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Citation for published version:

Agahi, R, Challinor, AJ, Carter, NB & Thomas, SP 2019, 'Earth-Abundant Metal Catalysis Enabled by Counterion Activation', *Organic letters*. <https://doi.org/10.1021/acs.orglett.8b03986>

Digital Object Identifier (DOI):

[10.1021/acs.orglett.8b03986](https://doi.org/10.1021/acs.orglett.8b03986)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Organic letters

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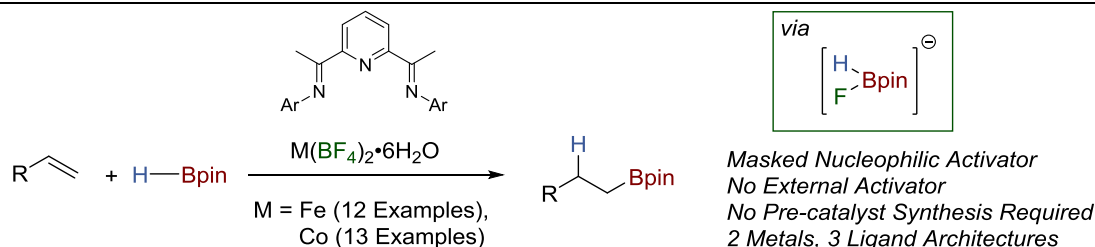


Earth-abundant Metal Catalysis Enabled by Counterion Activation

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Supporting Information Placeholder



ABSTRACT: A pre-catalyst activation strategy has been developed for Earth-abundant metal catalysis enabled by counterion dissociation and demonstrated through alkene hydroboration. Commercially available iron- and cobalt tetrafluoroborate salts were found to catalyze the hydroboration of aryl- and alkyl alkenes with good functional group tolerance (Fe, 12 substrates; Co, 13 substrates) with 3 structurally distinct ligands. Key to this endogenous activation was counterion dissociation to generate fluoride which indirectly activates the pre-catalyst by reaction with pinacol borane.

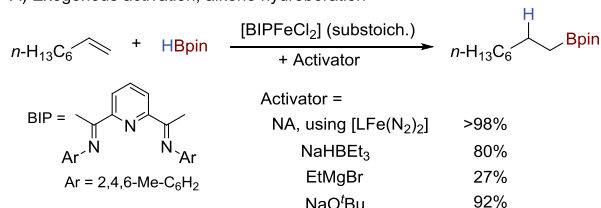
Catalytic protocols using precious metals such as platinum, palladium and rhodium have become routine in academia and industry due to the highly robust and reliable nature of these methods. However, beyond fine chemical and specialist applications, the low natural abundance, volatile cost and toxicity of these metals remains problematic. Therefore great interest and resource has been invested in the use of Earth-abundant metal-catalyzed processes, particularly for bulk and dispersive technologies.¹⁻⁶ Boronic esters are ubiquitous in chemical synthesis and readily prepared by metal-catalyzed hydroboration.⁷⁻¹² Great progress has been made towards operationally simple iron- and cobalt-catalyzed alkene hydroboration methods, but the state-of-the-art remains exogenous activation strategies where a bench-stable pre-catalyst is activated using an organometallic reagent (Scheme 1A).¹²⁻²³ The use of an alkoxide in place of the organometallic activator further simplified these catalytic manifolds, but still required an external reagent.^{24,25} Recently, endogenous (activator free) protocols have been reported using cobalt acetylacetonate complexes to catalyze enyne cyclisation-borylation^{26,27} and alkene diborylation,^{28,29} and iron- and cobalt carboxylate complexes to catalyze alkene hydrosilylation.³⁰⁻³² However, and to the best of our knowledge, only a single example of cobalt-catalysed hydroboration has been reported,^{33,34} while endogenous activation for iron-catalysed hydroboration is yet to be realized (Scheme 1B).

