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Magnesium-Catalyzed tandem dehydrogenation-dehydrocoupling: an atom economical access to alkynylboranes

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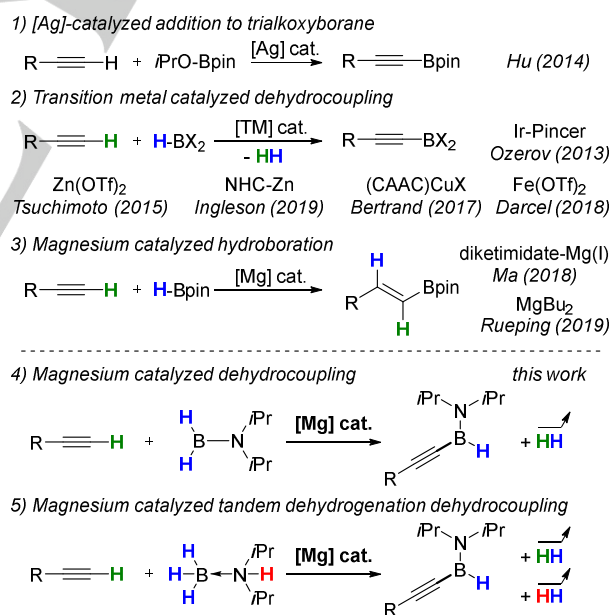
Abstract: Owing to the unusual reactivity of sterically hindered amine borane complexes, we designed a catalytic system based on magnesium salts to perform a tandem dehydrogenation-dehydrocoupling between terminal alkynes and boranes. The reaction is providing pure alkynylboranes within few minutes at room temperature, with only two molecules of hydrogen as a by-product.

Boron derivatives have long been used as key synthons in many organic transformations.^[1] Among those, alkynylboronates^[2] are no exceptions and already showed interesting reactivity in the transition metal-catalyzed formation of carbon-carbon^[3] or carbon-heteroatom^[4] bonds. Their synthesis is based on the C(sp)-H activation using a stoichiometric base or more recently, organometallic catalysis. The catalytic addition of silver-alkynide to *i*PrO-Bpin has been reported in 2014,^[5] and the first dehydrocoupling using Ir/Pd-pincer complexes^[6] was described only in 2013. Indeed, if many reports^[7] followed pioneering works by Smith,^[8] Hartwig^[9] on C-H borylation, these methods are limited to C(sp²)-H and C(sp³)-H activation, and only a few reported C(sp)-H dehydrocoupling. In addition to Ozerov seminal paper, it has been shown that dehydrocoupling can be catalyzed by Zn(OTf)₂,^[3, 10] NHC-Zn,^[11] (CAAC)CuX^[12] or Fe(OTf)₂,^[13] the borylating agent being pinacolborane (HBpin) or 1,8-diaminonaphthalenylborane (HBdan).

Earth-abundant metal catalysis has recently gained major interest, including catalysis using group 2 organometallic complexes.^[14] In all previously described cases, however, the reaction between a borane and earth alkali complexes resulted in the formation of metal-hydrides that subsequently reacted with terminal alkynes *via* hydrometallation. The following transmetalation to the boron would then lead to alkenylboranes, resulting from the formal hydroboration of the triple bond. This mechanism is highly represented in the literature, with transition metal such as Co^[15] or Fe^[16], but also Al^[17] and more recently Mg. Both Ma^[18] and Rueping^[19] groups described magnesium catalyzed hydroboration of alkynes using pinacolborane. In the mechanism, they proved that Mg-H^[20] could be involved in the key step, and excluded the formation of the magnesium alkynide. This was consistent with all previous reports of magnesium catalyzed^[14b] hydroboration of imine/aldehydes,^[21] ketones^[21b, 22] or esters.^[21b, 23]

