B,N-Heterocycles

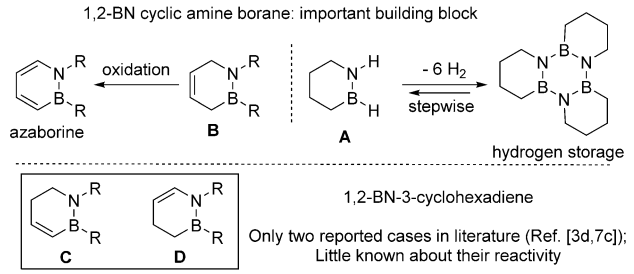
International Edition: DOI: 10.1002/anie.201604986
German Edition: DOI: 10.1002/ange.201604986

Regioselective Amine–Borane Cyclization: Towards the Synthesis of 1,2-BN-3-Cyclohexene by Copper-Assisted Triazole/Gold Catalysis

*Stephen E. Motika, Qiaoyi Wang, Novruz G. Akhmedov, Lukasz Wojtas, and Xiaodong Shi**

Abstract: *The combination of triazole/gold (TA-Au) and $Cu(OTf)_2$ is identified as the optimal catalytic system for promoting intramolecular hydroboration for the synthesis of a six-membered cyclic amine–borane. Excellent yields (up to 95%) and regioselectivities (5-exo vs. 6-endo) were achieved through catalyst control and sequential dilution. Good functional-group tolerance was attained, thus allowing the preparation of highly functionalized cyclic amine–borane substrates, which could not be achieved using other methods. Deuterium-labeling studies support the involvement of a hydride addition to a gold-activated alkyne with subsequent C–B bond formation.*

Boron-containing heterocycles have attracted attention because of their broad utility in chemical, biological, and materials research.[1] A prominent subgroup is the cyclic 1,2-amino-borane, which contains a N–B subunit that is isoelectronic to a C–C double bond.[2] The application of these compounds as hydrogen storage materials[3] or as precursors for the preparation of the aromatic 1,2-azaborine has garnered significant attention over the past few decades (Scheme 1).[4] The preparation of these compounds still remains challenging though, because of limited effective synthetic approaches. For this reason, new strategies which offer good functional-group tolerance, high efficiency, and scalability are desired. In this work, we report the synthesis of 1,2-BN-3-cyclohexene through a copper-assisted triazole/gold-catalyzed intramolecular hydroboration.



Scheme 1. 1,2-Aminoborane analogues.

[*] S. E. Motika, Dr. L. Wojtas, Prof. Dr. X. Shi
Department of Chemistry, University of South Florida
Tampa, FL 33620 (USA)
E-mail: xmshi@usf.edu
Dr. Q. Wang, Dr. N. G. Akhmedov
Department of Chemistry, West Virginia University
Morgantown, WV 26505 (USA)

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201604986.

Discrete subgroups of the six-membered 1,2-aminoborane can be identified based on oxidation states. This includes the fully oxidized aromatic aminoborane, cyclohexadiene **B** (Scheme 1), and cyclohexene **A**. Dewar and Marr[5] and White[6] first reported the synthesis of a monocyclic, aromatic azaborine, though these early works offered poor functional-group tolerance and operated under harsh reaction conditions. Later, work by Ashe and Liu led to the effective revival of this field through seminal reports on the synthesis of the fully aromatic 1,2-dihydro-1,2-azaborine (direct benzene isostere) through the synthesis and successive oxidation of **B**.[7] A key synthetic step involved a ring-closing metathesis (RCM) of di-allylic N–B precursors to afford the key cyclic scaffold.[8] Although this method has maintained a state-of-the-art status for simpler six-membered cyclic aminoborane, relatively expensive and highly reactive reagents are required with overall modest yields.

In the last several years, our group has developed new transition-metal catalysts containing the 1,2,3-triazole ligand.[9] Those extended efforts have led to the discovery of 1,2,3-triazole/gold (TA-Au) complexes as a new class of catalysts with improved stability.[10,11] By using these catalysts, we recently disclosed a unique strategy to access five-membered N–B-containing heterocycles through TA-Au-catalyzed alkyne hydroboration.[12] Key to this discovery was the need for heightened catalyst stability in the presence of a CN-modified amine–borane. Thus, when coupling the enhanced stabilizing effects of the TA ligand and a sterically influential XPhos primary ligand, excellent conversions and yields were attained, thus providing the cyclic amine–borane **2** (Figure 1 a). All other tested catalyst permutations absent of triazole led to rapid catalyst decomposition, therefore highlighting the crucial role of the triazole ligand in stabilizing the gold cation in a reducing reaction environment.

