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Cobalt-Catalyzed Ligand-Controlled Regioselective Hydroboration/Cyclization of 1,6-Enynes

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Cobalt-Catalyzed Ligand-Controlled Regioselective Hydroboration/Cyclization of 1,6-Enynes

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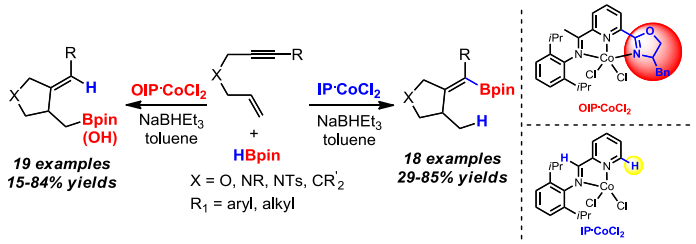
ABSTRACT: A ligand-controlled cobalt-catalyzed regioselective hydroboration/cyclization of 1,6-enynes with HBPin was developed by switching the size of the coordinated side arm to afford alkenylboronates and alkylboronates, respectively. The gram-scale reactions could be easily conducted which is benefit for further derivatizations. A primary mechanism was proposed based on substrate-controlled experiments and deuterium experiments.

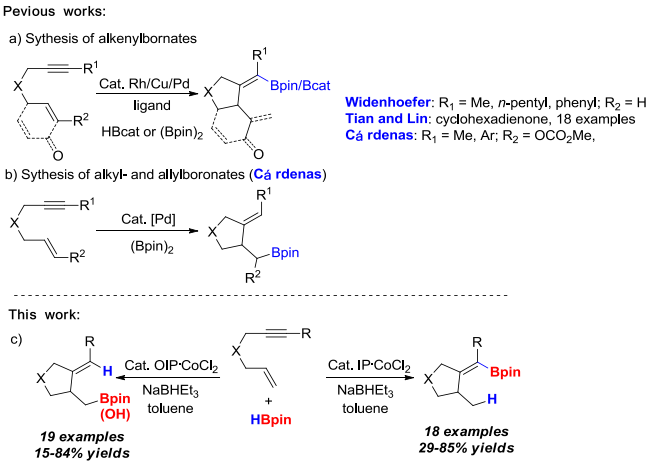


Selective hydroboration[1] of carbon-carbon multiple bonds is one of direct, atom-economic, and powerful methods to synthesize alkyl or alkenyl organoboron compounds,[2] which are very important intermediates for organic synthesis, material science and pharmaceutical.[3]

Cyclization of enynes is a direct and useful method to efficiently construct cyclic compounds.[4] However, hydroboration of 1,6-enynes with hydroboranes are less formulated. In 2006, Widenhoefer and co-works reported an effective rhodium-catalyzed protocol for asymmetric hydroboration/cyclization of 1,6-enynes with catecholborane followed by oxidation or arylation to afford the corresponding chiral cyclic compounds (Scheme 1, a).[5] Tian and Lin reported copper-catalyzed asymmetric borylative cyclization of cyclohexadienone-containing 1,6-enynes with bis(pinacolato)diboron (Scheme 1, a).[6] Cárdenas and co-workers[7] developed a series of facile palladium-catalyzed regioselectivity-controllable borylative cyclization of 1,6-enynes with $(BPin)_2$ by switching different protecting groups on substrates (Scheme 1, a and b). However, the *O*-tether and *N*-tether substrates have shown poor reactivities.

Although cobalt-catalyzed hydroboration of alkenes[8] or alkynes[9] have been explored, to the best of our knowledge, cobalt-catalyzed selective hydroboration/cyclization of 1,6-enynes with HBpin has not been previously reported. Herein, we developed a ligand-controlled regioselective cobalt-catalyzed hydroboration/cyclization reaction of 1,6-enynes to afford alkenylboronates and alkylboronates, respectively (Scheme 1, c).

