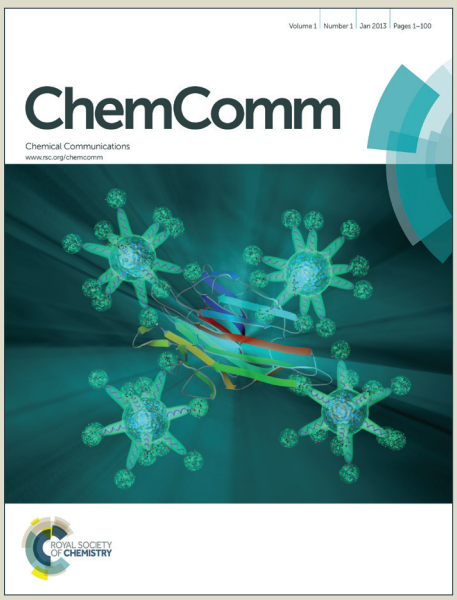
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

cis-Semihydrogenation of Alkynes With Amine Borane Complexes Catalyzed by Gold Nanoparticles Under Mild Conditions

Eleni Vasilikogiannaki,[¶] Ioannis Titilas,[¶] Georgios Vassilikogiannakis and Manolis Stratakis*

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

Supported gold nanoparticles catalyze the semihydrogenation of alkynes to alkenes with ammonia borane or amine borane complexes in excellent yields and under mild conditions. Internal alkynes provide *cis*-alkenes, making this protocol an attractive alternative of the classical Lindlar's hydrogenation.

Nanogold-catalyzed reductive processes using either H_2 or transfer hydrogenation pathways have recently received considerable attention.[1] In this context, little progress has been achieved in the reduction of π-systems by direct hydrogenation[2] due to the difficulty of formation of the labile gold hydride reducing species[3] on the surface of nanoparticulated Au catalysts (Au NPs). On the other hand, promising examples of heterogenized Au-catalyzed transfer hydrogenation protocols for π-systems are gradually starting to appear,[4] especially in the semireduction of alkynes using hydrosilanes/H_2O,[4a] or CO/H_2O,[4c] as reductants.

Our recent promising results in the transfer hydrogenation of nitro compounds using ammonia borane complex catalyzed by supported Au NPs[5] drove us to examine the potency of ammonia borane and other amine borane complexes in the reduction of π systems and especially alkynes, given that the semihydrogenation of alkynes into *cis*-alkenes is of significant interest in synthetic organic chemistry.[6] To achieve this transformation, organic chemists mainly hydrogenate alkynes in the presence of suitable catalysts (e.g. Lindlar's catalyst or frustrated Lewis pairs).[7] Yet, these processes require special apparatuses operating with flammable H_2 gas. More practical semireduction procedures would certainly be welcomed by researchers on the bench.[8]

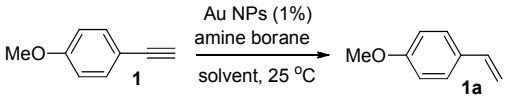
The reduction of *p*-methoxyphenylacetylene (**1**) was examined as a model substrate in the presence of different supported Au NPs catalysts,[9] amine borane complexes[10] and solvents. Note that the use of boron hydride substances as reductants of π-systems and especially alkynes is rather limited. The Pd-catalyzed reduction of akynes with $NaBH_4$,[11a] or $NaBHEt_3$[11b] provides alkanes, as the intermediate formed alkenes are also rapidly reduced. Ammonia borane has been used as reducing agent for transforming aryl alkynes into alkenes catalyzed by a Ni(0) complex under rather forcing

Department of Chemistry, University of Crete, Voutes 71003 Iraklion, Greece. Fax: +30 2810 545001; Tel: +30 2810 545087. E-mail: stratakis@chemistry.uoc.gr

† Electronic Supplementary Information (ESI) available: Spectroscopic data for all products and copies of ^1H and ^{13}C NMR. See DOI: 10.1039/b000000x/

[¶] These authors contributed equally to this work

Table 1. Reduction of *p*-methoxyphenylacetylene (**1**) with amine borane complexes catalyzed by supported Au nanoparticles.



