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Highly Efficient and Selective Hydroboration of Terminal and Internal Alkynes Catalysed by a Cobalt(II) Coordination Polymer

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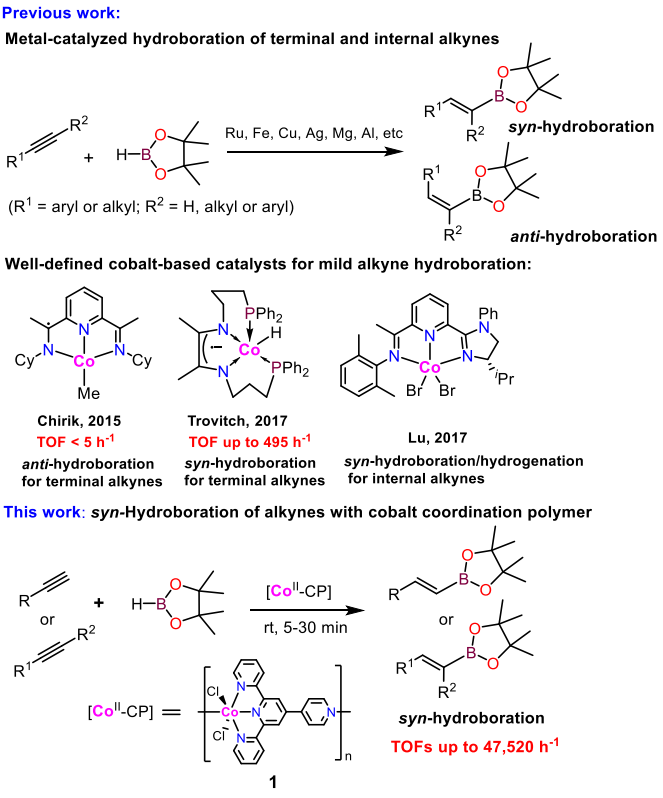
Hydroboration of terminal and internal alkynes has been carried out with extremely high efficiency by using bench-stable and inexpensive cobalt(II) coordination polymer as a precatalyst in the presence of potassium tert-butoxide (KO^{t}Bu). Good to high yields of alkenylboronate esters were obtained in 5-30 min with low catalyst loading (0.025 mol%). Good chemoselectivity for alkyne vs alkene hydroboration was observed. A possible catalytic cycle involving the in-situ formation of an active Co-H species is proposed based on additional experimental results. This work provides valuable implications for the design of efficient and practical base metal catalysts.

Introduction

The synthesis of alkenylboronate esters has long been a highly attractive topic, because they are used as key precursors in the classic Miyaura-Suzuki coupling reactions as well as other useful organic transformations.[1] Traditionally, these compounds were prepared from the reaction of Grignard or lithium reagents with trialkyl borates.[2] Despite useful, this method is not atom-economic and also largely limited by poor functional group tolerance. To develop more efficient routes to this important class of organic intermediates, catalytic methods for the direct hydroboration of alkynes have attracted considerable interests.[3] In the past decades, a number of catalysts have been observed to enable the hydroboration of alkynes under mild conditions using pinacolborane (HBpin) as a boron source, and metal-based catalysts have predominated.[4,5] Although precious metal-based catalysts (Pd, Pt, Ru, Rh, Ir, Au, Ag) displayed usually higher turnover frequencies (TOFs),[5] catalysts based on earth-abundant, early transition and main group metals are much desired, considering their low cost and environmental sustainability.[4a,6] Typically, both *syn*- and *anti*-selective hydroboration of terminal alkynes have been approached using certain metal catalysts, on the basis of effective ligand design (Scheme 1).[5,6] Recently, well-defined transition and main-group metal (Cu, Fe, Al, Mg, Na, Li, P, B)[7,8] catalysts have emerged and in particular, an iron complex was found to exhibit high turnover numbers (TONs of up to 710)[7d] for a range of terminal alkynes.



