Homogeneous Catalysis

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Synthesis of Cyclic Amine Boranes through Triazole-Gold(I)-Catalyzed Alkyne Hydroboration**

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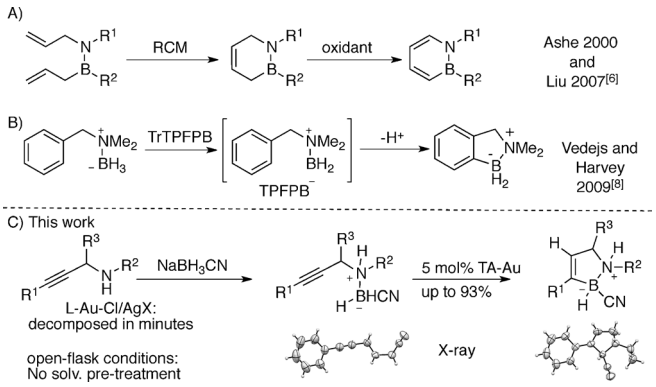
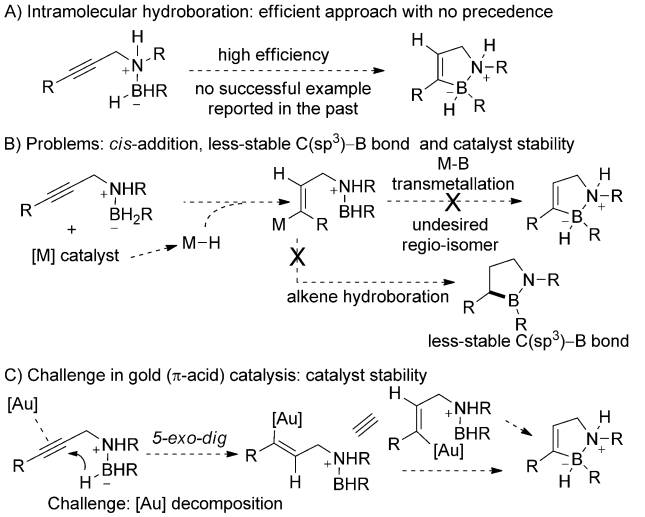
Abstract: *The first catalytic alkyne hydroboration of propargyl amine boranecarbonitriles is accomplished with triazole-Au^{I} complexes. While the typical [L-Au]$^{+}$ species decomposes within minutes upon addition of amine boranecarbonitriles, the triazole-modified gold catalysts (TA-Au) remained active, and allowed the synthesis of 1,2-BN-cyclopentenes in one step with good to excellent yields. With good substrate tolerability and mild reaction conditions (open-flask), this new method provides an alternative route to reach the interesting cyclic amine borane with high efficiency.*

The isoelectronic and isosteric relationship between B–N and C=C units initiated great interest in 1,2-azaborine research during the last several decades.[1] Despite the apparent similarity of these two units, there is relatively little known about the BN-containing heterocycles, which play a pivotal role for this class of BN-moiety-containing molecules.[2] Because of their broad applications in chemical, material, and energy storage research,[3] development of efficient methodologies for the synthesis of compounds or structures with BN moieties has become a topic of interest.[4]

The groups of Ashe,[5] Liu,[6] and Piers[7] have recently contributed to the preparation of the novel BN heterocycles based on a breakthrough strategy involving ring-closing-metathesis (Scheme 1 A). In addition, Vedejs and co-workers reported the formation of a labile B–I bond or a trivalent borenium ion as a superelectrophile[8] to facilitate the desired carbon substitution to access the BN heterocycle structure (Scheme 1 B). Despite these advances, most of the reported methods involved air- and moisture-sensitive starting materials or intermediates, which limited the synthetic applications. Thus, new strategies with high efficiency and good substrate tolerance are highly desirable. Herein, we report the triazole-gold complex catalyzed intramolecular hydroboration of alkynes (Scheme 1 C) as a new strategy for the preparation of cyclic amine boranes, in particular, 1,2-BN-cyclopentenes. This new transformation occurs under open-flask conditions with no requirement for solvent pre-treatment, and thus



Scheme 1. Synthesis of amine borane heterocycle.



