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Asymmetric Rhodium-Directed anti-Markovnikov Regioselective Boracyclopentannulation

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Supporting Information

ABSTRACT: A Shimoi-type activation of B−H bond of NHC-boranes by a diphosphane-ligated cationic Rh complex was applied in an unprecedented intramolecular hydroboration reaction of simple olefins. The use of NHC-boranes as hydroborating reagents is still undisclosed due to their nonreactivity toward alkenes which could be explained by the high stability of this complex rendering it unable to provide a "free" borane hydroborating reagent. B−H bond Rh activation of NHC-borane circumvents this limitation, and asymmetric Rh-directed anti-Markovnikov boracyclopentannulation reaction led to a library of enantioenriched cyclic boranes in high yield (up to 94%) with high regio- (up to 100%) and enantioselectivity (er up to 99.2:0.8). This new activation mode of NHC-boranes highlights their use in organometallic chemistry and offers a very good approach to access chiral cyclic NHC-boranes.

Since the isolation of stable N-heterocyclic carbenes (NHCs) by Arduengo and their intensive use in the past decade as ligands in organometallic catalysis[1] or catalysts in organic chemistry,[2] NHC-boranes emerged also as new reagents[3] in the NHC constellation. They were readily employed in radical[4] or ionic[5,6] reactions and as efficient co-initiators for photopolymerization processes.[7] Surprisingly, the use of NHC-borane as a hydroborating reagent of simple olefins is still undisclosed, unless a more specific activation is provided, as very recently reported with borenium ions in a racemic manner (Figure 1b).[8] The high stability to decomplexation of NHC-borane complexes could explain this nonreactivity toward alkenes, in sharp contrast with their amine[9] or phosphine[10] borane analogues, which lead to either inter- or intramolecular hydroboration reactions. In these cases, the conventional hydroboration step occurred *via* an early stage N−B or P−B bond dissociation mechanism, generally activated by heating (Figure 1a).[11]

Because NHC-boranes were unreactive in hydroborations compared to other labile borane−Lewis bases (BH_3•Me_2S or BH_3•THF), we were interested in their potential to be activated by an organometallic source. As it was already described, in the case of amine- or phosphine-boranes,[12] Braunschweig et al. have isolated NHC-borane adducts coordinated to a metal center (Mn, Cr, Mo, and W) through a B−H−M three-center two-electron bond.[13] From these observations, we have hypothesized that a Rh catalyst could activate the NHC-borane species in a Shimoi type complex,[14] leading to an alkene hydroboration process, which could be foreseen in an asymmetric version by using chiral Rh complexes (Figure 1c).

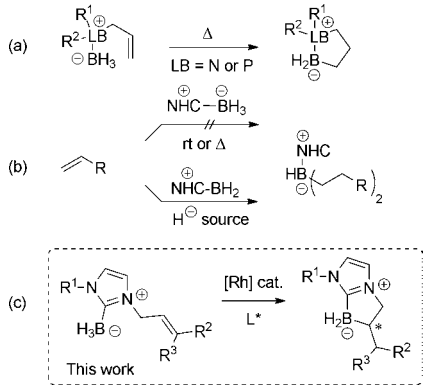
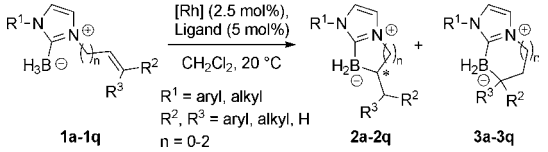


Figure 1. Lewis base−borane hydroboration of alkenes: (a) with amine or phosphine borane; (b) with no reaction with NHC-borane or reaction *via* an activation with a borenium species (see ref 8); (c) in this work.

Herein, we disclose our initial studies toward this goal and report an unprecedented asymmetric Rh-directed anti-Markovnikov regioselective boracyclopentannulation (Figure 1c).[15] NHC-boranes with a pendant allyl[4c] group moiety were chosen because of their nonreactivity as reducing or hydroborating agents. Regio- and enantioselectivity would be controlled by the right choice of Rh and chiral ligand sources which are well-known in the literature for the conventional hydroboration step of alkenes with borane derivatives.[16]

NHC-borane **1a** (R^1 = Ph, R^2, R^3 = H, n = 1) (Scheme 1)[17] was prepared according to a general procedure described in the literature.[4c] Dichloromethane was chosen as a noncoordinating solvent instead of tetrahydrofuran for conventional hydroboration reaction conditions with BH_3•SMe_2, and classical Rh sources were then evaluated in the catalytic process. To our

Scheme 1. Asymmetric Intramolecular Rhodium-Catalyzed Hydroboration of NHC-Boranes (1a−1q)