We hypothesized that aminoboranes reactivity could differ. Indeed, in the mechanism of magnesium-catalyzed dehydrogenation of diisopropylamine borane complex (DIPAB), the resulting magnesium aminoborohydride is basic enough to deprotonate the starting DIPAB.^[24] We envisioned this property could be used to regenerate the alkynide instead of leading to

hydromagnesiation like in Ma and Rueping's examples.^[18-19] This would provide the first magnesium catalyzed C-H/B-H dehydrocoupling as, to our knowledge, only heteroatom-boron bonds have been formed *via* dehydrocoupling using group 2 metal catalysis.^[14c, 25] Our first hypothesis was evaluated by adding a 1:1 mixture of hexyne and PhMgBr to 1 eq of diisopropylaminoborane (DIPOB) in THF. The conversion reached rapidly 90% and resulted in the clean formation of the hexynylaminoborane (¹¹B NMR δ = 42 ppm (d)) and the corresponding aminoborohydride (¹¹B NMR δ = -13 ppm (t)) as expected by previous results on the aromatic series. When the quantity of PhMgBr was decreased to 5 mol%, the reaction proceeded equally well.



Scheme 1. Relevant precedent in the literature.

We evaluated the influence of the magnesium salt, using 5 mol% of a commercially available solution of various Grignard reagents. Using PhMgBr, vinylMgBr, EtMgBr, *i*PrMgCl, or MeMgBr, the results are identical with complete conversion and the formation of the alkynyl aminoborane **2a** (Table 1, entries 1-5). When the quantity of MeMgBr was further decreased (entries 6-9), conversion after 10 minutes was not complete so we kept 5 mol% as a standard catalyst loading. One downside of DIPOB,

however, is related to its instability toward air which requires distillation before use.

Table 1. Alkyne dehydrocoupling using DIPOB – Catalyst variation

Entry	RMgX	Loading (mol%)	Conv ^[a] (%)
1	PhMgBr	5	100
2	VinylMgBr	5	100
3	EtMgBr	5	100
4	<i>i</i> PrMgCl	5	100
5	MeMgBr	5	100
6	MeMgBr	4	91
7	MeMgBr	3	89
8	MeMgBr	2	89
9	MeMgBr	1	87

^[a] Reactions were performed using 1 mmol of **1a**, 1 mmol of DIPOB, and 1 mL of dry MTBE. Conversions were evaluated by ¹H and ¹¹B NMR.

Nonetheless, as the same magnesium salts could be used in the dehydrogenation process,^[24-26] the requirement of using moderately stable aminoboranes could be circumvented by doing a tandem dehydrogenation-alkynylation of amine borane complexes. Among all tested amine borane complexes (see ESI), DIPAB turned out to be work best; other complexes led to some conversion, but usually with some side products and remaining starting material. Other magnesium bases (alkoxides, oxides, ...) were evaluated, but none of them worked as efficiently as the previously listed Grignard reagents (see ESI).

Table 2. Tandem dehydrogenation-dehydrocoupling - solvent variation.

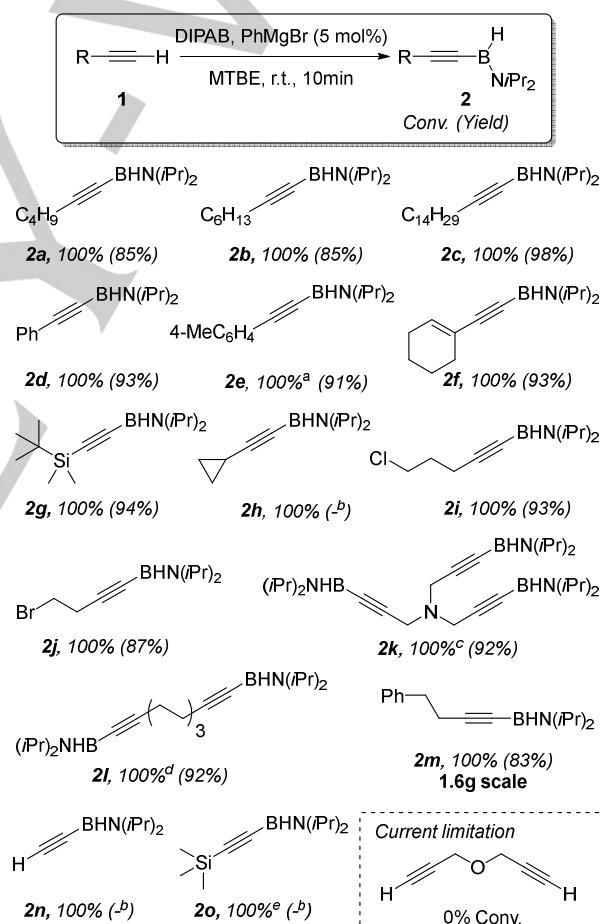
Entry	Solvent	Loading (mol%)	Conv ^[a] (%)
1	MTBE	5	100
2	THF	5	100
3	C ₆ D ₆	5	100
4	neat	5	100
5	Et ₂ O	5	100
6	Toluene	5	73 (100) ^[b]