Scheme 2. Amine-directed alkyne hydroboration.

presents a promising future as a general protocol in cyclic amine borane synthesis.

The amine-directed alkene/alkyne hydroboration could be a highly efficient approach for the preparation of cyclic amine borane derivatives (Scheme 2). Alkene hydroboration was used in cyclization transformations nearly a half century before, whereas, an alkyne hydroboration strategy has never been previously reported for cyclic amine borane synthesis.[9]

In general, amine-directed alkene hydroboration requires harsh conditions (high temperature) because of the reduced reactivity of boranes. With the application of I_2 as a catalyst/promoter (10% to 1 equiv), Vedejs and co-workers reported a successful alkene hydroboration performed at room tem-

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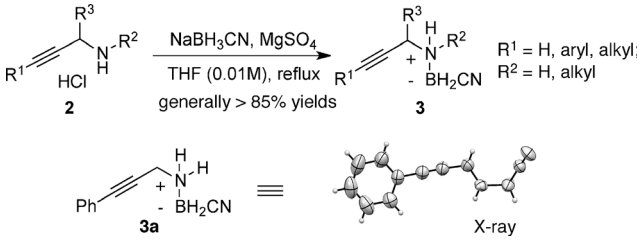
perature.[10] Although cyclic B–N compounds have been isolated in some cases, the yield (< 50 %) is moderate, and is likely due to the poor stability of the C(sp^3)–B bond.[11] This limitation decreased the potential of using this method for the synthesis of cyclic amine boranes.[10d] An amine-directed alkyne hydroboration will result in the formation of more stable vinyl boranes [C(sp^2)–B],[11] and could be more efficient for cyclic amine borane synthesis. However, to the best of our knowledge, this transformation has never been reported. In fact, because of the reduced reactivity of the alkyne, treatment of the propargyl amine borane **1** (HC≡CCH_2NH_2-BH_3) with I_2 (2 equiv, Vedejs protocol) gave no alkyne addition product after 24 hours.[12] The major challenges associated with this transformation are: 1) low reactivity of the alkyne; 2) the possibility of double addition rather than desired monohydroboration.

Although transition metal catalyzed hydroboration suffers from catalyst decomposition, successful examples have been reported.[13] To avoid the undesired catalyst decomposition (caused by borane reduction), almost all of the reported cases used metal cations which were able to form a metal hydride (M-H) bond. Meanwhile, the M-H *cis* addition to the alkyne led to the formation of the *trans* isomer, which is not suitable for the C–B bond cyclization (through M-B transmetallation, Scheme 2B). Thus, transition metal catalyzed alkyne hydroboration for the synthesis of cyclic amine borane has not been achieved in the past.

During the past decade, gold cations have been identified as one of the most effective π acids for alkyne activation.[14] Based on this activation mode, we hypothesized that cyclic amine boranes could be synthesized through the intramolecular alkyne hydroboration as shown in Scheme 2C, if an appropriate gold catalyst (that tolerates borane substrates) and amine borane precursor could be identified. Two practical concerns are: 1) the stability of active gold catalysts under the reductive conditions; 2) the feasibility of proposed Au–B transmetallation.

Our group has focused on the development of 1,2,3-triazole-coordinated metal complexes as new catalysts for challenging chemical transformations.[15] While interesting reactivity has been observed with the triazole/gold (TA-Au) complexes, the main advantage of this catalyst is the significantly improved stability.[16] Thus, we postulated that the TA-Au catalysts would provide the required π-acid reactivity toward alkyne activation while maintaining stability towards the borane, and thus afford a new and efficient synthesis of cyclic amine boranes under mild reaction conditions.