Received: September 11, 2012
Published: October 18, 2012

   dx.doi.org/10.1021/ja309018f | J. Am. Chem. Soc. 2012, 134, 17892−17895

delight, a highly regioselective cyclization occurred leading to cyclic NHC-borane **2a** (Scheme 1) in good yields in the case of neutral Rh species (Table 1, entries 1 and 2) and in low yield with a cationic Rh source (Table 1, entry 3). The structure was secured by X-ray diffraction analysis (Figure 4b). While the noncatalyzed hydroboration of alkenes with BH_3•SMe_2 gave the terminal-borylated Markovnikov adduct, we observed, predominantly, the five-membered ring α-borylated adduct **2a**.[18]

Table 1. Rhodium Source and Chiral Ligand Optimization for Racemic and Enantioselective Intramolecular Catalyzed Hydroboration of NHC-Borane 1a[a]

entry	Rh source	ligand	conv (%)[b]	yield (%) **2a**[c]	er (*R*:*S*)[d]
1	$[Rh(cod)Cl]_2$	–	50	45 (90:10)[e]	–
2	$Rh(PPh_3)_3Cl$	–	70	68 (98:2)[e]	–
3	$[Rh(nbd)_2]BF_4$	–	20	18 (90:10)[e]	–
4	$[Rh(cod)Cl]_2$	L1	90	–	–
5	$Rh(PPh_3)_3Cl$	L1	95	–	–
6	$[Rh(nbd)_2]BF_4$	L1	100	94	97.0:3.0
7	$[Rh(nbd)_2]BF_4$	L2	30	25	39.5:60.5
8	$[Rh(nbd)_2]BF_4$	L3	2	–	–
9	C4	–	70	40 (20)[f]	76.0:24.0
10	$[Rh(nbd)_2]BF_4$	L5	100	84	97.5:2.5
11	$[Rh(nbd)_2]BF_4$	L6	50	40	85.0:15.0

[a]Reactions were carried out in CH_2Cl_2 (1 mL) at 20 °C under an argon atmosphere containing **1a** (0.125 mmol), [Rh] (2.5 mol %), and ligand (5.0 mol %). [b]Determined by ^{1}H NMR. [c]Yield after purification by chromatography on silica gel. [d]Er determined by HPLC analysis (Chiralcel OD-3, hexane/isopropanol 95/5, 1 mL·min^{-1}); Absolute configuration *R* determined by VCD. [e]Ratio (**2a**:**3a**) determined for the crude mixture by ^{1}H NMR. [f]Isolated yield of **3a**.

Due to the impact of the ligand on the reactivity and regioselectivity of the hydroboration reaction, we next evaluated various diphosphane chiral ligands **L1**–**L6** (Figure 2),[19] and some results are summarized in Table 1 (entries 4–11). First, (*S*)-BINAP was tested with neutral Rh sources (Table 1, entries 4 and 5). Surprisingly, despite very good conversion rates, the cyclic NHC-borane **2a** or **3a** was not obtained and ^{1}H NMR analysis revealed a complex unidentified mixture. No significant signals were observed beyond those corresponding to an *N*-propyl substituent in an imidazolium environment, suggesting hydrogenation of the allyl group. Fortunately, the use of the cationic Rh complex $[Rh(nbd)_2]BF_4$ in the presence of (*S*)-BINAP (Table 1, entry 6) gave only **2a** in an excellent yield after 4 h, with a high enantioselectivity (er = 97.0:3.0) (regioisomer **3a** was not detected in the crude by ^{1}H and ^{11}B NMR). Other ligands were screened with the $[Rh(nbd)_2]BF_4$ source, and diphosphane ligands with C_2 axial symmetry (Table 1, entries 6, 10, and 11) were found to be the most efficient and selective, especially (*S*)-**L1** and (*S*)-**L5** (er = 97.0:3.0 and 97.6:2.4 respectively). Among the complexes tested, only electron-rich diphosphane ligated cationic rhodium **C4** ((*S*)-catASium) yielded the Markovnikov adduct as a minor regioisomer (**2a** and **3a** in a 2:1 ratio). It should be noted that each ligand, with a different symmetry element with an (*S*)-absolute configuration, gave the (*R*)-absolute configuration, which was determined by vibrational circular dichroism (VCD) with a good degree of confidence (see Supporting Information (SI)).