Scheme 1 The State-of-the-Art of Catalytic Regioselective Hydroboration of Alkynes.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

In last few years, cobalt proved to be one of the most promising base metals in hydrogenation and hydroboration catalysis of alkenes.[4,9] However, examples of well-defined cobalt-based catalysts for the hydroboration of alkynes appeared to be rare (Scheme 1).[10] In 2015, Chirik and coworkers reported active Co^{II}-alkyl complexes with bis(imino)pyridine ligands enabling *syn*- or *anti*-selective hydroboration of terminal alkynes by altering the substituents on the ligand scaffold.[10a] Later on, the Huang group reported a cobalt complex of chiral iminopyridine-oxazoline (IPO) ligand as a precatalyst for the sequential dihydroboration of terminal alkynes to afford 1,1-diboronate esters while being activated by $NaHBEt_3$.[10b] In 2017, the Trovitch group observed an α-diimine cobalt hydride complex that catalyses the *syn*-selective hydroboration of terminal alkynes, achieving the highest TON of 990 in 2 h (TOF = 495 h^{-1}) for several aliphatic alkynes.[10c] In addition, Co-catalysed sequential hydroboration/hydrogenation of internal alkynes leading to asymmetric alkylboronates has been reported by the Lu group.[10d]

It was noted that in these examples either highly sensitive cobalt complexes (Co-alkyl or Co-H) or activator ($NaHBEt_3$) were required for sufficient catalytic activity.[10] In addition, the synthesis and purification of ligands and their cobalt complexes were often not trivial and the obtained TONs and TOFs were still unsatisfactory with regard to practical, large-scale applications. Thus, a more efficient and practical method offering higher TOFs for regioselective hydroboration of alkynes is highly desired.

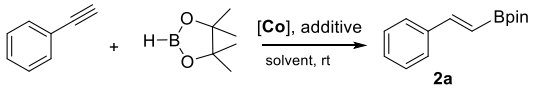
We have been recently interested in the development of earth-abundant metal (Fe, Co, Mn, Cu, Al, etc.) catalysts for hydrogenation and hydroboration catalysis[9,11] and have reported a bench-stable and readily available cobalt(II) coordination polymer (CP, **1**) based on a divergent tetradentate ligand, 4′-(4-pyridyl)-4,2′;6′,4′′-terpyridine (pytpy) that catalysed efficient hydroboration of carbonyl compounds with HBpin while using KO^tBu as an activator.[12] The same catalyst system was also found to be extremely efficient for hydroboration of a variety of aromatic and aliphatic alkenes, achieving excellent TOFs of up to ~47,520 h^{-1}.[13] Unusual branched-regioselectivity for a range of vinylarenes was also observed.[14] Encouraged by these results, we investigated the effectiveness of the same CP catalyst for the hydroboration of alkynes. Herein, we report a highly efficient regioselective hydroboration of terminal and internal alkynes with high TOFs of up to 47,520 h^{-1} at ambient temperature, representing the most active and efficient catalyst for alkyne hydroboration thus far. It is worth noting that metal-coordinated polymers/frameworks were sparsely investigated for hydroboration catalysis.[15]

Results and discussion

Initially, we used phenylacetylene as a model alkyne and the combination of cobalt CP **1** (0.1 mol % based on Co(**L**)Cl_2) and KO^tBu (1 mol %) as a catalyst at ambient temperature to test the catalytic reaction with HBpin. The results are summarized in Table 1. It was found that effective hydroboration (90% GC yield) was obtained in only 10 min at room temperature, affording exclusively *syn*-selective product, trans-styrenylboronate ester (**2a**) as the only regioisomer (entry 1, Table 1). Lowering the loading of **1** to 0.025 mol% did not change the yield and thus the reaction was also accomplished in 10 min corresponding to a TOF of 21,600 h^{-1} (entry 2), achieving the highest TOF for metal-catalysed alkyne hydroboration.[4-8]