We noted that counterion lability and nucleophilicity were common features of endogenous activation. Presumably, counterion lability gives a coordinatively unsaturated metal centre³⁵ and nucleophilicity generates a hydride activator by reaction

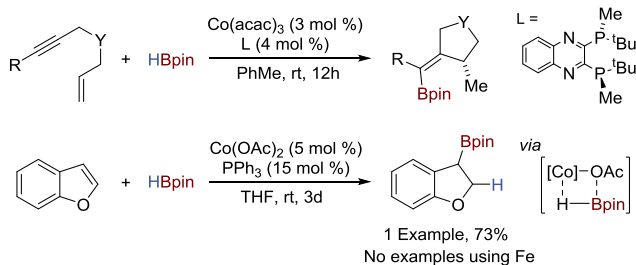
with the hydrometalloid reagent.²⁴ The tetrafluoroborate counterion is both weakly coordinating and known to undergo dissociation to BF_3 and fluoride,³⁶⁻³⁸ with the nucleophilicity of this fluoride having been exploited in precious metal catalysis.³⁹ We postulated that a similar mechanism could be applied as a general endogenous activation across iron- and cobalt pre-catalysts for hydroboration; with the dissociation of tetrafluoroborate giving a coordinatively unsaturated metal centre and the free fluoride reacting with pinacolborane to generate an *in situ* borohydride activator (Scheme 1C). This operationally simple procedure for Earth-abundant metal-catalyzed hydroboration would not require external activators and use only bench-stable, commercially available and easily handled reagents, so enabling the non-expert equal access to precious and non-precious metal catalysis alike.

Scheme 1. State-of-the-art for Activation in Earth-abundant Metal Catalysis

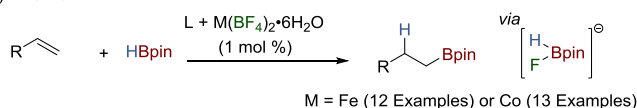
A) Exogenous activation; alkene hydroboration



B) Endogenous activation; 1,5-hydroborylative cyclisation and hydroboration



C) This work



Using the hydroboration of 1-octene as a model reaction, baseline reactivity was established for a strongly coordinating chloride anion (Table 1, Entry 1) and weakly coordinating triflate anion $[\text{EtBIPFe}(\text{OTf})_2]$ (Entry 2). Both reactions gave no alkene hydroboration. Using the preformed bisiminopyridine iron(II) tetrafluoroborate complex $[\text{EtBIPFe}(\text{BF}_4)_2]$ **1a** gave excellent conversion to the linear boronic ester **3a** with complete control of regiochemistry (Entry 3). Using the commercially available iron(II) tetrafluoroborate hydrate salt ($[\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}]$) and *in situ* ligand complexation gave a catalyst with equal reactivity and selectivity to that using the preformed, non-hydrated, complex **1a** (Entry 4). Significantly, application of the tetrafluoroborate activation to the analogous cobalt complex **1b** $[\text{EtBIPCo}(\text{BF}_4)_2]$ also gave the linear boronic

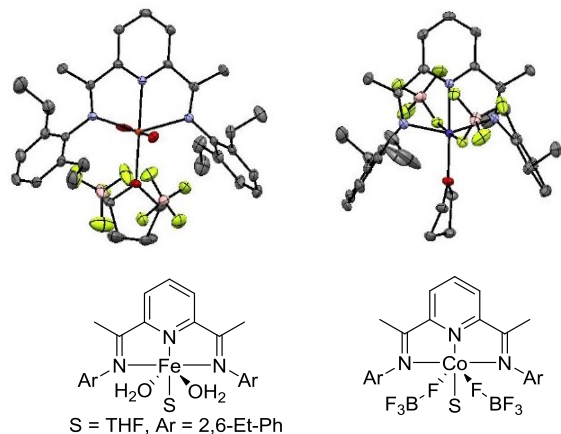


Figure 1. Crystal structure of $[\text{EtBIPFe}(\text{BF}_4)_2]$ (CCDC - 1563786) and $[\text{EtBIPCo}(\text{BF}_4)_2]$ (CCDC - 1563785). 50% probability of ellipsoids; hydrogen atoms and solvent molecules omitted for clarity; black=C, lilac=N, red=O, pink=B, yellow=F, orange=Fe, blue=Co.

ester in excellent yield and regioselectivity (entry 5). Single crystal X-Ray analyses of the iron- and cobalt complexes, **1a** and **1b**, revealed a free coordination site occupied by THF in both complexes (Figure 1). In the case of the iron complex **1a**, outer sphere $[\text{BF}_4]^-$ counterions were observed in the solid state, while fluoride contacts were present in the cobalt complex (**1b**).

