

Markovnikov-Selective Hydroboration of Vinylarenes Catalyzed by a Cobalt(II) Coordination Polymer

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(5) Supporting Information

ABSTRACT: Highly efficient and practical hydroboration of alkenes has been catalyzed by an inexpensive and air-stable cobalt(II) coordination polymer (CP) in the presence of KO^tBu. Complete conversion of alkenes to alkylboronates were performed within just 5 min with low catalyst loading (0.025 mol %), achieving the record high turnover frequencies of up to 47 520 h⁻¹. For a range of vinylarenes, unusual Markovnikov selectivity was observed.

H vdrofunctionalization of alkenes constitutes a class of key reduction reactions that have prominent applications in current synthetic and petroleum chemical industries.¹ Metalcatalyzed hydroboration of alkenes is one of the most attractive processes in this class, because it offers alkylboronates as key and versatile synthetic intermediates in a direct, one-step manner.² Earlier success on this reaction has been built on precious metal complex catalysts involving Ru, Rh, and Ir.³ Although good efficiencies (turnover frequency (TOF) values of up to 325 h^{-1})^{3g} and excellent chemoselectivity, regioselectivity, and enantioselectivity have been achieved with these metals, their applications in industrial manufacturing and sustainable synthesis are severely diminished by their low abundance, high cost, and inherent environmental toxicity. The requirement for replacing the precious-metal catalysts with Earth-abundant elements has thus emerged.^{4,5}

In the past decade, several alkene hydroboration catalysts have been developed based on Earth-abundant metals, with the majority being anti-Markovnikov selective for terminal alkenes.^{6–8} However, Markovnikov hydroboration were rarely approached with base-metal catalysts.⁹⁻¹² Along with sparse reports on $Cu^{I,9}$ Mn^{II,10} Ni^{II,11} and Fe^{II} (ref 12) complexes that induced Markovnikov selectivity (in all examples, TOFs were up to 330 h⁻¹), cobalt-based catalysts proved to be the most promising for high Markovnikov selectivity (Scheme 1). For example, in 2015, Chirik and co-workers reported a cobalt complex of terpyridine-catalyzed Markovnikov hydroboration of styrene using pinacolborane (HBpin) with a 25:1 branch/ linear (b/l) product ratio and a TOF of 300 $h^{-1.6d}$ Later, the Hollis group also revealed a (CCC)Co^{II}-catalyzed hydroboration of styrene in high Markovnikov selectivity with a TOF of 330 h⁻¹.¹³ Thomas and co-workers developed a more general (NNN)Co^{II} catalyst for Markovnikov hydroboration of a range of vinylarenes by using NaO^tBu as an activator, while reported TOFs were only up to 100 h^{-1} .^{14a} Very recently, the





Previous work:

Anti-Markovnikov hydroboration of alkenes

Markovnikov hydroboration of alkenes



 Chink, et al. 2015
 Hollis, et al. 2015
 Thomas, et al. 2017
 Zhang, et al. 2017

 1 example, TOF = 300 h⁻¹
 1 example, TOF = 330 h⁻¹
 24 example, TOF < 100 h⁻¹
 14 example, TOF < 50 h⁻¹

This work: High-efficiency Markovnikov selective hydroboration by Co-CP



Findlater group reported a simple $Co(acac)_3/PPh_3$ -catalyzed Markovnikov hydroborotion of styrenes with TOFs of up to 5 h⁻¹ for several active substrates.^{14b} We also observed cobalt(II) catalyst of a flexible N₃ ligand for Markovnikov hydroboration of vinylarenes with TOFs up to 50 h⁻¹,¹⁵ with connection to

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our recent interest in hydrogenation and dehydrogenation catalysis with cobalt. $^{16}\,$

Despite such progress, the catalysts developed thus far often suffer from tedious ligand synthesis and purification, the involvement of air-sensitive metal complexes or reagents, and high catalyst loading.^{4–12} A higher efficiency and practical method for catalytic alkene hydroboration is still unavailable. In this contribution, we wish to report a practical, extremely efficient, non-precious-metal, cobalt-catalyzed Markovnikov hydroboration of vinylarenes with outstanding TOFs of up to 47 520 h⁻¹ at ambient temperature. Furthermore, this catalyst also showed equally high efficiency toward internal alkenes and good functional group tolerance.

