ORGANOMETALLICS

Borenium-Catalyzed Hydroborations of Silyl-Substituted Alkenes and Alkynes with a Readily Available N-Heterocyclic Carbene– Borane

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S Supporting Information

ABSTRACT: Borenium-catalyzed hydroboration reactions of a stable, readily available N-heterocyclic carbene—borane with allyl-, alkenyl-, and alkynylsilane substrates provides either standard 1,2-hydroboration products or rearranged 1,1-hydroboration products, depending on the structure of the substrate. A competent catalyst can be generated in situ by addition of bis(trifluoromethane)sulfonimide or diiodine. In a typical 1,2-hydroboration, reaction of 1,3-dimethylimidazol-2-ylidine—borane (diMe-Imd-BH₃) with 1,2-bis(trimethylsilyl)ethene provides 1,3-dimethylimidazol-2-ylidine—(1,2-bis(trimethylsilyl)ethyl)borane (diMe-Imd-BH₂CH-



 $(TMS)CH_2TMS))$ as a stable product. In a typical 1,1-hydroboration, the reaction of diMe-Imd-BH₃ with bis(trimethylsilyl)-ethyne provides 1,3-dimethylimidazol-2-ylidine-bis(2,2-bis(trimethylsilyl)ethenyl)borane (diMe-Imd-BH(CH=C(TMS)_2)_2 again as a stable product.

INTRODUCTION

N-heterocyclic carbene complexes of borane (NHC-BH₃ or, more generally, NHC-boranes) have a rich chemistry that stems in part from their stability.¹ Unlike most complexes of borane (BH₃) and neutral Lewis bases, NHC complexes of BH₃ resist decomplexation even under forcing conditions. Classic reactions of borane such as hydroboration cannot be directly elicited. This means that NHC-boranes can be exposed to all kinds of reagents that standard borane–Lewis base complexes would not tolerate.^{1a}

Spurred by the pioneering amine–borenium ion chemistry of Vedejs,² we and Vedejs recently showed that the prohibitive barriers for direct hydroboration of alkenes by NHC–boranes can be overcome by in situ generation of an NHC–borenium ion catalyst (NHC-BH₂⁺, Figure 1a).³ The borenium ion (or a reactive equivalent^{2a}) is a highly electrophilic species with a potential vacant site for complexation. It can undergo rapid 1,2-hydroboration reactions with alkenes (Figure 1a, step 1). Turnover occurs when the resulting hydroborated borenium ion (NHC-BH⁺CH₂CH₂R) abstracts hydride from the starting NHC–borane to provide the neutral hydroborated product (NHC-BH₂CH₂CH₂R) while regenerating the catalyst (Figure 1a, step 2).

In a typical example (Figure 1b), 5-15% trifluoromethane sulfonimide (hereafter triflimide or Tf_2NH) is added to 1,3dimethylimidazol-2-ylidine—borane (1), followed by addition of 3-hexene.³ Rapid dihydroboration occurs to give the primary product, bis(3-hexylborane) **2**. This evolves over a few hours, presumably by reverse hydroboration, to provide the secondary product, bis(2-hexylborane) **3**. This product surprisingly resists further rearrangement to the bis(1-hexylborane).



Figure 1. NHC-borenium-catalyzed hydroboration reactions.

A related procedure that involves addition of a small amount of diiodine (I_2) in place of triflimide has recently been introduced.⁴ This procedure seems to be gentler, giving an expanded range of products from more substituted and more functionalized alkenes. The diiodine activation procedure often selectively forms monohydroboration products when a 1/1

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ratio of NHC-borane and alkene is combined. This is an advantage, because monoalkyl NHC-boranes tend to survive standard chromatographic purification and are stable to storage. In contrast, dialkyl NHC-boranes are stable for long periods in solution but often cannot be further purified by chromatography.⁵

We decided to study NHC–borenium-catalyzed hydroborations of silyl-substituted alkenes and alkynes because the existing hydroboration chemistry of these compounds is so rich and diverse. Borane and alkylboranes typically give 1,2-hydroboration products with these species, with regioselectivity often directed by the silicon atom.⁶ With alkynylsilanes, there are rare examples of 1,1-hydroboration reactions with silicon shifts in the carborane field.⁷ In contrast, 1,1-carboration reactions with silicon shift (the Wrackmeyer reaction) are rather common when alkylboranes are used.⁸ Products of silicon migration have been observed with 9-BBN,⁹ and boron migration can occur with bis(pentafluorophenyl)borane (HB- $(C_6F_5)_2$).¹⁰ Reactions of both alkenyl- and alkynylsilanes with electrophilic trihaloboranes (BX₃) often give silicon/boron exchange products.¹¹