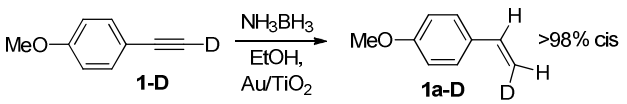
Entry	Catalyst	Solvent	Reductant (amine borane)	Molar equiv	Time (h)	Conv. (%)	Sel. (%)[a]
1	Au/TiO_2	EtOH	NH_3BH_3	1.0	0.2	100	94
2	Au/TiO_2	EtOH	NH_3BH_3	0.5	0.5	100	98
3	Au/TiO_2	EtOH	NH_3BH_3	0.35	2.0	85	>99
4	Au/TiO_2	DCM	NH_3BH_3	2.0	8.0	8	>99
5	Au/TiO_2	EtOAc	NH_3BH_3	2.0	1.0	16	>99
6	Au/TiO_2	THF	NH_3BH_3	2.0	1.0	11	>99
7	Au/TiO_2	THF/H_2O[b]	NH_3BH_3	2.0	1.0	100	93
8	Au/Al_2O_3	EtOH	NH_3BH_3	1.0	0.5	100	95
9	Au/ZnO	EtOH	NH_3BH_3	1.0	0.5	10	>99
10	Au/TiO_2	EtOH	$NH_2NH_2BH_3$	1.5	0.2	100	98
11	Au/TiO_2	EtOH	*t*-$BuNH_2BH_3$	3.0	1.0	15	>99
12	Au/TiO_2	EtOH	Me_2NHBH_3	0.5	0.5	100	>99
13	Au/TiO_2	EtOH	Me_2NHBH_3	1.0	0.2	100	99
14	Au/TiO_2	EtOH	$MeNH_2BH_3$	0.5	0.5	100	>99
15	Au/TiO_2	EtOH	Me_3NBH_3	3.0	1.0	0	

[a]Relative percent ratio of alkene **1a** to the corresponding alkane. [b]THF/H_2O=20/1.

conditions (80 °C, 24-72 h).[12] We found that using Au/TiO_2 (1 mol%) as catalyst and ethanol as solvent, smooth reduction of **1** to *p*-methoxystyrene (**1a**) took place with 0.5 molar equiv of ammonia borane (AB), or dimethylamine borane (DMAB), within 30 min at 25 °C and under non-inert atmosphere (Table 1). Using 1 molar equiv of AB, overreduction to the corresponding alkane was observed in 6% relative yield, while in the presence of 1 molar equiv of DMAB, the alkane side-product is formed in ~1% yield. The reduction proceeds sluggishly in non-protic solvents such as THF, ethyl acetate, or DCM, yet when adding 5% v/v H_2O in THF complete reduction occurs within 1 h with 2.0 equiv of AB, or DMAB. *tert*-Butylamine borane is less efficient, while in the presence of trimethylamine borane (Me_3NBH_3), no reduction was seen. Hydrazine borane on the other hand is exceptionaly reactive, however, it suffers from a relatively fast competing dehydrogenative decomposition,[10b,13] requiring thus 1.5 molar equiv excess to reduce **1** into **1a**. Hydrazine borane had been anticipated as a highly promising reductant, given the high

reactivity of ammonia borane and the fact that hydrazine itself is a potent reductant[14] in the presence of supported Au NPs. In addition, reduction of **1** with dimethyl sulfide borane complex or pinacol borane, in the presence of Au NPs does not take place. The reduction process is heterogeneous as under the reaction conditions Au leaking into the solution is below ppm level (ICP analysis). Au NPs are recyclable and resuable for 3 concecutive runs regarding the reduction of **1** with AB (0.5 equiv of AB in each run), without any deterioration of their activity. The recycling process consists of filtration, washing with ethanol and finally drying at 80 °C for 2 h.

Most importantly, even less than 0.5 molar equiv of AB, or DMAB, are necessary for a quantitative reaction (entry 3, Table 1),[15] indicating that the possible origins of the two new hydrogen atoms in product **1a** are the B-H of borane (hydride) and the N-H of amine (proton). Highly supportive of this proposal is the fact that trimethylamine borane, which lacks of N-H bond is completely unreactive, in sharp contrast to dimethylamine borane. In addition, the reduction of labelled **1-D**[17] with AB affords stereoselectively **1a-D**[17] (Scheme 1) indicative of a *cis*-addition pattern for the two hydrogen atoms.