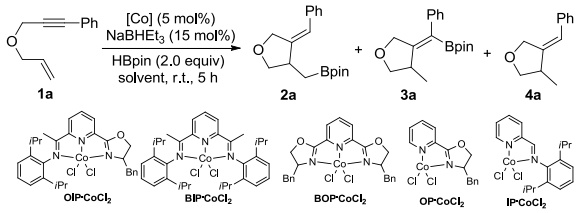
Scheme 1. Hydroboration/cyclization of 1,6-enynes



We began our studies by investigating the model reaction of 1,6-enyne **1a** with HBpin in the presence of 5 mol% of $OIP{\cdot}CoCl_2$ as a precatalyst and 15 mol% of $NaBHEt_3$ as a reductant in a solution of THF at ambient temperature for 5 h (table 1, entry 1). The alkylboronate cyclic product **2a** was observed in 66% yield. It should be noted that **2a** would decompose on silica gel and could be converted to the corres-

ponding alcohol **5a** through oxidation of **2a** with H_2O_2.[7c] Various solvents, such as Et_2O, dioxane, toluene and DCM (entries 2-5), were used instead of THF, toluene was more suitable to give **5a** in 72% yield. The reductant reagents ($NaBH^sBu_3$, $LiBHEt_3$, MeLi, MeMgBr, Et_2Zn) were also investigated to give **3a** in promising yields (SI Table 1). Interestingly, using BIP instead of OIP as a ligand, the reaction afforded the reductive cyclization product **4a** in 25% yield without any hydroboration products (entry 6). Using BOP or OP as ligands, the yields of **2a** were diminished (entries 7 and 8). Unexpectedly, when remove of the side arm oxazoline on OIP,[10-11] IP·$CoCl_2$ could catalyze the cyclization reaction to deliver a regioselectivity-switchable alkenyl boronate **3a** in 68% yield without **2a** (entry 9). The control experiments without reductant or catalyst or ligand did not afford any cyclic products (entries 10 and 11). Unfortunately, no enantioselectivities were observed when chiral OIP ligand was used.

Table 1. Optimizations of hydroboration/cyclization of 1,6-enynes[a]



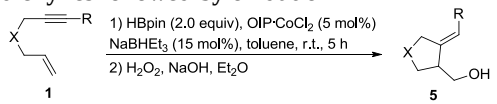
Entry	[Co]	Solvent	Yield of **2a**[a] (%)	Yield of **3a**[a] (%)	Yield of **4a**[a] (%)
1	OIP·$CoCl_2$	THF	66	0	0
2	OIP·$CoCl_2$	Et_2O	50	0	0
3	OIP·$CoCl_2$	toluene	72[b]	0	0
4	OIP·$CoCl_2$	Dioxane	69	0	0
5	OIP·$CoCl_2$	DCM	0	0	0
6	BIP·$CoCl_2$	Toluene	0	0	25
7	BOP·$CoCl_2$	Toluene	41	0	0
8	OP·$CoCl_2$	Toluene	7	0	0
9	IP·$CoCl_2$	Toluene	0	68[c]	0
10	OIP·$CoCl_2$	Toluene	0	0	0
11[d]	--	Toluene	0	0	0
12	$CoCl_2$	Toluene	0	0	0

[a] Yields determined by ^{1}H NMR analysis using TMSPh as an internal standard. [b]Isolated yield of the corresponding alcohol **5a** followed by oxidation of **2a**. [c]Isolated yield. [d] Without $NaBHEt_3$.