^[a] Reactions were performed using 1 mmol of **1a**, 1 mmol of DIPAB, 1 mL of dry solvent. Conversions were evaluated by ¹H and ¹¹B NMR ^[b] 4h reaction time

Despite the low propensity of other borohydrides to react as a base or to lose their hydride, we promptly tested organolithium and zinc, which could have widened the scope and the

generality of this dehydrocoupling. Whether the alkynyllithium or the lithiumaminoborohydride (LAB)^[27] was generated first, the reaction did not proceed efficiently even under stoichiometric conditions (See ESI). As a result, the addition of 10 mol% *n*BuLi, to a mixture of 1-hexyne and DIPAB, only led to 10 mol% of the corresponding alkynylaminoborane **2a** (See ESI). Other boranes with Grignard, such as pinacolborane (HBpin), catecholborane (HBcat), or 1,8-diaminonaphthalenyborane (HBdan) led to no conversion and full recovery of the starting materials when the reaction was performed in MTBE at room temperature (See ESI).

Overall we kept the DIPAB/PhMgBr combination which minimized the direct addition of PhMgBr onto the DIPOB^[28], hence leading to cleaner reaction mixtures. Using this system, solvent dependence was evaluated and in most cases (THF, Et₂O, MTBE, C₆D₆, Table 2, entries 1-5), conversions were complete after 10 minutes, with nearly quantitative yields. Only toluene (Table 2, entry 6) led to a slower reaction, which can be attributed to a slower DIPAB dehydrogenation process.



Reactions were performed using 1 mmol of **1a**, 1 mmol of DIPAB, 1 mL of dry MTBE. Conversions were evaluated by ¹H and ¹¹B NMR. (isolated yields after purification)

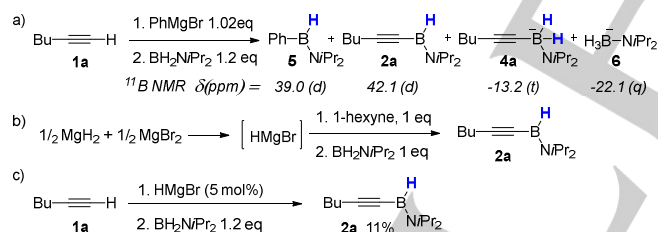
^a MeMgBr was used instead of PhMgBr ^b product with b.p. below MTBE b.p.

^c 3 eq of DIPAB ^d 2 eq of DIPAB ^e 1 eq of HCCMgBr was used

Scheme 2. Structural scope and limitation of alkyne borylation.

With good reaction conditions in hand, we evaluated the scope of the reaction by applying these conditions to various alkynes. In most cases, the conversion reached 100% and