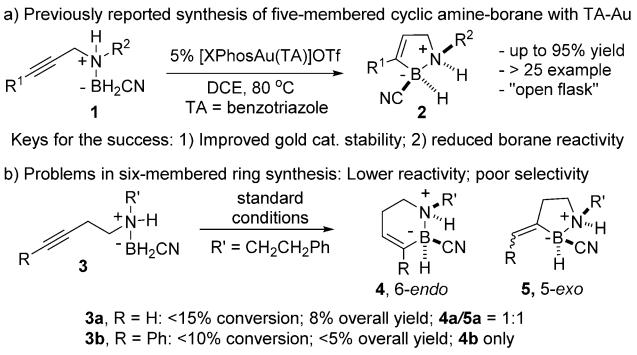


Figure 1. Challenges in the synthesis of 1,2-BN-cyclohexene. DCE = 1,2-dichloroethane, Tf = trifluoromethanesulfonyl.

We then sought to extend this protocol to access a modular synthetic platform for six-membered N–B cycles (Scheme 1; **C**). According to the literature, there are only two reported examples regarding the syntheses and applications of 1,2-BN-3-cyclohexadiene (**C** and **D**).[7c,3d] For this reason, there is also little known about this 1,2-aminoborane subgroup, which alone warrants further investigation.

When treating the homopropargyl amine derivatives **3a** and **3b** under the previously optimized reaction conditions, less than 15% conversion was obtained along with complete gold decomposition (based on ^{31}P NMR data) after 6 hours (Figure 1b). Moreover, the reaction of **3a** gave a mixture of the 6-*endo* product **4a** and 5-*exo* product **5a** in a 1:1 ratio. Absolute structural confirmation for the cyclization products **4a** and **4b** were obtained using single-crystal X-ray analysis (Figure 2). The structure of product **5** was characterized using comprehensive NMR analysis (see the Supporting Information). Notably, for both **4a** and **4b**, only *cis*-isomers were obtained based on X-ray crystallography and NMR spectroscopy.

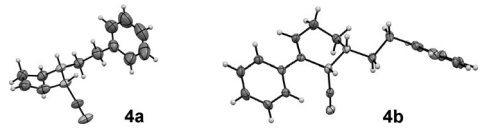
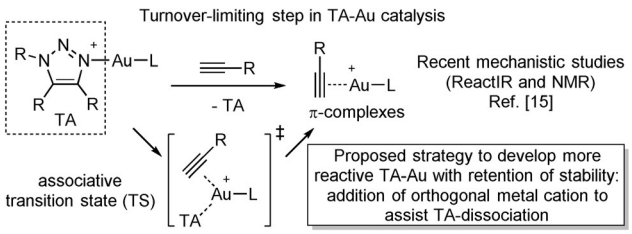


Figure 2. X-ray structures of BN-cyclohexene. Thermal ellipsoids shown at 50% probability.[21]

This result revealed two major challenges which were absent in our seminal NB-heterocycle synthesis: a) more subdued reaction kinetics requiring a more reactive catalyst which is still capable of withstanding reduction from the present borohydride; b) poor regioselectivity (desired 6-*endo* over kinetically favored 5-*exo*).