Control experiments revealed that the combination of either free terpyridine ligand or cobalt(II) chloride with KO^tBu was inactive and the reaction also did not proceed in the absence of cobalt CP **1** or without an additive (entries 4-7, Table 1). These results indicate the important role of the combined system **1**/KO^tBu in initiating the reaction. In contrast, when the discrete complex Co(tpy)Cl_2 was examined in the presence of KO^tBu, only moderate yield of **2a** was found (entry 8, Table 1). We further tested other additives such as NaO^tBu, KOH, NaOH, K_2CO_3 and $NaBH_4$ (entries 9-13, Table 1), yet relatively lower yields of **2a** were detected in all cases. The poor yield in the presence of $NaBH_4$ was partially due to the competing semihydrogenation of alkyne to form styrene in ~29% yield (entry 13, Table 1). Finally, we investigated the solvent effect with the same catalytic loading (entries 14-17, Table 1). It was found that the hydroboration proceeded with lower yields (between 62-75%) in all the solvents screened than that obtained in THF.

Table 1. Reactivity test for **1**-catalysed hydroboration of phenylacetylene with HBpin.[a]



2a

Entry	Catalyst	Additive	Solvent	Yield **2a**[b] (%)
1	**1**	KO^tBu	THF	90
2[c]	**1**	KO^tBu	THF	90
3[d]	**1**	KO^tBu	THF	76
4	**L**	KO^tBu	THF	-
5	$CoCl_2$	KO^tBu	THF	<5
6	**1**	-	THF	-
7	-	KO^tBu	THF	-
8	Co(tpy)Cl_2	KO^tBu	THF	60
9	**1**	NaO^tBu	THF	85
10	**1**	KOH	THF	81
11	**1**	NaOH	THF	75
12	**1**	K_2CO_3	THF	44
13	**1**	$NaBH_4$	THF	30[e]
14	**1**	KO^tBu	toluene	72
15	**1**	KO^tBu	pentane	62
16	**1**	KO^tBu	benzene	70
17	**1**	KO^tBu	Et_2O	75

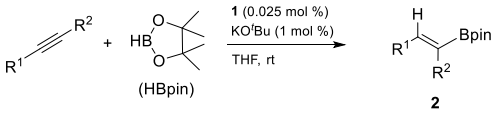
[a] Conditions: phenylacetylene (1.0 mmol), pinacolborane (1.1 mmol), catalyst (0.025 mol%), additive (1 mol%) and solvent (0.5 mL), rt, 10 min, N_2. [b] Determined by GC analysis with hexamethylbenzene as an internal standard. [c] Reaction run using 0.1 mol% of **1**. [d] Reaction run for 5 min. [e] Approximately 29% GC yield for styrene through semihydrogenation was found.

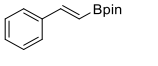
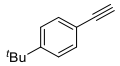
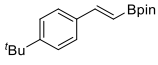
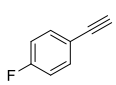
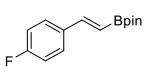
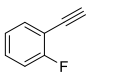
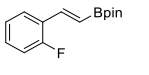
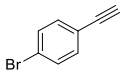
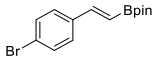
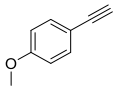
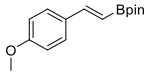
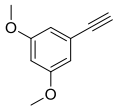
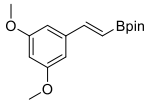
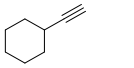
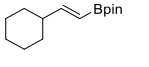
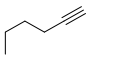
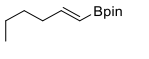
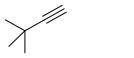
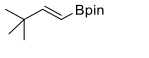
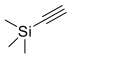
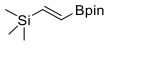
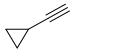
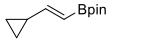
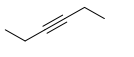
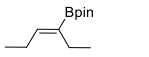
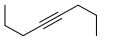
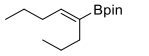
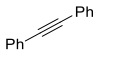
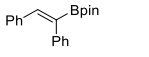
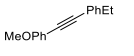
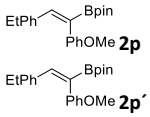
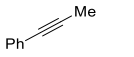
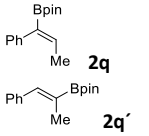
Next, we applied the optimized catalytic conditions (*i.e.* **1** (0.025 mmol%), KO^tBu (1 mol%), THF, rt) for the hydroboration of a series of substituted terminal and internal alkynes to