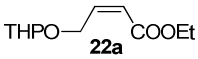
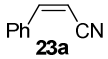
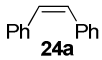
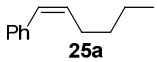
Scheme 1. Stereoselective *cis*-semihydrogenation of deuterium labelled *p*-methoxyphenylacetylene **1-D** with NH_3BH_3.

The potency of the Au-catalyzed triple bond semi-reduction was examined in a series of terminal and internal alkynes. Based on the optimum results from Table 1, ammonia borane (AB) and dimethylamine borane (DMAB) were chosen as reductants, ethanol as solvent, and the commercially available Au/TiO_2 (1 mol%) as catalyst. The results are summarized in Table 2 and reveal that the *cis*-semihydrogenation pathway observed in **1-D** is general. In most of the cases, no chromatographic purification of products is required. The reaction tolerates a series of functionalities such as a chloride, free alcohol, aryl-, silyl- or THP-protected alcohols, nitrogen containing alkynes, esters and nitrile. The highly sensitive under typical hydrogenation conditions benzyl ethers remain intact (product **18a**). The only functional group that does not tolerate the reaction conditions are aldehydes or ketones, which are known to be reduced smoothly by AB to alcohols under non-catalyzed conditions.[5,17] Thus, alkynal Ph-C≡C-CHO (**26**, not shown in Table 2) affords with 1.5 equiv of AB *cis*-alkenol **15a** in 85% yield, via intermediate formation of the corresponding alkynol **15** (GC-MS). Among all reactions examined, it was found that only α,β-unsaturated esters (e.g. Ph-C≡C-COOEt, **20**) exhibited a slow E/Z-unselective and uncatalyzed reduction. This competing reduction did not exceed 15-20% conversion after 12 h and was seen when large excess (5 molar equiv) of AB or DMAB were used. In certain cases of α,β-unsaturated esters (**20**, **22**) and nitrile **23**, the *cis*-reduction with DMAB proceeds in low yield, as competing addition of Me_2NH to the triple bond in a Michael fashion is also taking place, forming chromatographically labile adducts. Sterically hindered alkynes require a suitable excess of reducing agent, as while the reduction rate slows down, at the same time amine boranes

Table 2 *cis*-Semireduction of alkynes with ammonia borane or dimethylamine borane catalyzed by Au/TiO_2.

product	amine borane (molar equiv)	time (h)	yield (%)[a]	(Z/E)/alkane
Ph 2a	AB (1.0)	0.5	>99%[b]	(98)/2
	DMAB (1.0)	0.5	>99%[b]	(100)/0
Me_2N 3a	AB (1.0)	0.5	86%	(95)/5
	DMAB (1.0)	0.5	95%	(99)/1
TBSO, MeO 4a	AB (0.6)	1.0	85%	(96)/4
	DMAB (0.6)	0.8	95%	(100)/0
N 5a	AB (1.0)	1.5	97%[b]	(90)/10
	DMAB (1.0)	1.0	97%[b]	(100)/0
PhO 6a	AB (0.5)	0.5	78%	(98)/2
	DMAB (1.0)	1.0	93%	(100)/0
TBDPSO 7a	AB (0.7)	0.5	96%	(99)/1
	DMAB (0.7)	0.5	97%	(100)/0
THPO 8a	AB (1.0)	0.5	83%	(98)/2
	DMAB (1.5)	1.0	88%	(100)/0
BocHN 9a	AB (0.7)	0.5	92%	(96)/4
	DMAB (0.7)	0.5	97%	(100)/0
AcO 10a	AB (0.8)	0.5	90%	(99)/1
	DMAB (0.8)	0.5	91%	(100)/0
HO 11a	AB (1.5)	1.0	90%	(96)/4
	DMAB (0.7)	0.5	95%	(100)/0
OH 12a	AB (1.0)	0.5	91%	(97/2)/1
	DMAB (0.7)	1.0	95%	(99/1)/0
Pr HO 13a	AB (1.5)	1.5	82%	(91/5)/4
	DMAB (1.5)	3.0	93%	(99/1)/0
OH 14a	AB (5.0)	3.0	79%	(95/2)/3
	DMAB (4.0)	5.0	86%	(98/2)/0
Ph OH 15a	AB (0.5)	2.0	84%	(95/2)/3
	DMAB (0.5)	0.5	96%	(99/1)/0
Ph HO 16a	AB (1.0)	1.0	87%	(94/4)/2
	DMAB (1.0)	1.0	95%	(99/1)/0
Ph OH 17a	AB (3.0)	4.0	76%	(88/2)/10
	DMAB (1.5)	2.0	90%	(97/2)/1
O Ph 18a	AB (1.5)	1.0	82%	(95)/5
	DMAB (1.0)	1.0	95%	(100)/0
Cl 19a	AB (1.5)	4.0	15%[b]	(99)/1
	DMAB (1.5)	3.0	92%[b]	(100)/0
Ph COOEt 20a	AB (1.0)	1.0	78%	(91/6)/3
	DMAB (1.5)	2.0	51%[c]	(94/6)/0
COOEt 21a	AB (1.0)	0.5	82%	(94/2)/4
	DMAB (1.0)	1.0	92%	(98/2)/0