Here we show that allyl- and alkenylsilanes give products of 1,2-hydroboration in borenium-catalyzed hydroborations with NHC-boranes. In contrast, rearranged 1,1-hydroboration products are sometimes formed from alkynylsilanes. These products are the first alkenyl and dialkenyl NHC-boranes, and we find that they are rather stable. We also learn that activation by diiodine (I_2) is a valuable alternative to triflimide activation for such substrates.

RESULTS AND DISCUSSION

Allylsilanes. The results of hydroboration reactions of two typical allyl silanes by 1 are summarized in Scheme 1. Not

Scheme 1. Results of Borenium-Catalyzed Hydroborations of Allylsilanes



surprisingly, nothing happened when 1 and allyltrimethylsilane (4a) were mixed without a catalyst. In the catalytic method, 20% triflimide was first added to 1 to generate the catalyst, and then 2.2 equiv of allylsilane 4a was added. Rapid dihydroboration occurred to give the major product 5, which was characterized in situ by ¹H, ¹¹B, and ¹³C NMR spectroscopy. While stable in solution, this product did not survive automated flash chromatography.

We also reacted 1 first with 10% diiodine.⁴ This rapidly provides 20% of the corresponding NHC–boryl iodide (NHC-BH₂I) and dihydrogen (H_2) .¹² Addition of 2.2 equiv of allyltrimethylsilane (4a) again provided the dihydroboration product 5 rather cleanly in solution.

Hydroboration of 1,4-bis(trimethylsilyl)but-2-ene (**4b**; E/Z mixture) was also conducted by the triflimide procedure. This time, the monohydroboration product **6** predominated in the ¹¹B NMR spectrum of the reaction mixture, even though 2.2 equiv of **4b** was added. Monoalkylborane **6** was stable to flash chromatography and was isolated in 59% yield and fully characterized.

The results in Scheme 1 show similarities and differences in comparison to the borenium-catalyzed hydroboration of simple alkenes.³ On the one hand, the reaction of allyltrimethylsilane resembles that of 1-hexene. The dihydroborated product **5** is quickly formed in situ, but it is not stable to purification. On the other hand, the results with disubstituted **4b** are not so similar to results with comparable alkenes such as 3-hexene and 4-octene. The simple alkenes give dihydroboration products such as **2** that are subject to further migration of boron (to give **3** in Figure 1, for example). In contrast, **4b** gives the monohydroboration product **6**, which is not prone to further migration.

In short, there is no tendency for boron to migrate toward silicon in either 1,2-hydroboration product **5** or **6**. This is in contrast with related hydroborations by the highly electrophilic bis(pentafluorophenyl)borane ($(C_6H_5)_2BH$), which show a strong tendency for boron to migrate toward silicon as reaction times are extended.^{10b}

Alkenylsilanes. Scheme 2 summarizes the results of borenium-catalyzed hydroborations of the three 1,2-disubstituted alkenylsilanes 7a-c. In preliminary ¹¹B NMR experiments, hydroboration of (Z)-1,2-bis(trimethylsilyl)ethene (7a)

Scheme 2. Results of Borenium-Catalyzed Hydroborations of Alkenylsilanes



with 1 succeeded well with both the triflimide and the iodine activation procedures. In both cases, the monohydroboration product 8 was formed even though the alkene 7a was used in excess (3 equiv in NMR experiments). In a preparative experiment by the triflimide procedure, the hydroboration product 8 was isolated in 39% yield after flash chromatography.

With (Z)-1-(trimethylsilyl)-1-pentene (7b) and (Z)-1-(trimethylsilyl)-2-phenylethene (7c), the iodine procedure gave cleaner reaction products in NMR experiments; therefore, this was used for the preparative experiments. Both alkenes again gave only monohydroboration products, but now two regioisomers were formed. The reaction with 7b produced an inseparable 83/17 mixture of α -borylsilane 9 and β -borylsilane 10. The structure of the major isomer 9 was confirmed by oxidation of the crude product (H₂O₂, NaOH, MeOH) to give 1-(trimethylsilyl)-1-hexanol as the main product. The hydroboration reaction of 1 with 7c was unselective, giving the two analogous regioisomers 11 and 12 in about a 50/50 ratio in 72% isolated yield.