Table 1. Optimization of hydroboration reactivity

entry	[M]	additive	yield
1	EtBIPFeCl_2	-	0
2	$\text{EtBIPFe}(\text{OTf})_2$	-	0
3	$\text{EtBIPFe}(\text{BF}_4)_2$	-	>95%
4	$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O} + \text{EtBIP}$	-	>95%
5	$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O} + \text{EtBIP}$	-	>95%
6	$\text{EtBIPFe}(\text{PF}_6)_2$	-	0
7	$\text{EtBIPFe}(\text{BPh}_4)_2$	-	0
8	$\text{EtBIPFe}(\text{BPh}_4)_2$	TBAT	65%
9	$\text{EtBIPCo}(\text{BPh}_4)_2$	TBAT	64%
10	EtBIPFeCl_2	TBAT	10%
11	EtBIPCoCl_2	TBAT	88%
12	$\text{FeF}_2 + \text{EtBIP}$	-	0

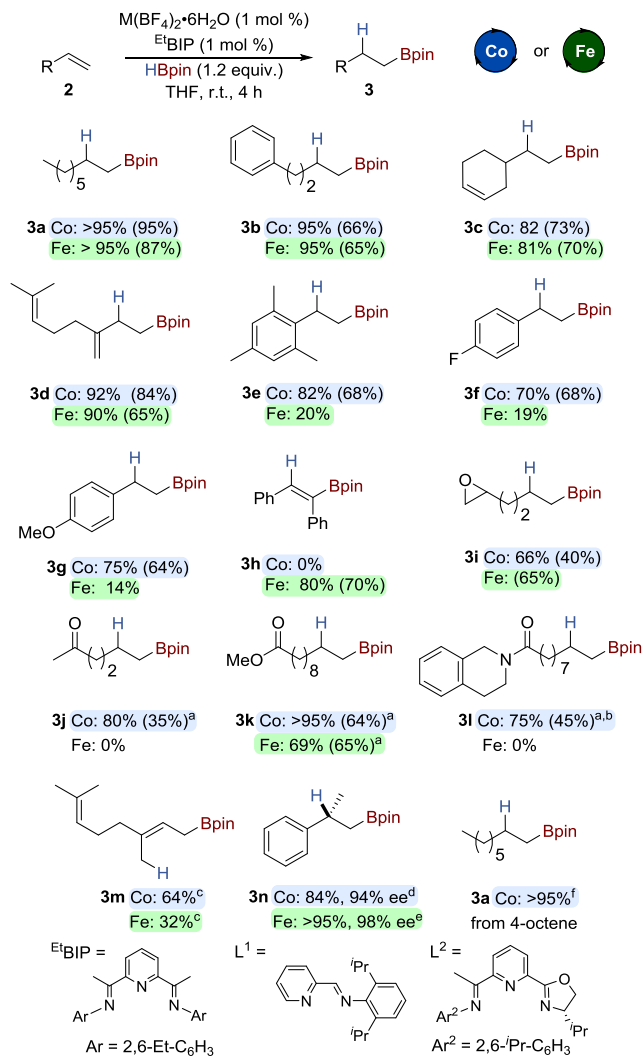
Conditions: Olefin (1.00 equiv.) with pinacolborane (1.20 equiv.), and metal salt (0.02 equiv.) stirred in THF (1 M) at ambient temperature; over 24 hours. Yields determined by ^1H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

In order to confirm the catalytic importance of dissociated fluoride, the analogous tetraphenyl borate $[\text{EtBIPFe}(\text{BPh}_4)_2]$ **1c** and hexafluorophosphate complexes were prepared as these bear non-coordinating counterions, but lack the ability to generate a nucleophile. Using either the tetraphenyl borate complex or the hexafluorophosphate salt gave no catalytic activity (Entries 6 and 7, respectively). Catalytic activity could be restored using both iron- and cobalt tetraphenylborate salt by addition of external fluoride, tetrabutylammonium difluorotriphenylsilicate (TBAT), clearly demonstrating the crucial role of free fluoride in catalysis (Entries 8 and 9). It was also possible to activate the more stable iron- and cobalt chloride pre-catalysts using TBAT (Entries 10 and 11). No catalytic activity was observed using iron(II) fluoride and ligand (Entry 12), suggesting that an iron-fluoride is not catalytically relevant.