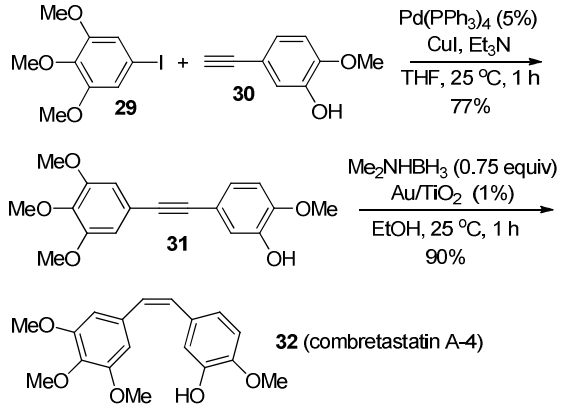
(continued)

 **22a**	AB (1.0) DMAB (1.5)	1.0 2.0	82% 22%[c]	(95/2)/3 (98/2)/0
 **23a**	AB (1.5) DMAB (2.0)	2.0 4.0	82% 49%[c]	(96/4)/1 (98/2)/0
 **24a**	AB (3.0) DMAB (1.0)	1.0 0.5	78% 95%	(91/6)/3 (98/2)/0
 **25a**	AB (6.0) DMAB (5.0)	12.0 12.0	52%[d] 78%	(89/6)/5 (94/5)/1

[a]Isolated yield. [b]Conversion yields by GC analysis. [c]The low yield is due to competing Michael-type addition of Me_2NH to triple bond. [d]75% conversion of alkyne **25**.

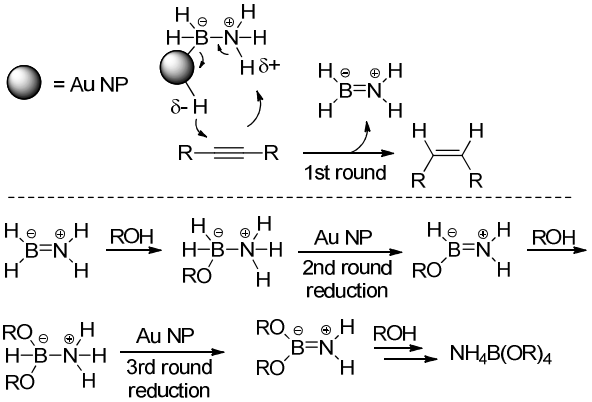
gradually undergo competing solvolytic destruction.[15] Also, the reduction of non-polar alkynes proceeds slowly (e.g. **25**), possibly due to their difficulty accessing the active catalytic sites of Au NPs on the polar support.[18]

The current stereoselective semireduction protocol was applied in the efficient synthesis of combretastatin A-4, a potent pharmaceutical stilbenoid isolated from *Combretum caffrum* (Scheme 2). Thus, the Au/TiO_2-catalyzed reaction of diaryl alkyne **31**[19] with DMAB (1.0 equiv) afforded combretastatin A-4 (**32**) in 90% yield and >96% geometrical purity. The analogous reduction with AB provided marginally inferior results in terms of stereoselectivity and yield. Alkyne **31** was easily prepared by the Sonogashira coupling of commercially available 5-iodo-1,2,3-trimethoxybenzene (**29**) and acetylene **30**, itself obtained in 2 steps from isovaniline.[20]



Scheme 2 A short stereoselective synthesis of combretastatin A-4 (**32**) employing as key step the catalytic reduction of alkyne **27** with DMAB.