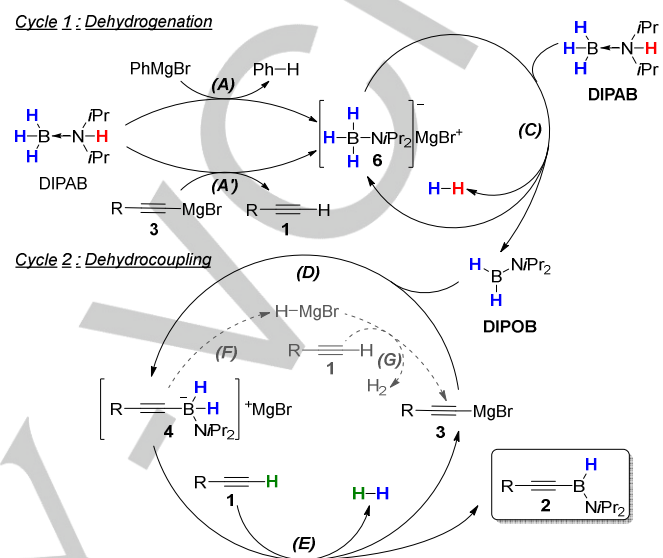
isolated yields were quite high (Scheme 2). Aliphatic terminal alkynes unsurprisingly reacted quite similarly to the model 1-hexyne, with 1-octyne and 1-hexadecyne leading to the corresponding alkynylboranes **2b-c** in 85% and 98% yield respectively. Phenylacetylene and 4-methylphenylacetylene reacted smoothly, and products **2d-e** were isolated in 93 and 91% yield; we found however that replacement of PhMgBr by 5 mol% of MeMgBr led to better yield in the last case. Enynes could also be used as substrate and **2f** was isolated in 93% yield. When a protected version of acetylene was used, namely tert-butyldimethylsilylacetylene, no desilylation was observed and the bifunctional silane-borane **2g** was isolated in 94% yield. Cyclopropylacetylene reacted equally well and was converted into the corresponding borane **2h** very cleanly. The reaction tolerates alkylhalide functions; 1-chloropent-4-yne and homopropargyl bromide were converted in aminoboranes **2i** and **2j** in 93% and 87% isolated yield, respectively. On poly-yne, the reaction was very efficient as well; the tris(propargyl)amine was converted in the tris(alkynylaminoborane) **2k** in 92% yield (97% yield per function), and dec-1,9-diyne led to the bisalkynylborane **2l** in 92% yield (96% yield per function). 3-Butyn-1-yl-benzene borylation was performed on a larger scale, leading to 1.6g of **2m**, in 86% isolated yield. TMS-acetylene, similarly to the TIPS protected alkyne, was converted to the expected aminoborane **2o**. The simplest alkynylaminoborane **2n** was obtained using 1 eq of ethynylmagnesium bromide which turns out to be more convenient than using acetylene gas. **2h** and the two last products **2n-o** were obtained in MTBE solution after filtration; attempts to isolate them under pure form failed due to a very low boiling point (below MTBE). Notwithstanding the high functional group compatibility, we found some limitations to the reaction and despite our attempts, bispropargylether remains unreactive.



Scheme 3. Reactivity of magnesium hydride and alkyne with amine boranes.

Some control experiments were performed to confirm the reaction mechanism. The amine borane dehydrogenation was already well established,^[24] and could be initiated by either the phenyl magnesium bromide (Scheme 4A) or the alkynylmagnesium bromide **3** (Scheme 4A') resulting from the reaction of the alkyne with the latter. In both cases, the dehydrogenation cycle (Scheme 4, pathway A/A'; cycle 1) was very efficient and 100% conversion in aminoborane was reached within a few minutes. The addition of hexynylmagnesium bromide **3a** generated from 1-hexyne **1a** and PhMgBr to DIPOB was performed in C₆D₆ (Scheme 3a). Within few minutes conversion reached a maximum leading to a mixture of 4 products: (1) diisopropylaminophenyl borane (**5**, ¹¹B NMR δ = 39ppm, d) resulting from the addition of remaining PhMgBr onto DIPOB; (2) the expected diisopropylaminohex-1-yn-1-ylborane

(**2a**, ¹¹B NMR δ = 42ppm, d), (3) magnesium diisopropylaminohex-1-yn-1-ylborohydride (**4a**, ¹¹B NMR δ = -13 ppm, t), albeit in very low quantity with respect to the other compounds and finally (4) magnesium diisopropylaminoborohydride (**6**, ¹¹B NMR δ = -22ppm, t) (See NMR in ESI). This product could result from the direct hydride transfer from **4a** to DIPOB without the formation of Mg-H as observed in the C=O Mg-catalysed hydroboration^[29]



Scheme 4. Tandem dehydrogenation-dehydrocoupling proposed mechanism.