Alkynylsilanes. Three of the alkynylsilanes selected for study, 13a-c, have the same substituents as the alkenylsilanes 7a-c to facilitate comparison, while the fourth (13a') is an analogue of bis(trimethylsilyl)ethyne (13a) with two different silyl groups. The results with the two bis(silyl)ethynes 13a and 13a' are summarized in Scheme 3. Hydroboration of 13a (3 equiv) with 1 by the triflimide procedure gave rapid conversion not to a monohydroboration product (as with alkenylsilane 7a) but to a dihydroboration product. Flash chromatography of the

Scheme 3. Reactions of Bis(silyl)ethynes 13a,a' Giving Normal (15) or Rearranged (14 and 18) Products Depending on the Order of Complexation and Hydroboration Steps



crude product provided pure 14 in 44% yield as a white solid, mp 84–86 °C. This is the first alkenyl NHC–borane to be isolated. Unlike many dialkyl NHC–boranes (see 5, for example), this dialkenyl NHC–borane survives chromatography and is stable to storage.

The spectra of 14 seemed at first glance consistent with the standard 1,2-hydroboration product 15, but there was a glaring problem. The alkenyl proton H^a resonated as a doublet at 7.93 ppm in the ¹H NMR spectrum with a coupling constant (J) of 6.4 Hz. We recorded an ¹¹B-decoupled ¹H NMR spectrum of 14 to show that this was the coupling of the remaining proton on boron (BH) to the alkenyl proton H^a. In this spectrum, the proton on boron is a triplet, J = 6.4 Hz, at 3.08 ppm. On the basis of the magnitude of the coupling constant, the C–H^a bond and the B–H bond must be vicinal. Therefore, the product is 14, the result of 1,1-hydroboration with silyl migration, not 15, the result of standard 1,2-hydroboration.

To solidify this structure assignment, we prepared an authentic sample of the 1,2-hydroboration product **15** by first hydroboration of **13a** with BH₃. THF (2 equiv).¹³ After 1 h, the resulting solution of dialkenylborane **16** was added to a solution of 1,3-dimethylimidazol-2-ylidene (**17**). The resulting dialkenyl NHC–borane **15** is a constitutional isomer of **14** that was again stable to flash chromatography and was isolated as a while solid in 34% yield, mp 68–70 °C. Now the lone alkenyl proton H^b is not coupled to the H on boron (J < 1 Hz) and resonates at 6.49 ppm in the ¹H NMR spectrum. There was no trace of resonance of **14** in the ¹¹B NMR spectrum of product **15** from the borenium-catalyzed hydroboration of **1**.

Adding in the step of complexation of 17 and BH_3 to make NHC-borane 1,¹⁴ the sequence of complexation followed by borenium-catalyzed hydroboration gives the rearranged product 14. In contrast, the sequence of direct hydroboration to make 16 followed by complexation gives the standard product 15.

In a separate experiment, we added 20% triflimide to a sample of pure 15. Although some decomposition occurred,¹⁵ much of 15 remained unreacted and no resonance for 14 appeared in the ¹¹B NMR spectrum. These results suggest that the borenium-catalyzed hydroboration of 13a by 1 does not initially form the standard 1,2-hydroboration product 15, which later rearranges. Instead, that reaction directly provides rearranged product 14.

Eventually we secured crystals of 1,1-hydroboration product 14 that were amenable to X-ray crystallography, and the resulting structure is shown in Figure S1 (Supporting Information). Likewise, we solved the X-ray structure of the 1,2-adduct 15, and this is shown in Figure S2 (Supporting Information).¹⁶

To probe the stereochemistry of the silyl migration, we hydroborated (triisopropylsilyl)(trimethylsilyl)ethylene with **13a'** by the triflimide procedure (Scheme 3). This time only monohydroboration occurred, presumably due to the bulky triisopropylsilyl (TIPS) group. The product **18** again is a formal 1,1-hydroboration product resulting from a silyl shift. It is also a single stereoisomer, though the assignment was difficult. The 2D NOE spectrum of **18** was notable for its absence of cross peaks. However, in a 1D experiment, irradiation of the alkenyl proton H^a at 7.88 ppm produced no enhancement of the signal for methyl protons on the trimethylsilyl group, but there was a 3% enhancement of the signal of the methyne protons of the triisopropylsilyl group. This suggests that **18** has the TMS group *trans* to the NHC–boryl group and the TIPS group *cis*.