Regarding the reaction mechanism, significant information was gained from the fate of ammonia borane during reduction. Based on direct ^{11}B NMR studies from the liquid phase of the Au-catalyzed reaction among ammonia borane and **1**, carried out in methanol-d4 as solvent, revealed that NH_3BH_3 (-24.4 ppm) transforms into $NH_4B(OCD_3)_4$. The borate salt exhibits a broad peak at 9.0 ppm (see Supporting Information) in accordance to literature data from the $RuCl_3$-catalyzed dehydrogenative methanolysis of AB.[21] Even at ~50% progress of reaction only the specific borate salt was seen; no other intermediate boron-bearing substances were detected. The formation of tetra-alkoxy borate salt indicates that a protic solvent is essential, participating into the reaction mechanism. In Scheme 3, the ideal case of reduction of 3 molecules of alkyne by 1 molecule of AB is depicted.[15] We propose that the reduction involves formation of Au-hydrides from insertion of B-H bond on Au,[22] that nucleophilically attack the triple bond, while the second hydrogen atom on the produced alkene derives from the N-H moiety, through an inner-sphere[23] addition mechanism. The first round of reduction delivers alkene and $H_2B{=}NH_2$. Then, $H_2B{=}NH_2$ reacts with the protic solvent (ROH) forming $(RO)H_2BNH_3$. The new ammonia alkoxyborane complex, which is expected to be more reactive relative to parent H_3BNH_3 due to the electron donating alkoxy substituent, undergoes a second round of alkyne reduction, forming as by-product $(RO)HB{=}NH_2$. Addition of ROH and third round of alkyne reduction, finally forms the identified $NH_4B(OR)_4$. We believe that the whole process resembles the metal-catalyzed alcoholysis or hydrolysis of AB,[21] with the only difference that the hydrogen atoms of AB are delivered on the alkyne instead of eliminated as H_2. We also point out that, although AB and related substances are in general sources of H_2,[24] in our case it is highly unlikely that reduction takes place via hydrogenation of the alkyne by the produced H_2, because Au NPs are inefficient catalysts for such transformation under mild conditions.[2] Supportive of the mechanism shown in Scheme 3 is the fact that when performing the reduction of **1** with AB in CD_3OD, or THF/D_2O, around 60-65% D incorporation was seen in **1a** on both carbon atoms of styrene (see Supporting Information), as based on our proposal, CD_3OD introduces D atoms on the intermediate borazine-type compounds ($X_2B{=}NH_2$, X = H or OR). Finally, our proposed mechanism nicely explains the high efficiency of Me_2NHBH_3 (Tables 1 and 2), although having only one N-H functionality.



Scheme 3 A mechanistic rational for the *cis*-semihydrogenation of alkynes by ammonia borane complex in the presence of Au NP, showing the fate of ammonia borane.

In conclusion, we present herein a highly efficent and simple protocol for the stereoselective *cis*-semireduction of functionalized alkynes with amine borane complexes (especially ammonia or dimethylamine borane), catalyzed by supported Au nanoparticles under very mild conditions. This protocol is a compelling alternative to the direct catalytic hydrogenation process. Given that supported Au nanoparticles are recyclable and resuable as described above, the value of this reduction protocol becomes even more apparent.

Acknowledgment: The authors acknowledge co-funding of this research by the European Regional Development Fund of the EU and national funds- Greek Ministry of Education and Religious Affairs, Sport and Culture/GGET – EYDE-ETAK, through the Operational Program Competitiveness and Entrepreneurship (OPC II), NSRF 2007-2013, Action "SYNERGASIA 2011" Project: THERA-CAN - No. 11ΣΥΝ_1_485.