To circumvent these issues, we first re-examined the general design of the triazole/gold catalyst. As shown in Scheme 2, the triazole effectively stabilizes the gold cation

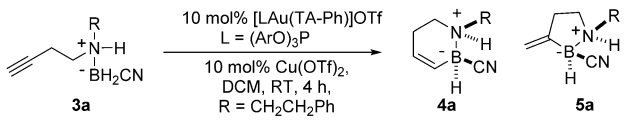


Scheme 2. Proposed new strategy: M^+-assisted TA-Au activation.

through formation of a coordinatively saturated [L-Au-TA]$^+$ complex, thereby reducing the net concentration of [L-Au]$^+$.[13] This feature explains the observed reduced reactivity of TA-Au compared to the corresponding [L-Au]$^+$ catalyst.[14] In fact, monitoring TA-Au-catalyzed reactions by ^{31}P NMR spectroscopy showed TA-Au as the dominant signal throughout the reaction (resting state). Using *React* IR and NMR spectroscopy, we recently reported the mechanistic studies of a TA-Au-catalyzed propargyl ester rearrangement.[15] The kinetic data clearly supports the formation of an alkyne–gold π complex as the turnover-limiting step, and explained the observed chemoselectivity when using the TA-Au catalyst (activation alkyne over allene).

With this mechanistic insight, we postulate that the addition of a Lewis-acidic metal cation will aid in the dissociation of the triazole ligand to yield an active gold catalytic system. Moreover, it is possible that the presence of triazole will beneficially assist in the deauration step through the formation of TA-Au.[16] Thus, the metal-assisted TA-Au catalysts may achieve improved reactivity with the retention of stability toward the borohydride. To test this idea, we charged **3a** with a combination of a gold catalyst and other Lewis acids. As expected, the addition of different metal cations significantly improved the TA-Au catalyst reactivity. Finally, with the combination of 10 mol% [$(ArO)_3$PAu(TA-H)]OTf and 10 mol% $Cu(OTf)_2$, 100% conversion of **3a** was achieved with **4a** and **5a** obtained in greater than 95% yield. Furthermore, no conversion of the starting material was observed when only a Lewis acid was used.[17] Several results obtained under alternative reaction conditions are summarized in Table 1. Typical cationic gold ([LAu]$^+$; entry 4) gave poor conversions and low yields of the cyclic aminoborane because of the rapid catalyst decomposition. The use of TA-Au alone (entry 2) also gave subdued conversions and yields because of the reduced reactivity of the gold catalyst. Interestingly, using PPh_3 as the primary ligand, the corresponding TA-Au catalyst gave slightly better yield than

Table 1: Optimization of catalysts.[a,b]



Entry	Variations from the standard reaction conditions	Conv. [%]	Yield [%] (**4a**+**5a**)	**4a**/**5a**
1	none	100	96	2:1
2	without $Cu(OTf)_2$	70	34	1:1
3	Other tested $M(OTf)_n$ salt instead of $Cu(OTf)_2$[c]	<70	<55	1:1
4	[Au]=10% $LAuNTf_2$ L=PPh_3, IPr, XPhos, $(ArO)_3P$	<40	<18	1:1
5	10 mol% [PPh_3Au(TA-H)]OTf without Cu	63	48	1:1
6	10 mol% [XPhosAu(TA-H)]OTf without Cu	75	41	1:1
7	10 mol% [$(ArO)_3$PAu(TA-H)]OTf without Cu	65	57	1:1
7	[Au]=10 mol% [PPh_3Au(TA-H)]OTf	70	34	2:1
8	[Au]=10 mol% [XPhosAu(TA-H)]OTf	84	55	2:1
9	[Au]=10 mol% [$(ArO)_3$P(TA-H)]OTf	90	85	2:1
10	[Au]=10 mol% [$(ArO)_3$P(TA-Me)]OTf	88	84	2:1
11	[Au]=5 mol% [$(ArO)_3$P(TA-Ph)]OTf	58	53	2:1

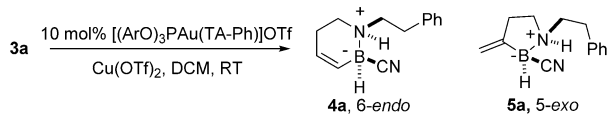
[a] General reaction conditions: **3a** (0.2 mmol), [Au cat.] (5–10 mol%), $Cu(OTf)_2$ (5–10 mol%), dichloromethane (0.2 M), RT. [b] ^{1}H NMR yields determined using 1,3,5-trimethoxybenzene as an internal standard. [c] $M(OTf)_n$ = $Ga(OTf)_3$, $Zn(OTf)_2$, $In(OTf)_3$, etc.; Ar = 2,4-di-*tert*-butylphenyl, DCM = dichloromethane, TA-Ph = *N*1-phenylbenzotriazole.

