.* **2013**, 135, 14094–14097. (c) Chen, D.; Zhang, X.; Qi, W.-Y.; Xu, B.; Xu, M.-H. Rhodium(I)-catalyzed asymmetric carbene insertion into B-H bonds: Highly enantioselective access to functionalized organoboranes. *J. Am. Chem. Soc.* **2015**, 137, 5268–5271. (6) (a) Horn, M.; Mayr, H.; Lacôte, E.; Merling, E.; Deaner, J.; Wells, S.; McFadden, T.; Curran, D. P. N-heterocyclic carbene boranes are good hydride donors. *Org. Lett.* **2012**, 14, 82–85. (b) Allen, T. H.; Curran, D. P. Relative reactivity of stable ligated boranes and a borohydride salt in rhodium(II)-catalyzed boron-hydrogen insertion reactions. *J. Org. Chem.* **2016**, 81, 2094–2098. (7) Allen, T. H.; Kawamoto, T.; Gardner, S.; Geib, S. J.; Curran, D. P. N-heterocyclic carbene boryl iodides catalyze insertion reactions of N-heterocyclic carbene boranes and diazoesters. *Org. Lett.* **2017**, 19, 3680–3683. (8) Ren, S. C.; Zhang, F. L.; Xu, A. Q.; Yang, Y.; Zheng, M.; Zhou, X.; Fu, Y.; Wang, Y. F. Regioselective radical  $\alpha$ -borylation of  $\alpha,\beta$ -unsaturated carbonyl compounds for direct synthesis of  $\alpha$ -borylcarbonyl molecules. *Nat. Commun.* **2019**, 10, 1934. (9) Yang, J.-M.; Zhao, Y.-T.; Li, Z.-Q.; Gu, X.-S.; Zhu, S.-F.; Zhou, Q.-L. Gold-catalyzed oxidative coupling of terminal alkynes and borane adducts: Efficient synthesis of  $\alpha$ -boryl ketones. *ACS Catal.* **2018**, 8, 7351–7355. (10) Su, X.; Huang, H.; Yuan, Y.; Li, Y. Radical desulfur-fragmentation and reconstruction of enol triflates: Facile access to  $\alpha$ -trifluoromethyl ketones. *Angew. Chem., Int. Ed.* **2017**, 56, 1338–1341. (11) Kawamoto, T.; Sasaki, R.; Kamimura, A. Synthesis of  $\alpha$ -trifluoromethylated ketones from vinyl triflates in the absence of external trifluoromethyl sources. *Angew. Chem., Int. Ed.* **2017**, 56, 1342–1345. (12) (a) Dolbier, W. R. Fluorinated free radicals. *Top. Curr. Chem.* **1997**, 192, 97–163. (b) Dolbier, W. R. Structure, reactivity, and chemistry of fluoroalkyl radicals. *Chem. Rev.* **1996**, 96, 1557–1584. (13) (a) Xiang, J.; Everts, J.; Rivkin, A.; Curran, D. P.; Fuchs, P. L. Use of allylic triflates for allylation of C-H bonds. *Tetrahedron Lett.* **1998**, 39, 4163–4166. (b) Xiang, J.; Jiang, W.; Gong, J.; Fuchs, P. Stereospecific alkenylation of C-H bonds via reaction with  $\beta$ -heteroatom substituted vinyl triflates. *J. Am. Chem. Soc.* **1997**, 119, 4123–4129. (c) Gong, J.; Fuchs, P. Alkynylation of C-H bonds via reaction with acetylenic triflates. *J. Am. Chem. Soc.* **1996**, 118, 4486–4487. (d) dos Passos Gomes, G.; Wimmer, A.; Smith, J. M.; König, B.; Alabugin, I. V.  $\text{CO}_2$  or  $\text{SO}_2$ : Should it stay, or should it go? *J. Org. Chem.* **2019**, 84, 6232–6243. (14) Lee, J. Y.; Lim, K.-C.; Meng, X.; Kim, S. Radical alkylations of alkyl halides and unactivated C-H bonds using vinyl triflates. *Synlett* **2010**, 2010, 1647–1650. (15) Allen, T. H. NHC-borane Hammett values derived from  $^{13}\text{C}$ NMR chemical shift correlations. Ph.D. Thesis, University of Pittsburgh, Pittsburgh, PA, 2018; Chapter 4.2.4, pp 104–107. Available at <http://d-scholarship.pitt.edu/34993/>. (16) Martínez, A. G.; Subramanian, L. R.; Hanack, M.; Williams, S. J.; Régnier, S. Trifluoromethanesulfonic anhydride. *Encyclopedia of Reagents for Organic Synthesis*; John Wiley: New York, 2016. (17) Wu, J. J.; Xu, J.; Zhao, X. Selenide-catalyzed stereoselective construction of tetrasubstituted trifluoromethylthiolated alkenes with alkynes. *Chem. - Eur. J.* **2016**, 22, 15265–15269. (18) Qin, L.; Ren, X.; Lu, Y.; Li, Y.; Zhou, J. Intermolecular Mizoroki-Heck reaction of aliphatic olefins with high selectivity for substitution at the internal position. *Angew. Chem., Int. Ed.* **2012**, 51, 5915–5919. (19) Ramachandran, P. V.; Kulkarni, A. S.; Zhao, Y.; Mei, J. Amine-boranes bearing borane-incompatible functionalities: Application to selective amine protection and surface functionalization. *Chem. Commun.* **2016**, 52, 11885–11888. (20) McFadden, T. Synthesis and study of amidine-borane complexes. Ph.D. Thesis, University of Pittsburgh, Pittsburgh, PA, 2018; Chapter 2, pp 68–99. Available at <http://d-scholarship.pitt.edu/33821/>. (21) Hioe, J.; Karton, A.; Martin, J. M. L.; Zipse, H. Borane-Lewis base complexes as homolytic hydrogen atom donors. *Chem. - Eur. J.* **2010**, 16, 6861–6865. (22) (a) Lacôte, E.; Curran, D. P.; Lalevé, J. NHC-boranes: Air- and water-tolerant co-initiators for type II photopolymerizations. *Chimia* **2012**, 66, 382–385. (b) Tehfe, M.-A.; Monot, J.; Brahmi, M. M.; Bonin-Dubarle, H.; Curran, D. P.; Malacria, M.; Fensterbank, L.