Notes and references

1 (a) L. McEwan, M. Julius, S. Roberts and J. C. Q. Fletcher, *Gold Bull.,* 2010, **43**, 298. (b) Y. Zhang, X. Cui, F. Shi and Y. Deng, *Chem. Rev.,* 2012, **112**, 2467. (c) M. Stratakis and H. Garcia, *Chem. Rev.,* 2012, **112**, 4469. (d) T. Mitsudome and K. Kaneda, *Green Chem.,* 2013, **15**, 2636. (e) B. S. Takale, M. Bao and Y. Yamamoto, *Org. Biomol. Chem.,* 2014, **12**, 2005. (f) X. Liu, L. He, Y.-M. Liu and Y. Cao, *Acc. Chem. Res.,* 2014, **47**, 793.

2 (a) A. S. K Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896. (b) Y. Segura, N. Lopez and J. Perez-Ramirez, *J. Catal.*, 2007, **247**, 383. (c) M. Haruta, *Angew. Chem., Int. Ed.*, 2014, **53**, 52. (d) D. Ren, L. He, L. Yu, R.-S. Ding, Y.-M. Liu, Y. Cao, H.-Y. He and K.-N. Fan, *J. Am. Chem. Soc.*, 2012, **134**, 17592. (e) G. Li and R. Jin, *J. Am. Chem. Soc.*, 2014, **136**, 11347. (f) L. Shao, X. Huang, D. Teschner and W. Zhang, *ACS Catal.*, 2014, **4**, 2369.

3 M. Boronat, P. Concepcion, A. Corma, S. Gonzalez, F. Illas and P. Serna, *J. Am. Chem. Soc.*, 2007, **129**, 16230.

4 (a) M. Yan, T. Jin, Y. Ishikawa, T. Minato, T. Fujita, L.-Y. Chen, M. Bao, N. Asao, M.-W. Chen and Y. Yamamoto, *J. Am. Chem. Soc.*, 2012, **134**, 17536. (b) M. Yan, T. Jin, Q. Chen, H. E. Ho, T. Fujita, L.-Y. Chen, M. Bao, M.-W. Chen, N. Asao and Y. Yamamoto, *Org. Lett.,* 2013, **15**, 1484. (c) S.-S. Li, X. Liu, Y.-M. Liu, H. He, K. Fan and Y. Cao, *Chem. Commun.*, 2014, **50**, 5626.

5 E. Vasilikogiannaki, C. Gryparis, V. Kotzabasaki, I. N. Lykakis and M. Stratakis, *Adv. Synth. Catal*., 2013, **355**, 907.

6 C. Oger, L. Balas, T. Durand and J.-M. Galano, *Chem. Rev.*, 2013, **113**, 1313.

7 (a) M. Crespo-Quesada, F. Cardenas-Lizana, A.-L. Dessimoz and L. Kiwi-Minsker, *ACS Catal.*, 2012, **2**, 1773. (b) J. Paradies, *Angew. Chem., Int. Ed.*, 2014, **53**, 3552.

8 Recent selected examples of transfer semihydrogenation protocols of alkynes employing metal catalysis other than gold: (a) P. Hauwert, G. Maestri, J. W. Sprengers, M. Catellani and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 2008, **47**, 3223. (b) J. Li, R. Hua and T. Liu, *J. Org. Chem.*, 2010, **75**, 2966. (c) K. Semba, T. Fujihara, T. Xu, J. Terao and Y. Tsuji, *Adv. Synth. Catal*., 2012, **354**, 1542. (d) A. M. Whittaker and G. Lalic, *Org. Lett.*, 2013, **15**, 1112.

9 Au/TiO_2, Au/Al_2O_3, Au/ZnO (1 wt% in Au) are commercially available having an average gold crystallite size of ~2-3 nm.

10 Ammonia borane (NH_3BH_3), dimethylamine borane (Me_2NHBH_3), *tert*-butylamine borane (*t*-$BuNH_2BH_3$) and trimethylamine borane (Me_3NBH_3) complexes are commercially available. Methylamine borane ($MeNH_2BH_3$) and hydrazine borane ($NH_2NH_2BH_3$) were prepared according to literature procedures: (a) Y. Kikugawae, *Chem. Pharm. Bull.*, 1987, **35**, 4988. (b) R. Moury, G. Moussa, U. B. Demirci, J. Hannauer, S. Bernard, E. Petit, A. van der Lee and P. Mielea, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1768.