XPhosAu(TA) (entries 5 and 6). This outcome suggests that the electronic and steric influences inherent to XPhos, which were pivotal in our previous study, play less of a role in this system. We then turned to an even weaker σ-donating phosphite ligand, $(ArO)_3P$, coupled with the TA ligands. As expected, significantly improved conversion and yield were observed (entry 7). Finally, the application of N-phenyl-substituted benzotriazole (TA-Ph) gave the optimal result, with 100% conversion of **3a** and formation of products (**4a** and **5a**) in greater than 95% overall yield. Notably, excellent stereoselectivity was observed for both **4a** and **5a** (d.r. > 20:1, *cis* only confirmed by X-ray). This result further validated the Lewis acid assistance in TA-Au activation.

Our next focus was to improve the poor regioselectivity. As seen in the screening conditions, the addition of $Cu(OTf)_2$ enhanced the final regioselectivity (from 1:1 to 2:1). This result suggested that the underlying mechanistic pathways might be different between the 5-*exo* and 6-*endo* routes. We speculated that the product variability could be a result of a competitive intermolecular versus intramolecular hydroboration.

To test this hypothesis, we conducted the reaction at dilute concentrations. As expected, different ratios were observed (Table 2). Fortunately, under dilute conditions, the desired **4a** was observed as the major product. With a 20% copper loading at 0.01M, excellent regioselectivity was obtained (13:1) with **4a** being isolated in an excellent yield (90%).

Table 2: Tuning the additive and concentration.[a,b]

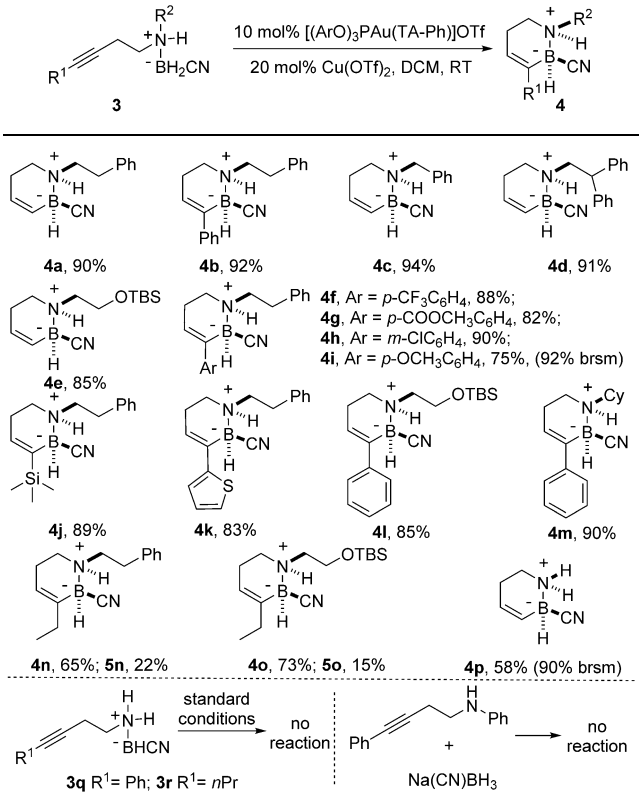


$Cu(OTf)_2$ (mol%)	[M]	Yield [%] 4a	5a	4a/5a	$Cu(OTf)_2$ (mol%)	[M]	Yield [%] 4a	5a	4a/5a
none	0.2	18	19	1:1	10	0.01	80	16	4.5:1
10	0.2	60	31	2:1	5	0.05	34	16	2.5:1
20	0.2	73	24	3:1	none	0.05	34	45	1:1.5
10	0.05	72	21	3:1	20	0.01	90	7	13:1

[a] General reaction conditions: **3a** (0.2 mmol), [Au cat.] (10 mol%), $Cu(OTf)_2$, dichloromethane, RT. [b] Yield determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