Having established optimal conditions for olefin hydroboration (Tables SI 1-3), we set out to investigate the scope of these reactions (Scheme 2). Aliphatic alkenes underwent successful hydroboration using both iron- and cobalt tetrafluoroborate pre-catalysts to give the linear boronic ester as the sole regioisomer in good yield **3a-c**. Chemoselectivity for the hydroboration of a

terminal alkene was observed over an internal alkene **3c**. In contrast to previous methods,^{19,20} the hydroboration of 1,3-dienes proceeded with 1,2-selectivity to give the homoallylic boronic ester **3d**. Cobalt catalysis proved highly effective for the hydroboration of styrene derivatives including the sterically demanding 2,4,6-trimethylstyrene **3e**, and those bearing electron-withdrawing **3f** and electron-donating substituents **3g**. In all cases hydroboration gave the linear regioisomer. Iron-catalyzed hydroboration of diphenylacetylene gave the alkenyl boronic ester **3h** as a single diastereoisomer. When terminal alkynes were tested, low reactivity and small amounts of alkyne hydrogenation were observed.⁴⁰ Good functional group tolerance was observed including epoxy **3i**, keto **3j**, ester **3k** and amido **3l** groups without a decrease in regioselectivity or reaction yield. Using a bidentate iminopyridine ligand L^1 , which has been applied in 1,4-hydroboration of 1,3-dienes,^{19,20} gave 1,4-hydroboration **3m**, with the same selectivity as those previously reported for this ligand. Enantioselective hydroboration of α -methylstyrene was achieved by replacing the bisiminopyridine ligand with an enantiopure ligand^{21,22} L^2 to give the alkyl boronic ester in high yield and enantioselectivity across both iron- and cobalt-catalyzed systems **3n**. This demonstrates the potential to apply this activation system in asymmetric catalysis, as well as the tolerance of this activation system for different ligand scaffolds. It was also possible to effect cobalt-catalyzed alkene isomerization-hydroboration,³³ with 4-octene reacting to give the linear boronic ester **3a** in excellent yield.

Scheme 2. Hydroboration Substrate Scope

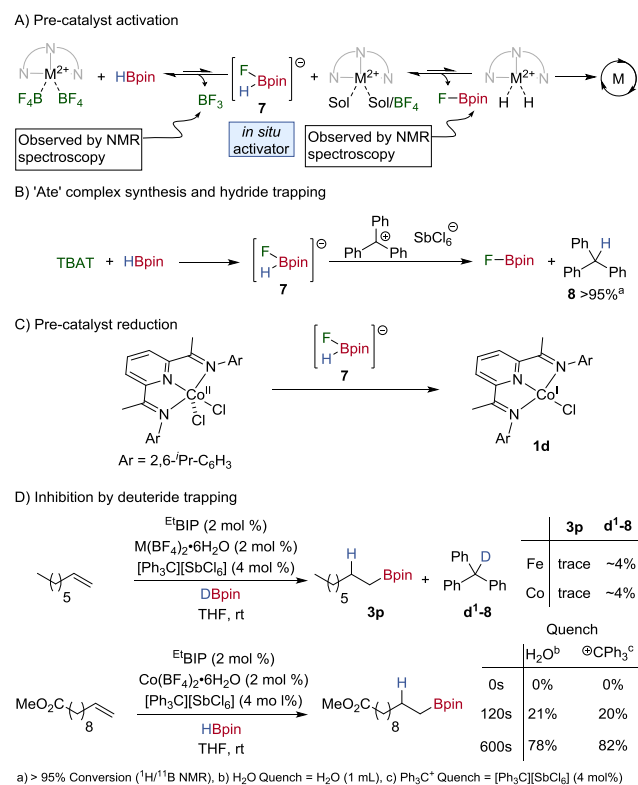


Conditions: Olefin (1.00 equiv.) with pinacolborane (1.20 equiv.), metal salt (0.01 equiv.) and ligand (0.01 equiv.) stirred in THF (1 M) at ambient temperature for 4 hours. Yields determined by ¹H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. Isolated yields (based on 1.5 mmol scale reactions) shown in parentheses. a) 2.4 equiv. HBpin, b) Isolated as alcohol following oxidation, c) Using L^1 as ligand, d) $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (3 mol %), L^2 (3 mol %) 5h, e) $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (5 mol %), L^2 (5 mol %) 5h, f) 80 °C.