To test our hypothesis, various gold and TA-Au catalysts, $[L\text{-}Au/TA]^+X^-$ ($L = PPh_3$, IPr, XPhos; $X^- = TfO^-$, F_6Sb^-), were tested in the hydroboration of **1** (see structure of **1** in Ref. [12]). Unfortunately, significant gold decomposition (formation of gold nanoparticle or gold mirror) occurred, even with the TA-Au catalysts. Corma and co-workers have recently reported the highly efficient alkyne hydration with small gold clusters.[17] Their work suggested the in situ formed Au^0 cluster was the active catalyst. Unfortunately, no reaction occurred after this reduction process by **1** (presumably because of the formation of catalytically inactive Au^0 species, which is clearly formed during the reaction process). To overcome this problem, we put our efforts into the development of less reactive amine boranes with the aim of slowing down the decomposition process of the gold catalysts. After extensive screening of various substrates, the cyano-substituted amine borane **3** was identified and accessible through the general synthetic route summarized in Scheme 3.

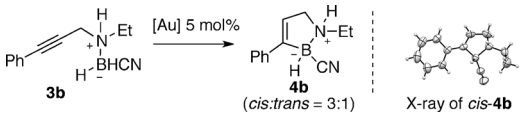


Scheme 3. Synthesis of the amine boranecarbonitrile **3**.

Under the optimal reaction conditions, **3** was prepared in good to excellent yields (generally > 85 %; see the Supporting Information). This method tolerated various substituents at the alkyne terminus. Both primary and aliphatic-substituted secondary propargyl amines worked well for the B–N formation. The aromatic-substituted propargyl amine (R^2 = Ar) could not give the corresponding complex **3** under the optimal reaction conditions, which is likely a consequence of the decreased basicity of the nitrogen atom. Nevertheless, this method allowed general access to the cyano-stabilized amine borane containing a less reactive borohydride (B–H).

With this new amine borane **3** in hand, we investigated its reactivity toward gold catalysts. Notably, compared to the terminal alkyne, the internal alkyne is usually much less reactive toward π-acid catalysts. Therefore, to better validate the feasibility of this gold catalyzed intramolecular hydroboration, **3b** was selected for our initial screening. The results are summarized in Table 1. Unlike **1** (which caused rapid gold decomposition), the **3b** gave the desired cyclic amine borane **4b** using the PPh^3AuCl/AgOTf catalyst, albeit with very low yield (17 %; entry 2). The structure of **4b** was determined by X-ray crystallography. Notably, the reaction gave 3:1 (*cis*/*trans*) isomer mixtures in solution. However, upon crystallization, all of the *trans* isomer was converted into the *cis* isomer. This process has been confirmed by NMR spectroscopy: the *cis* isomer was dissolved and a slow equilibrium was observed (up to 3 h), thus giving a 3:1 *cis*/*trans* mixture. Slowly evaporation of the solvent gave the pure *cis* isomer again (structure confirmed by X-ray). Overall, the success in obtaining **4b** greatly supported our hypothesis that the gold-catalyzed (π-acid) alkyne activation is a feasible approach for the preparation of cyclic amine boranes. To improve the reaction performance, we screened other gold catalysts. As shown in entries 1–4, although **3b** was a weaker reductant, the reaction still suffered from gold decomposition. Interestingly, the TA/Au catalysts, though giving no reaction, indicated better tolerance of **3b** given the decreased rate of gold mirror formation. To verify this result, we monitored the catalyst decomposition (upon treatment with **3b**) using

Table 1: Reaction condition screening.[a]



Entry	Catalyst	Solvent	*t* [h]	*T* [°C]	Conv. [%]	Yield [%]
1	PPh_3AuCl	CH_2Cl_2	72	RT	< 5	n.d.
2	PPh_3AuCl/AgOTf	CH_2Cl_2	0.5	RT	19	17
3	IPrAuCl/AgOTf	CH_2Cl_2	0.5	RT	15	11
4	XPhosAuCl/AgOTf	CH_2Cl_2	24	RT	< 5	n.d.
5	$[PPh_3Au\text{-}TA]^+TfO^-$	CH_2Cl_2	72	RT	< 5	n.d.
6	$[XPhosAu\text{-}TA]^+TfO^-$	CH_2Cl_2	72	RT	< 5	n.d.
7	PPh_3AuCl	DCE	72	80	< 5	n.d.
8	$[PPh_3Au\text{-}TA]^+TfO^-$	DCE	24	80	35	24
9	$[XPhosAu\text{-}TA]^+TfO^-$	DCE	72	80	> 99	93
10	$[XPhosAu\text{-}TA]^+TfO^-$	THF	72	65	85	73
11	$[XPhosAu\text{-}TA]^+TfO^-$	DMF	72	80	84	63
12	$[XPhosAu\text{-}TA]^+TfO^-$	toluene	72	90	39	36
13	$[XPhosAu\text{-}TA]^+TfO^-$	MeCN	72	80	88	65