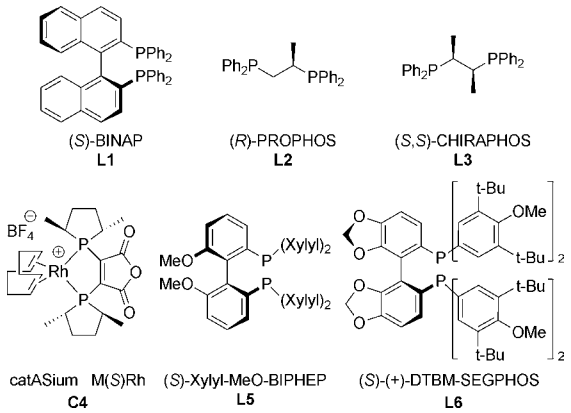


Figure 2. Ligands and rhodium complex structures.

To optimize these results, several parameters were modified based, first, on the catalytic system $[Rh(nbd)_2]BF_4$ (2.5 mol %), (*S*)-**L1** (5.0 mol %). Solvent influence, metal/ligand ratio, catalytic load, concentration, and temperature were evaluated in the reaction; however no improvement in conversion, regioselectivity, and enantioselectivity was observed.[20] Nevertheless, it was found that the use of $[Rh(nbd)_2]BF_4$, (*S*)-BINAP in a 1:1 ratio with a 5.0 mol % catalytic load drastically enhanced the reaction rate (2 min, 100% conv, 95% yield) and maintained high enantioselectivity (er = 97.0:3.0). In view of these results, this catalytic system was retained thereafter.

The scope of the NHC-borane intramolecular asymmetric Rh-catalyzed hydroboration reaction was then evaluated with **L5**.[21] First, we investigated the influence of the NHC-borane aryl group, in the enantioselective hydroboration step (Figure 4, **2a**–**2h**). The enantioselectivity was slightly improved from the phenyl (**2a**, er = 97.6:2.4) to mesityl group (**2b**, er = 98.5:1.5), but too much steric hindrance led to a lower enantioselectivity with the 2,6-diisopropylphenyl group (**2c**, er = 94.5:5.5). With the alkyl group, high enantioselectivities were obtained, more particularly with a methyl substituent (**2e**, er = 95.8:4.2) instead of a *tert*-butyl group (**2d**, er = 92.0:8.0), probably due to the higher steric hindrance in the latter case. Attempts with vinyl (**1f**), allyl (**1g**), and homoallyl (**1h**) substituted boranes were conducted to evaluate the chemoselectivity of the reaction and the feasibility of two consecutive intramolecular hydroboration steps. Unfortunately, **1f** did not react in the catalytic Rh hydroboration procedure giving **2f** in only trace amounts, and **1f** was fully recovered at the end of the reaction. However, **1g** and **1h** gave the corresponding cyclic NHC-boranes **2g** (er = 96.9:3.1) and **2h** (er = 97.3:2.7) in high yields, chemoselectivities (only hydroboration of the allyl group moiety), and enantioselectivities. Nevertheless, tricyclic NHC-boranes, which could be derived from a second intramolecular hydroboration step, were not detected. Crystallographic data of **2a** (Figure 3b) indicated that the two fused cycles were quasi

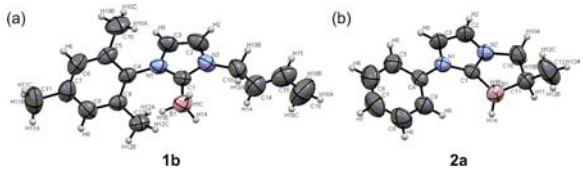


Figure 3. ORTEP diagrams of (a) **1b** and (b) **2a**, with thermal ellipsoids at 50% probability. Selected bond distances (Å) and angles (deg). **1b**: B1–C1 1.593(4); B1–C1–N1 129.3(2), B1–C1–N2 126.2(2), N1–C1–N2 104.5(2). **2a**: B1–C1 1.594(5), B1–C11 1.629(5); B1–C1–N1 143.0(3), B1–C1–N2 111.6(2), C1–B1–C11 99.4(2).