Results in the hydroborations of 1-(trimethylsilyl)-1-pentyne (13b) and (trimethylsilyl)phenylethyne (13c) are summarized in Scheme 4. Reactions of 13b and 1 by both the triflimide and

Scheme 4. Results of Borenium-Catalyzed Hydroborations of Silylalkynes 13b,c



the iodine activation procedures were followed by ¹¹B NMR spectroscopy. The triflimide procedure gave a mixture of three products, the bis-1,2-hydroboration product **19** (71%), the bis-1,1-hydroboration product **21** resulting from double migration (8%), and the bis-hydroboration product **20** (21%), in which one of the alkenyl groups has a migrated silyl group and the other does not. No monohydroboration products were detected by ¹¹B NMR spectroscopy, and the ratio of products **19/20/21** did not evolve after the hydroboration reaction was complete. By the diiodine activation procedure, the same three products were formed more slowly but with somewhat better selectivity for the bis-1,2-hydroboration product: **19**, 86%; **20**, 8%; **21**, 6%.

Flash chromatographic purification of the crude product from the triflimide reaction provided pure samples of the two major products; **19** was obtained in 43% yield and **20** in 10% yield. (The minor product **21** was not isolated; therefore, its structure is tentative.) The structures of the two purified products follow from both ¹¹B NMR and ¹H NMR spectroscopy. In the ¹¹B spectra, the boron atom in the 1,2-product **20** resonated upfield in comparison to the 1,1-product **19** (the same trend is seen with **14** and **15** in Scheme 3). In the ¹H NMR spectra, **19** has two equivalent alkenyl protons (H^b) while **20** has two different protons (H^a and H^b). The alkenyl proton appears further downfield when it is geminal to boron (H^a, 6.78 ppm in **20**) in comparison to when it is vicinal (H^b, 5.86 ppm in **19** and 5.99 ppm in **20**). The structure of **19** was also confirmed by oxidation, which occurred with some difficulty (**19** is rather stable; see the Supporting Information) but finally produced hexanoic acid. The Z geometries of the alkenes in **20** and **21** are tentative and were inferred from the structure of **18**.

Hydroboration of 13c by 1 worked best by the iodine activation method, providing the major monohydroboration product 22, which was assigned as resulting from 1,2-hydroboration with the boron atom located geminal to the silyl group. The product was isolated by flash chromatography in 34% yield, though it was only about 90% pure by ¹¹B NMR spectroscopy. The sample was further purified by crystallization, and the structure of 22 was confirmed by solving the X-ray crystal structure of this sample (see the Supporting Information, Figure S3). The minor contaminant was also a monoadduct (triplet in the ¹¹B NMR spectrum), but it is not clear whether this is the regioisomer of 22 (1,2-hydroboration in the other direction) or a silyl migration product (1,1-hydroboration).

The results show that the bis-silyl alkynes are highly prone to silyl migration to give 1,1,-hydroboration products (Scheme 3), while the monosilyl alkynes are less so, giving predominately 1,2-hydroboration products (Scheme 4). All of the alkenes, whether allylsilanes or alkenylsilanes, gave 1,2-hydroboration products (Schemes 1 and 2).

Figure 2 shows two possible pathways for formation of the 1,1-hydroboration product 18, which was isolated from the



Figure 2. Two plausible pathways for the 1,1-hydroboration reaction of the unsymmetrical bis-silyl-ethyne 13a'.

unsymmetrical silane 13a' bearing TMS and TIPS groups. We assume in both paths that the NHC-boryl group attaches itself to the carbon bearing the smaller TMS group. Both paths also avoid the intermediacy of the standard 1,2-hydroboration products (such as 15), because the results in Scheme 3 suggest that they do not rearrange to 1,1-products.