With the optimal reaction conditions in hand, we explored the reaction scope. The results are shown in Table 3. Various terminal and internal alkynes could be tolerated under the optimal reaction conditions, thus providing the BN-cyclohexenes in excellent yields and regioselectivities. Initially, terminal alkyne substrates containing different nitrogen substitution were assessed. Excellent yields were observed in all cases, even in the presence of increasingly more reactive benzylic hydrogen atoms (**4a**, **4c**, and **4d**). A sterically hindering cyclohexyl group at the nitrogen position showed no adverse effect (**4m**; 90% yield). The Lewis-basic OTBS group was well tolerated, thus giving the desired cyclization product in excellent yields (**4e** and **4l**). The aniline derivative

Table 3: Reaction scope.[a,b]



[a] General reaction conditions: **3a** (0.2 mmol), [Au cat.] (10 mol%), $Cu(OTf)_2$ (10 mol%), dichloromethane (0.01 M:0.2 M = terminal/internal alkyne), RT. [b] Yield of isolated product. TBS = *tert*-butyldimethylsilyl.

could not be assessed though, as the starting material was unstable at room temperature.[18]

Generally, both neutral and electron-withdrawing groups on aryl-substituted internal alkynes worked well, thus giving the products in excellent yields (**4b**, **4f**, **4g**, **4h**; Table 3). In the case of the more-electron-rich aryl alkyne **4i**, incomplete conversion was observed, but a high yield was attained (based on recovered starting material). The heterocycle-substituted alkyne **4k** and TMS-substituted alkyne **4j** both worked well, and further highlights the mild nature of this method.

It was evident that primary amine derivatives underwent the reaction with much lower reaction rate, thus leading to incomplete conversions (Table 3). The terminal alkyne **4p** gave low overall conversion, while a less reactive internal alkyne provided no reaction at all under the optimized reaction conditions. In general, alkyl-substituted internal alkynes gave reduced regioselectivity (**4n**/**5n** = 3:1; **4o**/**5o** = 5:1), even under dilute conditions. As discussed above, it is reasonable to suggest that the five-membered-ring formation may occur by an intermolecular process given the strong dilution effect. However, for the six-membered-ring cyclization, both steric and/or electronic factors could strongly influence the final regioselectivity (i.e. Markovnikov's rule), thus leading to the observed reduced selectivity. Overall, the exact reaction path of this new transformation is interesting

and may be complicated. Detailed mechanistic investigations are ongoing.

Following the successful optimization of cyclization conditions, we submitted the cyano-hydride product **4** to $LiAlH_4$ for B–CN cleavage. As shown in Figure 3, the desired

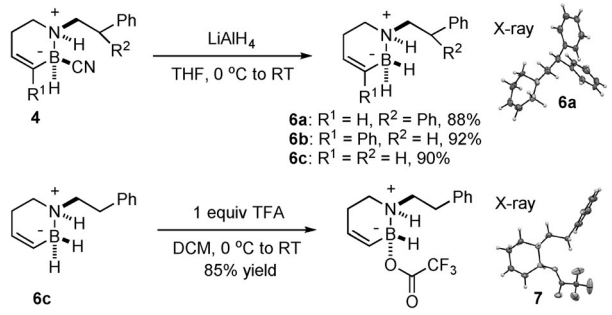


Figure 3. Post-cyclization functionalization approaches. X-ray structures[21] with thermal ellipsoids shown at 50% probability. TFA = trifluoroacetic acid.

reduced products (**6a–c**) were observed in excellent yields. Treating the borane **6c** with TFA (1.0 equiv) gave the dehydrogenation product **7**. Structures of **6** and **7** were unambiguously confirmed by X-ray crystallography.[19]

Some mechanistic probes were performed using deuterium-labeled samples. To confirm the initial hydride addition mechanism, we synthesized two deuterium-labeled precursors to monitor potential isotope scrambling (Figure 4). For the

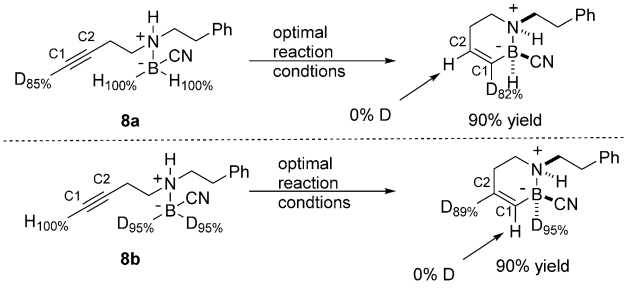


Figure 4. Mechanistic study with deuterium-labeled samples.