dx.doi.org/10.1021/ja309018f | J. Am. Chem. Soc. 2012, 134, 17892–17895

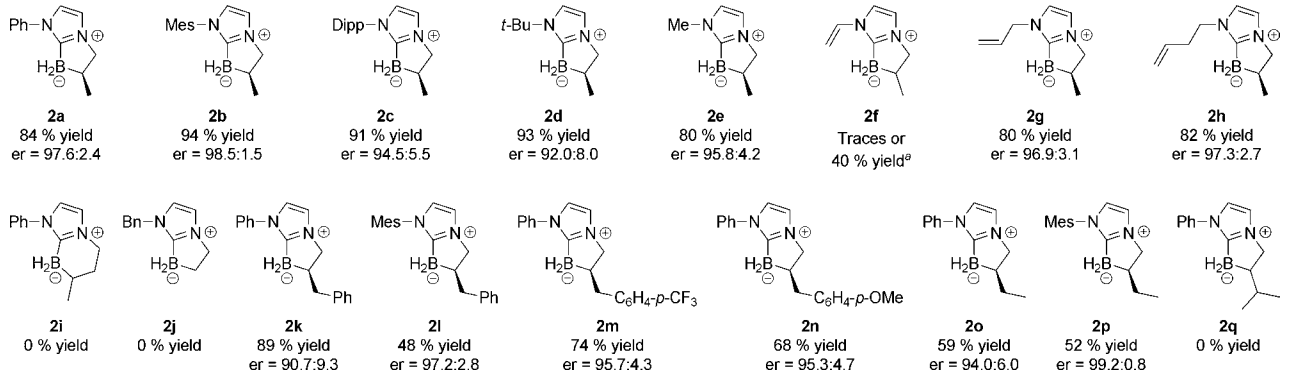


Figure 4. Scope and limitations of NHC-borane asymmetric intramolecular rhodium-catalyzed hydroboration with L5. [a]With a stoichiometric amount of catalyst $[Rh(nbd)_2]BF_4$, (*rac*)-BINAP.

coplanar, and the B1−C1−N1 (143.0°) and B1−C1−N2 (111.56°) angles were very different and clearly displaced compared to the case of the initial NHC-borane **1b** (B1−C1−N1, 129.3°, B1−C1−N2, 126.2°).

So, from bis-allyl-NHC-borane **1g**, a fused tricyclic compound would be too strained to be stable; nevertheless, in the case of **2h** (more flexible), it seems reasonable to obtain a tricyclic fused NHC-borane. Another explanation would be that, under these conditions, the hydrogen atoms from the cyclic NHC-borane **2g−2h** would not be sufficiently activated by the Rh catalytic system for a second hydroboration step. In fact, the catalytic reaction conducted on **1i** and **1j** showed, undoubtedly, that the Rh-catalyzed hydroboration step did not occur on vinyl or homoallyl side chains of the NHC-borane. In order to explain the nonreactivity of **1f**, in contrast to that of **1g−1h**, we postulated that the electron-rich vinyl group (that could be compared to an enamine group) would coordinate the Rh catalytic species as a ligand and would poison the catalytic reaction. To observe the hypothetic enamine coordinated species by ^{1}H NMR at 20 °C, attempts using a stoichiometric amount of the complex $[Rh(nbd)_2]BF_4$-(*rac*)-**L1** and **1f** led finally to **2f** in 40% yield in 18 h. A large excess in Rh catalyst seemed to overcome the poisoning effect and slowly catalyzed the hydroboration reaction.

The scope was extended to allyl-(α,β)-disubstituted NHC-boranes (**1k−1p**). In all cases, the asymmetric intramolecular Rh-catalyzed reaction was totally regioselective and only the 5-membered cyclic NHC-borane adducts were formed. Cyclic NHC-boranes (**2k−2p**) were isolated in fair to good yields,[22] albeit with excellent enantioselectivities (**2p**, er = 99.2:0.8; Figure 4). In these cases, the reaction rate strongly decreased and a complete reaction was obtained after 18 h, certainly due to the steric hindrance on the double bond of the allyl group. No effect was observed on reactivity and enantioselectivity by changing the electronic properties of the double bond (see **2k**, **2m−o**). However, attempts to cyclize trisubstituted allyl-NHC-borane **1q** into **2q** failed. From these observations, we thought that boracyclopentannulation would occur only when both olefin and B−H bonds are simultaneously activated by the Rh catalyst species. Thus, geometry around the rhodium, including agostic B−H−Rh and ligated olefin bonds, must be ideal, while too long tether or steric hindrance near the olefin subunit is unfavorable for the intramolecular hydroboration.

Finally, to verify if the Rh-catalyzed hydroboration process was fully an intramolecular process, some deuterated experiments were conducted. First, mesityl-borane-D_3 adduct (Figure 5, **1b•D$_3$**) (^{11}B NMR, s, −37.8 ppm) was prepared and then engaged in the Rh-catalytic procedure. Only the formation of