Alternatively, it can intermediately go through HMgBr loss which was proven to occur after addition of PhMgBr to HBpin for example.^[30] To evaluate its potential implication in the catalytic process, HMgBr was separately prepared by reaction between magnesium hydride and magnesium bromide.^[31] When 1 equivalent of HMgBr was added to **1a** and DIPOB, the expected aminoborane **2a** was obtained albeit less efficiently than in the catalytic process with PhMgBr (Scheme 3b). With 5 mol% HMgBr, the reaction yielded 11% of the alkynylaminoborane **2a** witnessing a catalytic process which was at least ten times less effective than under classical conditions (Scheme 3c).

In summary, after dehydrogenation (cycle 1), the magnesium alkyne adds to the diisopropylaminoborane (Scheme 4D). The resulting borohydride is thought to be unstable, directly reacting with the alkyne as a base (Scheme 4E), as proven by the stoichiometric deprotonation of alkyne using LAB. Alternatively, it can lose HMgBr (Scheme 4F) which can also act as a base (Scheme 4G) leading to the magnesium alkyne. Regardless of the base nature, the magnesium alkyne regeneration completes the second catalytic cycle (Scheme 4, pathway C-G; cycle 2). Using the standard reaction conditions, the conversion was monitored using ¹H NMR, ¹¹B NMR and released H₂ volume. Although originating from the two catalytic cycles, hydrogen evolution was correlated to product **2a** formation with a single kinetic constant (Figure 1). Moreover, a low concentration of DIPOB was present at all times as witnessed in ¹¹B NMR (See ESI), corroborating that dehydrogenation was the rate-determining catalytic cycle.

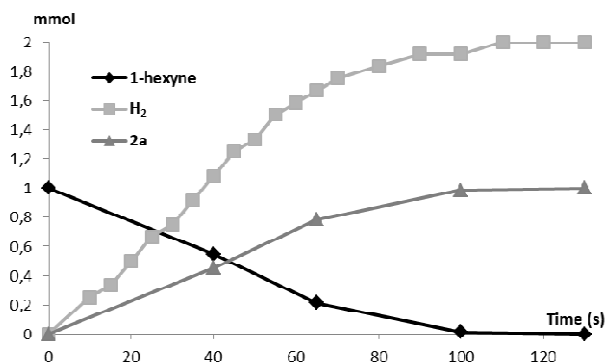


Figure 1. Kinetic analysis using 5 mol% PhMgBr at rt in MTBE.

Noticeably, amine borane complexes are known to react with metal-centered catalysts. It usually leads to dehydrogenation and dehydrocoupling products (polyaminoborane) which has widely been exploited as a source of hydrogen for the reduction of multiple bonds. In our case, the dehydrogenation process is combined with the formation of a carbon-boron bond releasing within a few minutes an alkynylborane with hydrogen as a sole by-product. Arguably, triple carbon-carbon bonds are also valuable functional groups and make alkynylboron derivatives interesting highly functionalized two-carbon building blocks.^[32] On a large scale, these compounds are mostly prepared by stoichiometric deprotonation followed by addition onto trialkoxyboranes resulting in moderate yields.^[33] Owing to the simplicity and the robustness of our procedure, we think that this magnesium catalyzed dehydrocoupling could greatly ease the access to these derivatives and extend their interest in organic synthesis or material science.

Acknowledgements

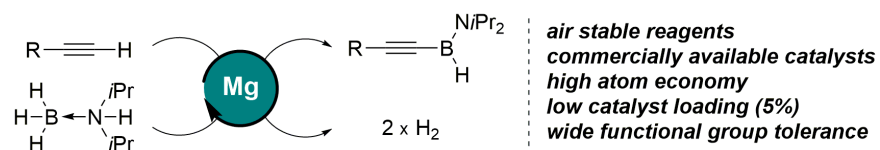
This work was funded by the Université de Bordeaux and the CNRS. M.B. thanks the Ministère de l'Éducation Nationale, de l'Enseignement Supérieur et de la Recherche for a fellowship. V.L. thanks Aquitaine Sciences Transfer (AST) for funding.

Keywords: Magnesium • Alkynylborane • Aminoboranes • Dehydrocoupling • Dehydrogenation

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Entry for the Table of Contents



An efficient synthesis of alkynylaminoborane was developed using a magnesium catalyst at room temperature. The reaction proceeds within few minutes in high yields releasing hydrogen through a tandem dehydrogenation/dehydrocoupling original mechanism.