[a] All conversions and yields determined by NMR spectroscopy with *p*-xylene as an internal standard. n.d. = not determined. DMF = *N*,*N*-dimethylformamide, THF = thetrahydrofuran.

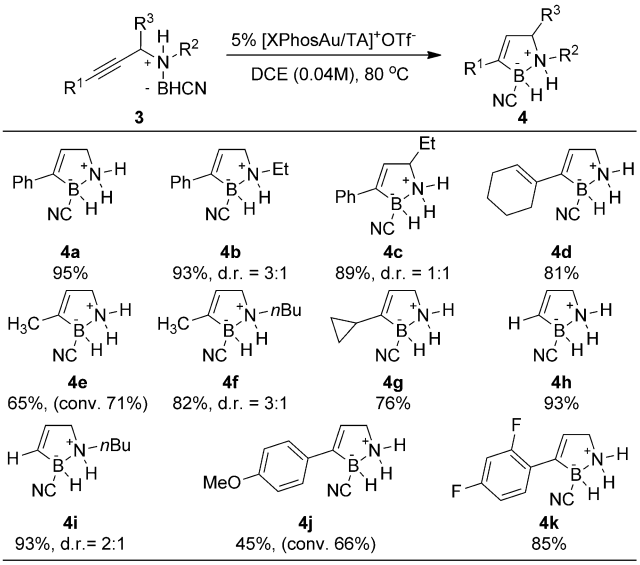


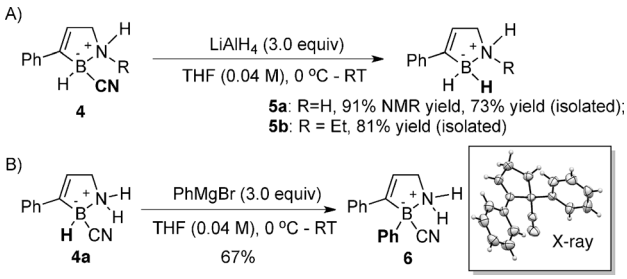
Figure 1. Reaction substrate scope: conversion, yield, and d.r. values were determined by NMR spectroscopy. Gram-scale synthesis of **4a** was conducted and product was isolated in 85% yield.

^{31}P NMR spectroscopy (see S-Figure 1 in the Supporting Information).

As shown in the ^{31}P NMR data, treating $[L\text{-}Au]^+$ species with **3b** caused immediate decomposition, even with XPhos as the primary ligand. Interestingly, with the 1,2,3-triazole-modified gold complexes, much slower decomposition was observed. The bulky XPhos ligand further improved the gold cation stability, thus giving little decomposition even after 20 hours at room temperature. With this improved catalyst stability, we further evaluated the reaction conditions at elevated temperature. To our great delight, with the XPhos-based TA-Au catalyst at 80 °C, all **3b** was consumed and **4b** was isolated in excellent yield (93%; Table 1, entry 9). Solvent screening revealed DCE as the optimal choice. Other factors, such as counter anions (SbF_6^- or Tf_2N^-) and MeCN-stabilized $[L\text{-}Au]^+$,[18] have also been screened. The triazole/gold complex gave the best result because of the superior stability under the reductive conditions (see the Supporting Information).