We have previously reported that a cobalt(II) CP (1) assembled from 4'-(4-pyridyl)-4,2';6',4"-terpyridine and CoCl₂ catalyzed the hydroboration of carbonyl compounds in the presence of KO^tBu as an activator.^{17,18} The structure of 1 features a one-dimensional linear polymer with Co^{II} being in a N₄Cl₂ environment that is similar to otherwell-defined cobalt-based hydroboration catalysts (Scheme 1). An initial catalytic test was performed using styrene as a model substrate and the combination of 1 (0.1 mol%) and KO^tBu (1 mol%) as a catalyst at ambient temperature; it was found that effective hydroboration (>99%) was accomplished within only 5 min, affording good Markovnikov regioselectivity with a b/l product ratio (2/3) of 90:10 (Table 1, entry 1). Further reducing the loading amount of 1 to 0.025 mol% did not affect the catalytic

Table 1. Reactivity Test for 1-Catalyzed Hydroboration of Styrene with HBpin^a

Dnin

Ĉ	о + НВ О	[Co], add solvent,	itive 25 °C	+	Bpin
entry	precatalyst	additive	solvent	yield ^b (%)	ratio, $2/3^{c}$
1^d	1	KO ^t Bu	THF	>99	90:10
2 ^e	1	KO ^t Bu	THF	82	92:8
3	1	KO ^t Bu	THF	99	92:8
4 ^{<i>f</i>}	1	KO ^t Bu	THF	64	90:10
5	L	KO ^t Bu	THF	_g	_h
6	$CoCl_2$	KO ^t Bu	THF	_g	_h
7	1	none	THF	g	_h
8	none	KO ^t Bu	THF	g	_h
9	1	NaO ^t Bu	THF	99	78:22
10	1	КОН	THF	95	79:21
11	1	LiO ⁱ Pr	THF	99	80:20
12	1	LiNTf ₂	THF	34	87:13
13	1	$NaBH_4$	THF	98	86:14
14	1	KO ^t Bu	toluene	95	78:22
15	1	KO ^t Bu	pentane	80	83:17
16	1	KO ^t Bu	benzene	92	78:22
17	1	KO ^t Bu	Et_2O	99	87:13
18	1	KO ^t Bu	CH_2Cl_2	44	86:14
19 ⁱ	1	KO ^t Bu	CH_2Cl_2	<4	_h
20	1	KO ^t Bu	none	99	74:26

^{*a*}Conditions: styrene (1.0 mmol), pinacolborane (1.1 mmol), precatalyst (0.025 mol%), additive (1 mol%), and solvent (0.5 mL), 25 °C, 5 min, N₂. ^{*b*}Yield of 2 + 3, determined by GC analysis with hexamethylbenzene as an internal standard. ^{*c*}Determined by GC analysis. ^{*d*}Reaction run using 0.1 mol% of 1. ^{*e*}Reaction run for 3 min. ^{*f*}0.5 mol% KO'Bu was used. ^{*g*}No reaction. ^{*h*}No ratio to measure or ratio not measured. ^{*i*}Reaction run in air.

activity. The yield of alkylboronates 2 and 3 were determined to be 82% in 3 min and 99% in 5 min, while improving the 2/3ratio slightly to 92:8, corresponding to a TOF of 47 520 h^{-1} (Table 1, entries 2 and 3). This represents the most efficient alkene hydroboration catalyst thus far.³ Decreasing the amount of KO^tBu led to a lower yield, although comparable regioselectivity was observed (Table 1, entry 4). Several control experiments revealed that the combinations of free terpyridine ligand or cobalt(II) chloride with KO^tBu were inactive and the reaction did not proceed in the absence of cobalt precatalyst 1 or without an additive (Table 1, entries 5-8). These results indicate the importance of the combined system 1/KO^tBu for generating an active catalyst species. We further tested other basic additives (Table 1, entries 9-13) and determined that, while NaO^tBu, LiO^tPr, and NaBH₄ were identically effective activators, the regioselectivities have decreased in all cases. Finally, solvent effects were studied under the same conditions (Table 1, entries 14-20). The reactions conducted in nonpolar solvents and CH₂Cl₂ were less efficient, yet those conducted in diethyl ether or under neat conditions showed the same efficiency as in THF, despite the regioselectivities being lower than that observed in THF. It was also determined that, when the reaction was performed in CH₂Cl₂ and in air, only trace alkene hydroboration was detected (Table 1, entry 18).