Lacôte, E.; Lalevée, J.; Fouassier, J.-P. N-heterocyclic carbene-borane radicals as efficient initiating species of photopolymerization reactions under air. *Polym. Chem.* **2011**, *2*, 625–631. (c) Walton, J. C.; Makhlof Brahmi, M.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Chu, Q.; Ueng, S.-H.; Solov'yev, A.; Curran, D. P. EPR studies of the generation, structure, and reactivity of N-heterocyclic carbene borane radicals. *J. Am. Chem. Soc.* **2010**, *132*, 2350–2358.

(23) Lalevée, J.; Telitel, S.; Tehfe, M. A.; Fouassier, J. P.; Curran, D. P.; Lacôte, E. N-heterocyclic carbene boranes accelerate type I radical photopolymerizations and overcome oxygen inhibition. *Angew. Chem., Int. Ed.* **2012**, *51*, 5958–5961.

(24) (a) Ren, S.-C.; Zhang, F.-L.; Qi, J.; Huang, Y.-S.; Xu, A.-Q.; Yan, H.-Y.; Wang, Y.-F. Radical borylation/cyclization cascade of 1,6-enynes for the synthesis of boron-handled hetero- and carbocycles. *J. Am. Chem. Soc.* **2017**, *139*, 6050–6053. (b) Qi, J.; Zhang, F.-L.; Huang, Y.-S.; Xu, A.-Q.; Ren, S.-C.; Yi, Z.-Y.; Wang, Y.-F. Radical borylative cyclization of 1,6-dienes: Synthesis of boron-substituted six-membered heterocycles and carbocycles. *Org. Lett.* **2018**, *20*, 2360–2364. (c) Jin, J.-K.; Zhang, F.-L.; Zhao, Q.; Lu, J.-A.; Wang, Y.-F. Synthesis of diverse boron-handled N-heterocycles via radical borylative cyclization of N-allylcyanamides. *Org. Lett.* **2018**, *20*, 7558–7562.