deuterium-labeled terminal alkyne **8a**, complete deuterium transfer at C1 was obtained with no C–D bond formation at C2. This result clearly confirmed the absence of scrambling of the hydrogen between C1 and C2. Furthermore, the reaction of deuterium-labeled **8b** gave the C–D bond at C2 with no deuterium at C1 (based on comprehensive NMR analysis). These studies clearly demonstrated the B–H (or B–D) bond as an effective nucleophile to attack the gold activated alkyne. In addition, the fact that no isotope scrambling was observed in both cases strongly suggested that the formation of either gold or copper acetylide was unlikely in this case.

The compounds **4**, **6**, and **7** were all submitted to several conditions to access the benzene isostere.[4h,5,7b,d,20] After numerous attempts, complex reaction mixtures were obtained with the benzene derivative observed in very low yields (< 5%). With the goal to develop a practical synthesis of BN-containing organic compounds (gram-scale synthesis and good functional group tolerability), our group is currently focused on investigations towards determining the optimal reaction conditions for both oxidation (to azaborine) and reduction (to BN-cyclohexane). Those results will be reported in due course.

In summary, we report a novel cyclization protocol towards the synthesis of 1,2-BN-3-cyclohexenes. The combination of a Lewis acid and a triazole/gold complex provides improved catalyst reactivity with good stability. Critical dilution led to excellent regioselectivity, thus suggesting a possible intermolecular reaction pathway for the 5-*exo*-*dig* cyclization. Although final reaction conditions for oxidation and reduction of this BN-cyclohexene have not been revealed at this moment, the reported work initiated the critical step in developing the gold-catalyzed hydroboration as a novel and practical protocol for the synthesis of N–B-containing compounds with diverse substitute patterns and excellent overall efficiency.

Acknowledgments

We acknowledge the NSF (CHE-1619590) and NSFC (21228204) for financial support.

Keywords: boranes · copper · heterocycles · gold · reaction mechanisms

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 11582–11586
Angew. Chem. **2016**, *128*, 11754–11758

[1] a) B. J. Wang, M. P. Groziak in *Advances in Heterocyclic Chemistry*, *Vol. 118* (Eds.: E. F. V. Scriven, C. A. Ramsden), Academic Press, San Diego, **2016**, pp. 47–90; b) D. Frath, J. Massue, G. Ulrich, R. Ziessel, *Angew. Chem. Int. Ed.* **2014**, *53*, 2290–2310; *Angew. Chem.* **2014**, *126*, 2322–2342.

[2] a) J. S. A. Ishibashi, J. L. Marshall, A. Maziere, G. J. Lovinger, B. Li, L. N. Zakharov, A. Dargelos, A. Graciaa, A. Chrostowska, S.-Y. Liu, *J. Am. Chem. Soc.* **2014**, *136*, 15414–15421; b) E. R. Abbey, S.-Y. Liu, *Org. Biomol. Chem.* **2013**, *11*, 2060–2069; c) M. J. D. Bosdet, W. E. Piers, *Can. J. Chem.* **2009**, *87*, 8–29; d) Z. Liu, T. B. Marder, *Angew. Chem. Int. Ed.* **2008**, *47*, 242–244; *Angew. Chem.* **2008**, *120*, 248–250.

[3] For examples of N–B systems in hydrogen storage, see: a) G. Chen, L. N. Zakharov, M. E. Bowden, A. J. Karkamkar, S. M. Whittemore, E. B. Garner III, T. C. Mikulas, D. A. Dixon, T. Autrey, S.-Y. Liu, *J. Am. Chem. Soc.* **2015**, *137*, 134–137; b) W. Luo, P. G. Campbell, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 19326–19329; c) G. Alcaraz, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2010**, *49*, 7170–7179; *Angew. Chem.* **2010**, *122*, 7326–7335; d) P. G. Campbell, E. R. Abbey, D. Neiner, D. J. Grant, D. A. Dixon, S.-Y. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 18048–18050.