Next, we explored the applicability of the optimized conditions for a range of alkene substrates. Typically, the reactions were performed in a 2 mmol scale using 1 (0.025 mol %) and KO^tBu (1 mol %) as a catalyst in THF at ambient temperature. The reaction mixture was examined and analyzed via gas chromatography-mass spectroscopy (GC-MS) after 5 min and then the major regioisomer was isolated by column chromatography on silica. The results are summarized in Table 2. The branched alkylboronate (2a) resulting from styrene hydroboration could be obtained in a good isolated yield (82%), and a 92:8 branched/linear selectivity. The hydroboration of sterically hindered 2-methylstyrene proceeded with equal efficiency (TOF = 47 520 h^{-1}) with decreased isolated yield and slightly lower regioselectivity (80:20). Halogenated styrenes are also suitable substrates for Markovnikov hydroboration, providing good isolated yields of branched products (2c-2f) and comparable selectivity, although the TOFs were relatively lower (in the range of $7840-23760 \text{ h}^{-1}$). Styrenes bearing electron-donating groups in the 4-position, such as 4methoxystyrene and 4-acetoxystyrene, were hydroborated in high TOFs (47 040 and 47 520 h^{-1}) and good yields of products 2g and 2h were isolated. In contrast, 4-trifluoromethylstyrene containing strongly electron-withdrawing group was found to be a more challenging substrate, and, in this case, only 66% conversion was detected in 1 h, while the Markovnikov selectivity remained good (88:12). 2-Vinylnaphthalene was fully converted to the boronic esters in high branched/linear regioselectivity (93:7) within 30 min, corresponding to a TOF of 7920 h⁻¹. In addition, several internal alkenes were examined for regioselective hydroboration. Trans- β -methylstyrene was hydroborated selectively with **2k** being isolated in 92% yield and the TOF was as high as 47 520 h^{-1} . In this case, only trace amounts of two other regioisomers were observed. Equally high efficiency was obtained when 2,3-benzofuran was used, along with a complete control of regioselectivity for the C-B bond formation at the benzylic position (Table 2, entry 12). Thus, product 2l has been isolated in a high yield of 94%. Note that selective



		or + O	THF, 25 °		or 3			
		R ² (HBpin)			Bpin			
		R'		F	$R^1 R^2$			
entry	alkene	product (2)	time /min	GC yield of 2 + 3 (%)	ratio of 2/3	isolated Yield of 2 (%)	TOF (h ⁻¹)	
1	$\bigcirc \frown$	Bpin	5	99	92:8	82 (2a)	47,520	
2		Bpin	5	99	80:20	63 (2b)	47,520	
3	F	Bpin	10	99	82:18	77 (2c)	23,760	
4	CL	Bpin	20	96	82:18	75 (2d)	11,520	
5	CI	Bpin	10	98	80:20	76 (2e)	23,520	
6	Br	CI- Spin	30	98	79:21	72 (2f)	7,840	
7		Br' Bpin	5	98	76:24	71 (2g)	47,040	
8		Bpin O	5	99	81:19	76 (2h)	47,520	
9	F ₃ C	Bpin	60	66	88:12	54 (2i)	2,640	
10	$\bigcirc\bigcirc\bigcirc$	Bpin	30	99	93:7	89 (2 j)	7,920	
11	\bigcirc	Bpin	5	99	98:1:1 ^b	92 (2k)	47,520	
12		Bpin	5	99	1:99	94 (2I)	47,520	
13	Ph Ph	Bpin Ph	5	99	-	95 (2m)	47,520	
14	Ph	Bpin Ph	5	99	-	96 (2m)	47,520	
15		Bpin	300	26	75:25	-	208	
16	$\widetilde{\checkmark}$	Bpin	5	99	58:42	-	47,520	
17	$\sim\sim\sim\sim$	Bpin	5	96	36:64	-	46,080	
18	<u> </u>		5	88	10:90°	72 (2n)	42,240	

<u>ь</u>.