establish the scope of substrates. Typically, the reactions were performed in a 1 mmol scale and the reaction mixture was examined and analysed by GC-MS after 10-30 min, and then the hydroboration products were isolated by column chromatography with silica gel. The results are summarized in Table 2. First, the exclusively *syn*-selective alkenylboronate (**2a**) resulting from hydroboration of phenylacetylene could be isolated in 82% yield. Substituted phenylacetylenes with 4-tert-butyl, 4-fluoro, 2-fluoro, 4-bromo and 4-methoxy substituents are all suitable substrates affording the corresponding *syn*-selective products with appreciable yields in 10-30 min, and the corresponding TOFs were between 5,520-17,040 h^{-1} (entries 2-6, Table 2). 3,5-Dimethoxyphenylacetylene was, however, hydroborated more efficiently to the alkenylboronate **2g** with a higher TOF of 33,600 h^{-1} (entry 7, Table 2). Five aliphatic terminal alkynes were then examined (entries 8-12, Table 2) and the results showed that they are all highly active substrates for hydroboration with HBpin, yielding selectively linear aliphatic alkenylboronates **2h-l** with 91-99% GC yields. Excellent isolated yields were obtained for these examples and the TOFs reached as high as 47,520 h^{-1}. Unfortunately, terminal alkynes with functional groups such as 4-ethynylbenzonitrile and 1-ethynylcyclohexylamine were not tolerated with the current catalytic method, giving no detectable products after 16 h.

In contrast to terminal alkynes, internal alkynes are challenging substrates for hydroboration reaction and metal-catalysed examples for internal alkynes are extremely rare. In 2016, the Thomas and Cowley group reported a DIBAL/$AlEt_3$·DABCO system that catalysed both terminal and alkyl-alkyl internal alkynes with 10 mol% catalyst loading at 110 °C.[8d] This catalyst was, however, not applicable for aryl-alkyl internal alkynes. Later on, Petit and co-worker revealed a $HCo(PMe_3)_4$-catalysed hydroboration of a range of internal alkynes under harsh conditions (160 °C in toluene).[16] In addition, Lu reported the hydroboration of internal alkynes followed sequentially by enantioselective hydrogenation of alkenylboronates using a chiral Co^{II} pincer complex at ambient temperature (Scheme 1).[10d] Very recently, Rueping and coworkers revealed a $MgBu_2$-catalysed hydroboration of both terminal and internal alkynes.[8a] This method could be applied for both alkyl-alkyl and aryl-alkyl alkynes to form regioselective products and alkenylboronates when 10 mol% of $MgBu_2$was utilized in 80 °C. However, in these examples, the reported TOFs for internal alkyne hydroboration were very low.

Table 2 Substrate scope of CP-Catalysed Hydroboration of Alkynes.[a]