11 (a) A. T. Tran, V. A. Huynh, E. M. Friz, S. K. Whitney and D. B. Cordes, *Tetrahedron Lett.*, 2009, **50**, 1817. (b) T. S. Carter, L. Guiet, D. J. Frank, J. West and S. P. Thomas *Adv. Synth. Catal*., 2013, **355**, 880.

12 R. Barrios-Francisco and J. J. Garcia, *Appl. Catal. A,* 2010, **385**, 108.

13 Hydrazine borane in ethanol releases H_2 gas in the presence of Au/TiO_2 at a profound fast rate obvious by naked eye.

14 P. L. Gkizis, M. Stratakis and I. N. Lykakis, *Catal. Commun.*, 2013, **36**, 48.

15 In the presence of 0.35 molar equiv of AB, 85% conversion of **1** to **1a** was seen. Based on our mechanistic suggestions, the reaction stoichiometry requires 1 mol of AB or DMAB per 3 mol of alkyne. Yet AB and DMAB undergo a slow Au/TiO_2-catalyzed alcoholytic decomposion with evolution of H_2, which can be followed by ^1H NMR in methanol-d4 using an internal standard. The decomposition of AB, or DMAB, proceeds much slower than the case of hydrazine borane.

16 Y. Yabe, Y. Sawama, Y. Monguchi and H. Sajiki, *Chem.-Eur. J.*, 2013, **19**, 484.

17 L. Shi, Y. Liu, Q. Liu, B. Wei and G. Zhang, *Green Chem.*, 2012, **14**, 1372.

18 The Au/TiO_2-catalyzed reduction of the highly unpolar 1-tetradecyne (**27**) into 1-tetradecene (**27a**), reaches merely 40% conversion after 6 h, even in the presence of 6 molar equiv of ammonia borane. The same holds with internal 5-decyne (**28**) which provides under similar conditions *cis*-5-decene (**28a**) in merely 15% relative yield (GC-MS).

19 For previous syntheses of combretastatin A-4 employing reduction of alkyne **27** by other means, see: (a) G.-H. Wang, H.-Y. Bin, M. Sun, S.-W. Chen, J.-H. Liu and C.-M. Zhong, *Tetrahedron*, 2014, **70**, 2175. (b) C. Belgera and B. Plietker, *Chem. Commun.*, 2012, **48**, 5419. (c) A. F. Lara-Ochoa and G. Espinosa-Perez, *Tetrahedron Lett.*, 2007, **48**, 7007. (d) O. I. Petrov, M. S. Gerova, C. D. Chanev and K. V. Petrova, *Synthesis*, 2011, 3711. (e) R. Furst, I. Zupko, A. Berenyi, G. F. Ecker and U. Rinner, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 694. (f) A. Giraud, O. Provot, A. Hamze, J.-D. Brion and M. Alami, *Tetrahedron Lett.*, 2008, **49**, 1107. (g) N. J. Lawrence, F. A. Ghani, L. A. Hepworth, J. A. Hadfield, A. T. McGown and R. G. Pritchard, *Synthesis*, 1999, 1656.

20 C. M. Ahn, W.-S. Shin, H. B. Woo, S. Lee and H.-W. Lee, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 3893.

21 P. V. Ramachandran and P. D. Gagare, *Inorg. Chem.*, 2007, **46**, 7810. We also carried out the Ru(III)-catalyzed dehydrogenation of NH_3BH_3 in methanol-d4, and found that the anticipated borate salt $[NH_4B(OCD_3)_4]$ has identical ^{11}B NMR spectrum to the by-product resulting from NH_3BH_3 in our Au-catalyzed semireduction process.

22 For a recent discussion of Au-hydrides arising from a boron hydride substance, see: S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G. S. Armatas and I. N. Lykakis, *ACS Catal.*, 2014, **4**, 3504.

23 For previous examples of inner-sphere mechanism in Au-catalyzed addition to alkynes, see: (a) K. D. Hesp and M. Stradiotto, *J. Am. Chem. Soc.*, 2010, **132**, 18026. (b) C. Gryparis, M. Kidonakis and M. Stratakis, *Org. Lett.*, 2013, **15**, 6038. (c) C. Gryparis and M. Stratakis, *Org. Lett.*, 2014, **16**, 1430. (d) Joost, M.; Estevez, L.; Sonia Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.*, 2014, **136**, 10373.

24 A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.,* 2010, **110**, 4079.