"Conditions: alkene (2.0 mmol), pinacolborane (2.2 mmol), 1 (0.025 mol%) and KO^tBu(1 mol%) in THF (1 mL), room temperature, N₂. ^bRatio of three possible regioisomers. 'Ratio of two regioisomers of the major alkene hydroboration products. The minor doubly hydroborated product was isolated in 11% yield; see the SI.

hydroboration of 2,3-benzofuran was only sparsely explored in the literature.^{6c} The same conversion and selectivity were achieved by using the Chirik's catalyst (PPh₃)₃CoH(N₂) (5 mol%) after 2 h (TOF < 10 h⁻¹). Both *cis*- and *trans*-stilbenes were also effective substrates, furnishing the reactions with 95% and 96% isolated yields, respectively. The disubstituted terminal alkene, α -methylstyrene, was found to be a challenging substrate, affording the alkylboronates with 26% conversion after 5 h, although a reasonable Markovnikov selectivity was obtained (75:25; see Table 2, entry 15). For alkyl alkenes, rapid hydroboration was also observed. For instance, 1-hexene furnished the reaction with a TOF of 47 520 h⁻¹; however, the selectivity was poor (b/l = 58:42). In contrast, in the case of 1-octene as a substrate, the reaction favors anti-Markovnikov selectivity with a b/l ratio of 36:64. Trans-4-octene was also tested for the hydroboration; however, the products include a complicated mixture of both alkylboronate and octene isomers resulting from isomerization–hydroboration,^{6b} which will deserve further studies on the optimization of selectivity. Finally, 5-hexen-2-one containing both alkene and ketone functional groups was selectively hydroborated on the alkene, with good anti-Markovnikov selectivity (b/l = 10:90). The ketone-containing alkylboronate **2n** was isolated in 72% yield, even though a

minor product (2n') resulting from double hydroboration of both ketone and alkene moieties was obtained in 11% yield (see the Supporting Information (SI)). The regioselectivity observed here is markedly different from that observed in the work of Thomas, using discrete (NNN)CoCl₂ as a precatalyst, where the linear ketone-containing alkylboronate product was obtained with a 70:30 b/l selectivity.^{14a}

To further investigate the functional group tolerance of the present 1-catalyzed Markovnikov hydroboration, we conducted a fast robustness screen of reducible functional groups by using the method introduced by Glorius.¹⁹ Thus, styrene hydroboration was examined under the optimized conditions with added chemicals (1.0 equiv) containing different functional groups and the results are summarized in Table 3. It is shown

Table 3. Robustness Screen of 1-Catalyzed Hydroboration of Styrene a



"Conditions: styrene (1.0 mmol), pinacolborane (1.1 mmol), 1 (0.025 mol%)/KO^fBu(1 mol%), additive (1.0 mmol, 1.0 equiv) and solvent (0.5 mL), 25 °C, 5 min, N₂. ^bYield of 2 + 3, determined by GC analysis with hexamethylbenzene as an internal standard."Determined by GC analysis. ^d>95% hydroboration of ketone was found. ^f76% hydroboration of aldehyde was found.

that the presence of benzonitrile reduced the yield of 2 and 3 to 60% with a decreased b/l ratio (82:18). However, other additives including *N*-heterocycles, imine, and ester did not influence the reactivity and efficiency, despite the regioselectivity being slightly poorer, compared to the reaction with styrene alone. Amide is also a compatible functionality, leading to a small decrease in both yield and selectivity. In these

examples (Table 3, entries 1-6), the additives were determined not to be hydroborated, based on GC-MS analysis. However, this catalyst showed different selectivity for styrene hydroboration in the presence of ketones and aldehydes (Table 3, entries 7-9).¹⁷

In conclusion, we developed a highly efficient and practical cobalt-catalyzed method for selective hydroboration of alkenes. The simple combination of air-stable cobalt(II) coordination polymer and KO^tBu constitutes, thus far, the most efficient catalyst for alkene hydroboration, achieving outstanding TOFs of up to 47 520 h⁻¹. Remarkably, the Markovnikov selectivity observed for vinylarenes also represents one of the rare examples for base-metal-catalyzed hydroboration. This work implicates a new approach to effective catalysts based on Earthabundant metals that outcompete non-precious-metal catalysts.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b03431.

Additional experimental details and copies of NMR spectra and crystallographic data (PDF)

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Notes

The authors declare no competing financial interest.

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