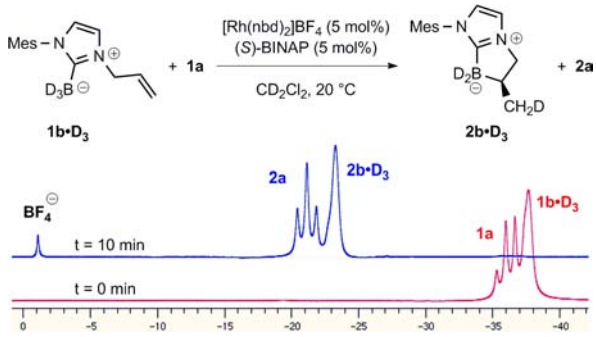


Figure 5. Deuterated scrambling study in CD_2Cl_2 (1.0 mL), ^{11}B NMR (128 MHz). Equimolar addition of **1a** and **1b•D$_3$** (0.125 mmol). Red spectrum, t = 0 min before [Rh(nbd), (*S*)-BINAP]BF_4 (5 mol %) addition; Blue spectrum, t = 10 min, after completion of the Rh-catalyzed hydroboration.

2b•D$_3$ was observed by ^{1}H NMR and ^{11}B NMR (s, −23.2 ppm) spectroscopies, with similar enantioselectivity that in the case of **2b** (er = 98.7:1.3) revealing no noticeable isotopic effect. A scrambling study (Figure 5) was also conducted by mixing **1a** and **1b•D$_3$** in an equimolar ratio. After completion of the reaction, only cyclic boranes **2a** and **2b•D$_3$** were observed by ^{1}H NMR and ^{11}B NMR without the migration of hydride or deuteride *via* a hypothetical [Rh]-H/-D exchange.

In summary, we have developed the unprecedented activation of a B−H bond of NHC-boranes by a diphosphane-ligated cationic Rh complex and applied this reaction in intramolecular hydroborations of alkenes. Independent of the unreactive *N*-substituent, *N*-allyl NHC boranes yielded a library of enantioenriched cyclic boranes in high yield (up to 94%), regio- (up to 100%) and enantioselectivity (up to 99.2:0.8). This new activation mode of NHC-boranes highlights their use in organometallic chemistry[5a,23,24] and further investigations of metal-catalyzed intermolecular hydroboration using NHC boranes are underway and will be reported in due course. Emerging recently as new promising reagents, these new cyclic NHC-boranes could be useful tools, notably as chiral hydride donors.[5b,6]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Contains complete experimental details and additional copies of NMR and VCD spectra, HPLC traces, CIF for structures **1b** (CCDC 892960) and **2a** (CCDC 892959). 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.

ACKNOWLEDGMENTS

This work was supported by the French Research Ministry (Grant 2010-2013, M.T.), Aix Marseille Université, and CNRS (UMR 7313). We thank Dr. M. Giorgi for the X-ray diffraction studies, and Dr. J.-V. Naubron for the vibrational circular dichroism spectra (www.spectropole.fr).

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(17) Structures and yields of **1a−1q** are described in the SI (see Part 3, Table 1).

(18) The ratio **2a:3a** was evaluated for the crude mixture by ^{1}H NMR, because the small amount of Markovnikov regioisomer adduct **3a** was not recovered after purification on silica gel.

(19) The complete ligand library evaluated is described in the SI (see Part 5, Table 2).

(20) Detailed optimization parameters considered in this reaction were described in the SI (nature of solvents, metal/ligand ratios, catalytic load, concentration, and temperature) (see Part 5, Tables 3−5).

(21) Both (*S*)-**L1** and (*S*)-**L5** were evaluated in the scope of the reaction, and generally, **L5** gave a slightly higher er. Enantiomeric ratios with **L1** are given in the SI (see Part 5, Figure 1).

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(24) In this context, treatment of **1b** in the standard Rh-catalyzed intramolecular hydroboration reaction, followed by the oxidation/hydrolysis process (30% aqueous H_2O_2/NaOH in MeOH), led to the functionalized hydroxyl-NHC salt **4b** (79% yield) (see SI Part 6). These products would have interesting applications as chiral bidentate NHC ligand precursors. For selected examples in the literature, see: (a) Arnold, P. L.; Rodden, M.; Wilson, C. *Chem. Commun.* **2005**, 1743. (b) Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2004**, 1612. (c) Tissot, M.; Poggiali, D.; Hénon, H.; Müller, D.; Guénée, L.; Mauduit, M.; Alexakis, A. *Chem.—Eur. J.* **2012**, *18*, 8731. (d) Hénon, H.; Mauduit, M.; Alexakis, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9122. (e) Martin, D.; Kehrli, S.; d'Augustin, M.; Clavier, H.; Mauduit, M.; Alexakis, A. *J. Am. Chem. Soc.* **2006**, *128*, 8416. (f) Tissot, M.; Hernandez, A. P.; Muller, D.; Mauduit, M.; Alexakis, A. *Org. Lett.* **2011**, *13*, 1524.