[4] a) A. W. Baggett, M. Vasiliu, B. Li, D. A. Dixon, S.-Y. Liu, *J. Am. Chem. Soc.* **2015**, *137*, 5536–5541; b) X.-Y. Wang, J.-Y. Wang, J. Pei, *Chem. Eur. J.* **2015**, *21*, 3528–3539; c) M. Baranac-Stojanović, *Chem. Eur. J.* **2014**, *20*, 16558–16565; d) E. R. Abbey, A. N. Lamm, A. W. Baggett, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2013**, *135*, 12908–12913; e) G. E. Rudebusch, L. N. Zakharov, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 9316–

9319; *Angew. Chem.* **2013**, *125*, 9486 – 9489; f) S. A. Brough, A. N. Lamm, S.-Y. Liu, H. F. Bettinger, *Angew. Chem. Int. Ed.* **2012**, *51*, 10880 – 10883; *Angew. Chem.* **2012**, *124*, 11038 – 11041; g) P. G. Campbell, A. J. V. Marwitz, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074 – 6092; *Angew. Chem.* **2012**, *124*, 6178 – 6197; h) A. Chrostowska, S. M. Xu, A. N. Lamm, A. Mazière, C. D. Weber, A. Dargelos, P. Baylère, A. Graciaa, S.-Y. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 10279 – 10285; i) A. N. Lamm, E. B. Garner III, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2011**, *50*, 8157 – 8160; *Angew. Chem.* **2011**, *123*, 8307 – 8310; j) S. Xu, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 20152 – 20155; k) R. Carion, V. Liegeois, B. Champagne, D. Bonifazi, S. Pelloni, P. Lazzeretti, *J. Phys. Chem. Lett.* **2010**, *1*, 1563 – 1568; l) A. J. V. Marwitz, S. P. McClintock, L. N. Zakharov, S.-Y. Liu, *Chem. Commun.* **2010**, *46*, 779 – 781; m) M. Lepeltier, O. Lukoyanova, A. Jacobson, S. Jeeva, D. F. Perepichka, *L. Chem. Commun.* **2010**, *46*, 7007 – 7009; n) J. Pan, J. W. Kampf, A. J. Ashe III, *Org. Lett.* **2007**, *9*, 679 – 681; o) P. J. Fazen, L. A. Burke, *Inorg. Chem.* **2006**, *45*, 2494 – 2500; p) J. Pan, J. W. Kampf, A. J. Ashe, *Organometallics* **2006**, *25*, 197 – 202.

[5] M. J. S. Dewar, P. A. Marr, *J. Am. Chem. Soc.* **1962**, *84*, 3782 – 3782.

[6] D. G. White, *J. Am. Chem. Soc.* **1963**, *85*, 3634 – 3636.

[7] a) W. Luo, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 13006 – 13009; b) A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973 – 977; *Angew. Chem.* **2009**, *121*, 991 – 995; c) E. R. Abbey, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 7250 – 7252; d) A. J. V. Marwitz, E. R. Abbey, J. T. Jenkins, L. N. Zakharov, S.-Y. Liu, *Org. Lett.* **2007**, *9*, 4905 – 4908; e) A. J. Ashe, X. D. Fang, X. G. Fang, J. W. Kampf, *Organometallics* **2001**, *20*, 5413 – 5418.

[8] A. J. Ashe, X. D. Fang, *Org. Lett.* **2000**, *2*, 2089 – 2091.

[9] a) X. Ye, Z. He, T. Ahmed, K. Weise, N. G. Akhmedov, J. L. Petersen, X. Shi, *Chem. Sci.* **2013**, *4*, 3712 – 3716; b) W. Yan, X. Ye, K. Weise, J. L. Petersen, X. Shi, *Chem. Commun.* **2012**, *48*, 3521 – 3523; c) W. Yan, Q. Wang, Y. Chen, J. L. Petersen, X. Shi, *Org. Lett.* **2010**, *12*, 3308 – 3311; d) H. Duan, S. Sengupta, J. L. Petersen, X. Shi, *Organometallics* **2009**, *28*, 2352 – 2355.