With this optimized reaction conditions in hand, we explored the reaction substrate scope. The results are summarized in Figure 1. As shown, this method tolerates a large substrate scope. First, both terminal and internal alkynes were suitable for this transformation. The more reactive terminal alkynes gave excellent yields (**4h** and **4i**). Most of the tested internal alkynes also worked well under these reaction conditions. The alkyne terminal (R^1) can be alkyl, aryl, cyclopropanyl, and even alkenyl (from enyne). The aliphatic internal alkynes were less reactive, thus giving slightly lower yields (**4e** and **4f**) compared to the aromatic internal alkynes. Alkynes substituted with electron-donating groups (**3j** to **4j**) reacted slowly under the reaction conditions (even with an extended reaction period, 4 days). The reaction was quenched upon the observed decomposition of the starting material **3j**. The overall yield was moderate when compared with the obtained with the electron-deficient substrate **3k**. No ring-opening product was observed in the cyclopropane-modified alkyne (**4g**), thus excluding single-electron process mechanism in this transformation. Both primary and secondary propargyl amines were tolerated, thus giving cyclic amine borane products as a mixture of *cis* and *trans* isomers with different ratios (**4b**, **4f**, and **4i**). The overall reactivity of these two types of amines was similar. Substitution at the propargyl position (R^3) had little influence on the reactivity, thus giving **4c** in excellent yield. Overall, the good functional-group tolerance at alkyne terminus (R^1), the propargyl position (R^3), and amine (R^2) highlights the potential of this method for the preparation of cyclic amine boranes with broad substrate scope.

The cyano group on boron was originally introduced to overcome the undesired gold catalyst decomposition. Thus, to further extend this methodology as a general protocol for potential cyclic amine borane synthesis, we investigated the post-cyclization derivatization with the expectation of introducing diverse functional groups on boron. Two representative transformations on the boron position are summarized in Scheme 4. First, treatment of the cyclic amine borane **4a**/**4b** with $LiAlH_4$ gave the corresponding reduction product **5a**/**5b** in good to excellent yields (Scheme 4A).[19] Notably, the



Scheme 4. Introducing functional groups at boron position.

nonsubstituted amine borane **5a** was not stable to air. Thus, excellent yields (91%) were observed by NMR spectroscopy, but only 73% product was isolated. This product loss was probably because of the loss of H_2 and sequential decomposition. Nevertheless, considering the fact that the BH_3-based amine borane **1** (see Ref. [12]) caused rapid gold decomposition and was not suitable for this transformation at all, this cyano borane modification provided an alternative solution to extend the reaction scope. Moreover, reaction of **4a** with 3 equivalents of PhMgBr gave the corresponding phenyl substituted cyclic amine borane **6**, the structure of which was confirmed by X-ray crystallography. The two strategies in Scheme 4 resulted in ready functionalization of boron, and highlights the scope of cyclic amine borane synthesis facilitated by TA-Au catalysis.[20]

Overall, we have reported a novel strategy for highly efficient preparation of cyclic amine boranes. With the newly developed cyano-modified amine borane and stable XPhos-based TA-Au catalyst, the challenging alkyne hydroboration was achieved successfully. The overall transformation operates under open-flask conditions. The excellent substrate tolerance and readily available derivatization methods make this transformation an efficient approach for cyclic amine borane synthesis. Preparation of other BN/CC isosteric derivatives (such as benzene and indole) and use of the resulting compounds in H_2 storage and catalysis are currently under investigation in our lab and will be reported in due course.

Experimental Section

4a: $[XPhosAu(TA)]^+TfO^-$ (9.3 mg, 5 mol%) was added to a solution of **3a** (0.2 mmol, 1.0 equiv) in 1,2-dichloroethane (5 mL, 0.04 M) at room temperature. The reaction mixture was stirred at 80°C and monitored by TLC. Upon completion, solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/hexanes = 1:2, V/V) to give **4a** as white solid.

For explicit experimental data, including spectroscopic data, see the Supporting Information.

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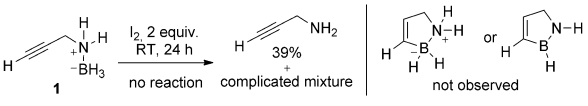

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