In the "1,2-silvl shift" pathway (Figure 2a), the borenium ion $NHC-BH_2^+$ (or its reactive equivalent) is a strong electrophile that adds to the alkyne to form vinyl cation 23, which suffers a standard 1,2-shift of the silvl group¹⁷ to give α -NHC-boryl vinyl cation 24. This cation may abstract a hydride from NHC-BH₃ to provide the product 18 directly. Alternatively, a 1,2-hydride shift from boron to carbon could occur to form a rearranged borenium ion (not shown, but this is analogous to the reaction of 26 below), which in turn abstracts hydride from NHC-BH₃ to continue the cycle. It is not immediately clear what the stereochemistry-determining step in this mechanism is; thus, accounting for the selective formation of 18 as the E isomer (TIPS and NHC-boryl trans) is not straightforward. In addition, if a pathway such as this was being followed, then silylalkenes 7a-c might also be expected to suffer analogous silvl shifts, but they do not (Scheme 2).

In the "boron-silicon exchange" pathway (Figure 2b), the NHC-borenium ion exchanges with the silicon of the TMS group to provide 25, which can be viewed as a silylenium ion complex of an alkyne. Now a 1,2-shift of a hydride *trans* to the TMS group provides the borenium ion 26, which abstracts hydride from 1 to continue the cycle. Alternatively, 25 may abstract hydride direct from NHC-BH₃, again in a *trans* fashion, to give product 18 and turn over the cycle.

CONCLUSIONS

In summary, the results herein with allyl-, alkenyl-, and alkynylsilanes continue to solidify the generality of boreniumcatalyzed hydroborations of functionalized compounds. The original triflimide-activation procedure³ is convenient because reactions are faster, but the newer procedure with the less expense diiodine activator⁴ seems more general because it gave cleaner crude reaction products in a number of the examples in Schemes 2–4.

These hydroborations continue to be unusual in that one typically obtains selectively either the mono- or the dihydroboration product. To date, the two are never mixed, even when the stoichiometry is chosen to favor one or the other. In early work,³ it looked as if mono- and disubstituted alkenes favored dihydroboration, while tri- and tetrasubstituted alkenes favored monohydroboration. However, as the studies have expanded,⁴ it now looks like many disubstituted alkenes (such as the allyl- and alkenylsilanes in this work) also favor monohydroboration. Simple dialkyl-substituted alkenes are the exceptions that favor dihydroboration, provided that the alkyl groups are small. We suspect that this selectivity results from a direct competition of the initial hydroborated borenium ion, which can undergo either a second hydroboration (dihydroborated product results) or hydride transfer (monohydroborated product results).

In the TMS-alkyne series, bis-hydroboration products are produced when the second alkyne substituent is another TMS group or a small alkyl group (Bu), while monohydroboration occurs when the alkyne has a phenyl group or a bulky TIPS group. The reactions with the bis-silylalkynes are rare examples of formal 1,1-hydroboration reactions that occur by silyl shifts.

The alkenyl NHC–boranes isolated in this work are the first examples of such compounds. Significantly, they are more robust than the analogous dialkylboranes. All of the major dialkenylboranes in this work survived chromatography and are stable products,¹⁸ whereas most dialkyl NHC–boranes do not survive chromatography.⁵ We suspect that this means that dialkyl NHC–boranes are subject to decomplexation of the

NHC group on silica gel, but dialkenylboranes are not. This might be an indication that alkenylboranes are somewhat stronger Lewis acids than the comparable alkylboranes; therefore, they hold onto the NHC Lewis base more tightly.¹⁹

In the big picture, the results show that borenium ion catalyzed hydroborations exhibit a number of attractive features, including ease of reaction and workup. In addition, reagent 1 is a stable solid that is easy to make, store, and handle. However, the unique feature in comparison to most other hydroboration methods is that many of the primary boroncontaining products are not especially reactive because the NHC group remains complexed to the boron atom. This offers a number of options, including direct isolation and storage of the products.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and a CIF file giving complete experimental details and compound characterization data, ¹H, ¹³C, and ¹¹B NMR spectra of hydroboration products, and a crystal structure and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) In addition to the resonance for NHC–borane **15**, the ¹¹B NMR spectrum showed a broad resonance at 50.6 ppm. The ¹H NMR spectrum showed resonances for a 1,3-dimethylimidazolium salt along with **15**. These spectra are shown in the Supporting Information.

(16) Both crystals were problematic, and the final *R* values were rather high (26-30%). Still, the connectivity of the molecules is clear; they are constitutional isomers. CIF files of both crystal structures are available from the Cambridge Structural Database as personal communications from Stephen J. Geib, 2013, file nos. 967205 and 967206.

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