Having shown that simply using non-coordinating counterions failed to initiate catalysis (Table 1, entries 6 and 7) and that fluoride was essential for catalysis (Table 1, entries 8 and 9), we sought to clarify the mechanism of the tetrafluoroborate activation and role of free fluoride. We postulated that dissociation of the tetrafluoroborate counterion gave fluoride, which on reaction with the HBpin gave a hydridic boronate complex **7**,²⁴ along with BF_3 (Scheme 3A). Hydride transfer to the metal centre would then give a metal-hydride complex which, following reductive elimination, would generate the catalytically active low oxidation-state metal complex.^{1,2} Assuming this mechanism is in operation, BF_3 would be produced by fluoride dissociation from $[\text{BF}_4]^-$ and F-Bpin would be generated as a byproduct of hydride transfer from the boronate complex **7**. The presence of F-Bpin, ¹¹B (20.8 ppm) and ¹⁹F (155 ppm), and BF_3 , ¹¹B (0.0 ppm) and ¹⁹F (153 ppm), under reaction conditions were confirmed by *in situ* NMR and comparison to authentic samples, (Scheme 3A, Scheme S117).⁴¹

Although the direct observation of the borohydride 'ate' complex **7** was not possible, independent synthesis of the fluoroborohydride **7** and use as an activator was explored. Reaction of fluoroborohydride **7** with trityl cation gave F-Bpin and triphenyl methane, HCPH₃, establishing the role of fluoroborohydride **7** as a hydride donor (Scheme 3B). The role of the fluoroborohydride **7** in pre-catalyst activation was confirmed by stoichiometric reaction with a cobalt(II) pre-catalyst to give a catalytically active cobalt(I) species **1d**,⁴²⁻⁴⁴ indicating the reductive role of the 'ate' complex **7** (Scheme 3C). In order to probe the catalytic role of a metal hydride, the addition of trityl cation, a hydride trap, to a standard reaction was investigated (Scheme 3D). The addition of trityl cation caused the complete loss of catalytic activity. Use of D-Bpin in a standard reaction inhibited by trityl cation gave d¹-triphenylmethane, DCPH₃ (as observed by ²H NMR analysis), showing that the hydride/deuteride originates from H/DBpin. Importantly, even after activation the addition of trityl cation completely inhibited catalysis. Quenching of a standard reaction with water or trityl cation gave equal outcomes (Scheme 3D). This demonstrates that in addition to preventing pre-catalyst activation, catalytic turnover was stopped by trapping of a hydride, underlining the catalytic activity of a metal-hydride complex.

Scheme 3. Mechanistic Investigations



A new method for iron- and cobalt-catalyzed hydroboration of alkenes and alkynes has been developed without the need for an external activator, specialist equipment or extensive (pre)catalyst synthesis. Mechanistic studies indicate that pre-catalyst activation results from the formation of a hydridic 'ate' complex by dissociation of fluoride from the counterion ([BF₄]⁻), reaction with HBpin and transfer of hydride to the metal pre-catalyst. It is hoped that this work can be applied to a range of iron- and cobalt-catalyzed transformations, in streamlining the

discovery of new reactivity, and, ultimately, in the replacement of precious metals with their Earth-abundant counterparts.

ASSOCIATED CONTENT

Supporting Information

Supporting Information includes characterization data for pre-catalysts, substrates and for compounds made for mechanistic studies (PDF)

The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

† R.A. and A.J.C. contributed equally.

Notes

Any additional relevant notes should be placed here.

ACKNOWLEDGMENT

RA and SPT thanks the Royal Society for funding a PhD studentship. AJC and SPT thank Syngenta for part funding a PhD studentship. SPT thanks the Royal Society for a University Research Fellowship. All thank the University of Edinburgh and the School of chemistry Technical Staff for generous support. We thank prof. Zheng Huang (Shanghai Institute of Organic Chemistry) for kindly donating ligand L².

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