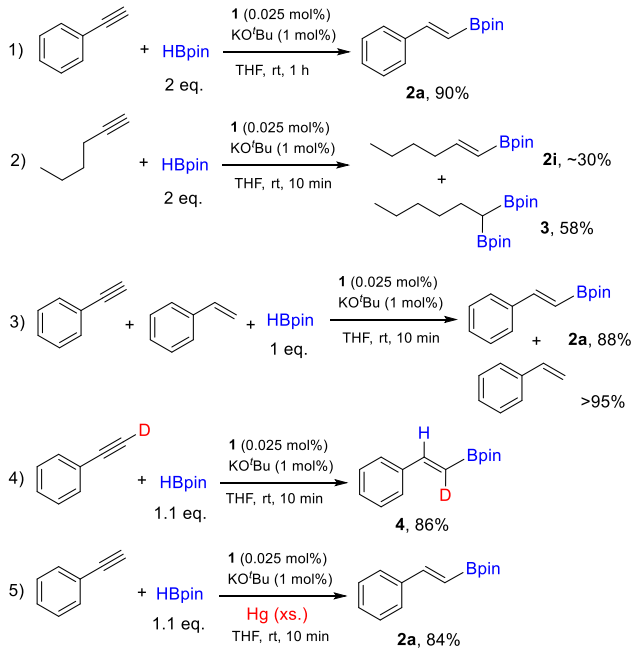
Entry	Alkyne	Product **2**	Time /min	Yield (%)[b]	TOF (h^{-1})[c]
1			10	90 (82) (**2a**)	21,600
2			10	60 (54) (**2b**)	14,400
3			10	71 (62) (**2c**)	17,040
4			20	82 (74) (**2d**)	9,840
5			10	65 (60) (**2e**)	15,600
6			30	69 (62) (**2f**)	5,520
7			5	70 (65) (**2g**)	33,600
8			5	99 (90) (**2h**)	47,520
9			5	95 (82) (**2i**)	45,600
10			5	99 (80) (**2j**)	47,520
11			5	91 (85) (**2k**)	43,680
12			5	99 (86) (**2l**)	47,520
13			10	96 (88) (**2n**)	23,040
14			10	72 (65) (**2m**)	17,280
15			30	61 (55) (**2o**)	4,880
16			30	90 (84) (**2p**/**2p´**)[d]	7,200
17			30	56 (52) (**2q**/**2q´**)[e]	4,480

[a] Conditions: alkene (2.0 mmol), pinacolborane (2.2 mmol), **1** (0.025 mol%) and KO^{t}Bu(1 mol%) in THF (1 mL), rt, N_2. [b] Ratio of three possible regioisomers. [c] Ratio of two regioisomers of the major alkene hydroboration products. [d] Two regioisomers **2p** and **2p´** were isolated as a mixture in a 1:1 ratio as identified by NMR (see SI). [e] Two regioisomers **2q** and **2q´** were isolated as a mixture in a 2.5:1 ratio as identified by NMR (see SI).

Considering the excellent activity of our cobalt CP catalyst displayed for the hydroboration of internal alkenes, we were interested to investigate the applicability of the current methodology for internal alkynes. Thus, several substrates involving both aliphatic and aromatic internal alkynes were examined and the results are listed in Table 2 (entries 13-17). To out delight, both alkyl-alkyl (entries 13 and 14) and aryl-aryl (entries 15 and 16) alkynes furnished the **1**-catalysed hydroboration in 10 and 30 min, respectively, affording moderate to good yields of branched alkenylboronates **2n**-**2p** with TOFs up to 23,040 h^{-1}. For unsymmetrical aryl-aryl alkyne (entry 16, Table 2), two regioisomers (**2p** and **2p´**) by syn-hydroboration have been isolated as a mixture in 84% yield and

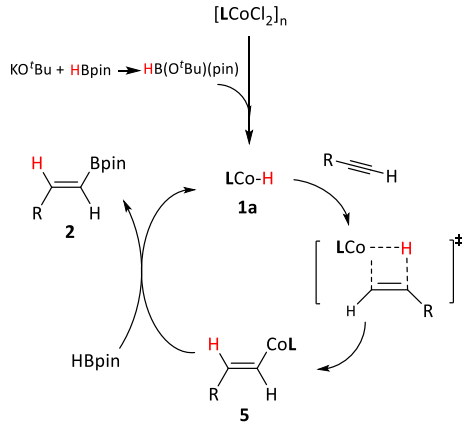
the ratio was determined to be 1:1 by ^{1}H NMR. Finally, another unsymmetrical aryl-alkyl alkyne, 1-phenylpropyne, was also used for **1**-catalysed hydroboration for 30 min (entry 16, Table 2), likewise, a mixture of two regioisomers (**2q** and **2q´**) was isolated in 52% yield, and a moderate regioselectivity (**2q** : **2q´** = 2.5:1) was found in this case. Nevertheless, the mildness and high-efficiency of this methodology make the **1**/KO^{t}Bu system the most active and practical catalyst for hydroboration of internal alkynes.