[10] a) B. Dong, Y. Xi, Y. Su, N. G. Akhmedov, J. L. Petersen, X. Shi, *RSC Adv.* **2016**, *6*, 17386 – 17389; b) S. Hosseyni, S. Ding, Y. Su, N. G. Akhmedov, X. Shi, *Chem. Commun.* **2016**, *52*, 296 – 299; c) S. Hosseyni, L. Wojtas, M. Li, X. Shi, *J. Am. Chem. Soc.* **2016**, *138*, 3994 – 3997; d) S. E. Motika, Q. Wang, X. Ye, X. Shi, *Org. Lett.* **2015**, *17*, 290 – 293; e) S. Hosseyni, Y. Su, X. Shi, *Org. Lett.* **2015**, *17*, 6010 – 6013; f) Y. Xi, B. Dong, E. J. McClain, Q. Wang, T. L. Gregg, N. G. Akhmedov, J. L. Petersen, X. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 4657 – 4661; *Angew. Chem.* **2014**, *126*, 4745 – 4749; g) Y. Xi, D. Wang, X. Ye, N. G. Akhmedov, J. L. Petersen, X. Shi, *Org. Lett.* **2014**, *16*, 306 – 309.

[11] For reviews of gold catalysis, see: a) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* **2012**, *41*, 2448 – 2462; b) L.-P. Liu, G. B. Hammond, *Chem. Soc. Rev.* **2012**, *41*, 3129 – 3139; f) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232 – 5241; *Angew. Chem.* **2010**, *122*, 5360 – 5369; j) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208 – 3221; k) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266 – 3325; c) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239 – 3265; d) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766 – 1775; h) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351 – 3378; g) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395 – 403; i) A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410 – 3449; *Angew. Chem.* **2007**, *119*, 3478 – 3519; e) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896 – 7936; *Angew. Chem.* **2006**, *118*, 8064 – 8105.

[12] Q. Wang, S. E. Motika, N. G. Akhmedov, J. L. Petersen, X. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 5418 – 5422; *Angew. Chem.* **2014**, *126*, 5522 – 5526.

[13] H. Duan, S. Sengupta, J. L. Petersen, N. G. Akhmedov, X. Shi, *J. Am. Chem. Soc.* **2009**, *131*, 12100 – 12102.

[14] a) D. Wang, Y. Zhang, R. Cai, X. Shi, *Beilstein J. Org. Chem.* **2011**, *7*, 1014 – 1020; b) D. Wang, L. N. S. Gautam, C. Bollinger, A. Harris, M. Li, X. Shi, *Org. Lett.* **2011**, *13*, 2618 – 2621; c) D. Wang, X. Ye, X. Shi, *Org. Lett.* **2010**, *12*, 2088 – 2091.

[15] Y. Xi, Q. Wang, Y. Su, M. Li, X. Shi, *Chem. Commun.* **2014**, *50*, 2158 – 2160.

[16] W. Wang, M. Kumar, G. B. Hammond, B. Xu, *Org. Lett.* **2014**, *16*, 636 – 639.

[17] a) D. J. Faizi, A. Issaian, A. J. Davis, S. A. Blum, *J. Am. Chem. Soc.* **2016**, *138*, 2126 – 2129; b) M. M. Hansmann, R. L. Melen, M. Rudolph, F. Rominger, H. Wadepohl, D. W. Stephan, A. S. K. Hashmi, *J. Am. Chem. Soc.* **2015**, *137*, 15469 – 15477.

[18] For aniline derivatives, only trace amounts of the desired acyclic precursor could be observed by crude NMR spectroscopy. Isolation proved futile, as complete decomposition was evident under various purification protocols.

[19] Investigations towards N–B dehydrogenation were performed following B–CN cleavage. At this point, modest yields of the desired dehydrogenated product have been attained. We include the trifluormethylation, as this represents a better leaving group compared to $^{-}$CN. The TFA adducts have been the most effective in further N–B dehydrogenation and will published in due course.

[20] Several reported oxidation procedures were attempted, see: a) E. R. Abbey, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 11508 – 11511; b) M. J. S. Dewar, B. P. Robinson, G. J. Gleicher, *J. Am. Chem. Soc.* **1964**, *86*, 5698 – 5699.

[21] CCDC 1479621 (**4a**), 1479623 (**4b**), 1479620 (**6a**), and 1479622 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: May 21, 2016
Published online: August 17, 2016