Since we have previously revealed the high reactivity of the **1**/KO^{t}Bu catalyst for hydroboration of alkenes, we were curious whether the hydroborated products, alkenylboronates could be further hydroborated should an excess amount of HBpin be introduced to the reaction. Thus, we conducted the standard catalytic reaction for phenylacetylene in the presence of 2 equiv. of HBpin (eq. 1, Scheme 2). It was found that even with elongated reaction time (1 h) only mono-hydroborated product **2a** was detected in 90% yield. However, when 1-hexyne was used as the starting alkyne in the presence of 2 equiv. of HBpin, a mixture of both mono- and bis-hydroborated products was obtained (eq. 2, Scheme 2). In this case, the regioselective product **3** with terminal bis-hydroboration was isolated in 58% yield, indicating the potential of the Co-CP catalyst for bis-hydroborating functionalization of aliphatic terminal alkynes. Furthermore, chemoselective hydroboration was observed for alkyne over alkene when an equimolar mixture of styrene and phenylacetylene was employed (eq. 3, Scheme 2).



Scheme 2 Additional catalytic experiments for chemoselectivity and mechanistic studies.

Deuterium-labeling experiment utilizing phenylacetylene-D and HBpin was carried out and the product **4** with D retained in the terminal carbon was isolated in high yield (eq. 4, Scheme 2). Finally, the mercury-poisoning experiment was conducted for the standard hydroboration of phenylacetylene with added mercury metal (xs.) and the results showed no obvious drop on the yield of **2a**, indicating the catalysis was likely to undergo under homogeneous conditions (eq. 5, Scheme 2), although the insoluble cobalt(II)-CP was used as a precatalyst. This is consistent with the fact that when HBpin was added to a suspension of **1**/KO^{t}Bu in THF, a dark solution rapidly developed. We envisioned that the reaction of **1**/KO^{t}Bu with HBpin has led to the formation of soluble oligomeric species that features active Co-hydride catalytic sites.



Scheme 3. Plausible cycle for Co^{II}-catalysed hydroboration of alkynes.

Based on previous work and our own results on the base metal-catalysed hydroboration of alkynes, we propose a catalytic cycle for the present Co^{II}-CP catalysed reaction (Scheme 3). We assume that initially a more active reducing agent, HB(O^{t}Bu)(pin), should form through the reaction between HBpin and KO^{t}Bu, as previously evidenced by Thomas and coworkers.[17] Then, the reaction of Co^{II}-CP with this reducing agent would produce the active Co-H species (**1a**) that is responsible for the catalytic cycle. Insertion of alkyne into the Co-H bond of **1a** leads to an intermediate **5** that favors the formation of terminal-C-Co bond due to the steric encumbrance. The intermediate **5** subsequently reacts with HBpin to generate the alkenylboronate product (**2**), while releasing the active catalyst **1a** for the next catalytic cycle.

Conclusions

In summary, in this work we present a highly efficient, cobalt-catalysed method for the *syn*-selective hydroboration of both terminal and internal alkynes. The cobalt(II)-CP precatalyst is bench-stable and easily prepared from a ditopic terpyridine ligand. The catalytic reactions could be performed at ambient temperature with very low catalyst loading. This method achieved the highest atom-efficiency among all known examples of metal-catalysed alkyne hydroboration. We have demonstrated the utilization of the present **1**/KO^{t}Bu for the synthesis of a variety of aromatic and aliphatic alkynes, achieving excellent TOFs of up to 47,520 h^{-1}, comparable to precious metal catalysts. This work expands the application of CP catalysts built with earth-abundant metals in efficient and practical hydroboration catalysis, implicating the advantage of using CP catalysts over small molecular catalysts in valuable organic transformations.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work is supported by the US National Science Foundation (CHE 1900500). We also acknowledge the generous support from the PSC-CUNY awards (61321-0049 and 62154-0050), the PRISM program and a Seed grant from the Office for Advancement of Research at John Jay College of City University of New York.

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