With standard conditions in hands, the scope of the OIP·$CoCl_2$-catalyzed hydroboration/cyclization followed by oxidation was illustrated in Table 2. Oxygen-, nitrogen- or carbon-linkers would be tolerated; The enynes with a methyl group at *para*-, *meta*-, or *ortho*-position of aryl rings could be delivered to the corresponding products **5f-h** in 46-60% yields; The enynes with electron-rich aryl rings underwent hydroboration/cyclization reaction to give products in good yields, however, the reactions of electron-deficient enynes were messy; Naphthalene (**1n**), thiofuran (**1o**), and indole (**1p**) were tolerated to afford cyclic products in 31-64% yields; The alkyl enynes (**1q-r**) could also be converted to cyclic products in 50% yields; 1-En-6,8-diyne could be reacted with HBpin to give **5s**, albeit in 16% yield. The reaction of terminal or Me_3Si-substituted alkynes (**1x-y**) did not occur.

The IP·$CoCl_2$-catalyzed hydroboration/cyclization with various enynes was summarized in **Table 3**. It should be noted that the reactions were conducted in 5.0 mmol scale. 1,6-Enynes with various linkers such as *O*-tether, *N*-tether, *C*-tether were tolerated to give **3a-3e** in 36-68% yields; The reaction of sterically hindered *ortho*-methylphenyl enyne **1f** afforded a mixture of regioisomers **3f** and **2f** in 30% and 14% yields, respectively; *meta*- and *para*-methylphenyl enynes were delivered to the corresponding products **3g** and **3h** in 65% and 64% yields, respectively; The reactions of enynes containing electron-donating and withdrawing groups, such as methoxyl (**3i, 3t**), phenyl (**3m**), chloro (**3u**) and cyano (**3v**) groups could smoothly undergo hydroboration/cyclization to afford the cyclic products in 29-63% yields; Alkyl substituted enynes (**1q-r**) could be reacted to give cyclic products in 19-56% yields. The terminal alkynes (**1x**) would be converted to **3x** in 41% yield. Me_3Si-substituted alkyne (**1y**) could not be suitable. The stereochemistry of hydroboration products was determined by X-ray diffraction of compound **3m**.[12]

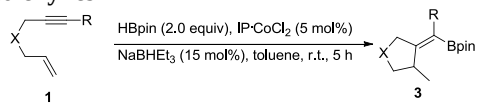
Table 2. OIP·$CoCl_2$-catalyzed hydroboration/cyclization of 1,6-enynes followed by oxidation[a]



Entry	Enynes	Products	Yield (%)[b]
1	**1a**	**5a** : X = O, R = Ph	72
2	**1b**	**5b** : X = NMe, R = Ph	71
3	**1c**	**5c** : X = NBn, R = Ph	49
4	**1d**	**5d** : X = NTs, R = Ph	84
5	**1e**	**5e**: X=  , R = Ph	75
6	**1f**	**5f** : X = O, R = 2-MeC_6H_4	46
7	**1g**	**5g** : X = O, R = 3-MeC_6H_4	60
8	**1h**	**5h** : X = O, R = 4-MeC_6H_4	52
9	**1i**	**5i** : X = O, R = 4-$MeOC_6H_4$	44
10	**1j**	**5j** : X = NTs, R = 4-$MeOC_6H_4$	74
11	**1k**	**5k** : X = NTs, R = 3-$MeOC_6H_4$	63
12	**1l**	**5l** : X = NTs, R = 4-MeC_6H_4	67
13	**1m**	**5m** : X = NTs, R = 4-PhC_6H_4	62
14	**1n**	**5n** : X = NTs, R = 1-naphthyl	31
15	**1o**	**5o** : X = NTs, R = 2-thienyl	64
16	**1p**	**5p** : X = NTs, R = 2-(*N*-methyl)-indolyl	56
17	**1q**	**5q** : X = NTs, R = Me	50
18	**1r**	**5r** : X = NTs, R = nC_4H_9	50
19	**1s**	**5s** : X = O, R = PhCC	16
20	**1x**	**5x**: X = NTs, R = H	0
21	**1y**	**5y**: X = NTs, R = $SiMe_3$	0

[a]OIP-conditions: **1** (1 mmol), HBPin (2 mmol), OIP·$CoCl_2$ (5 mol%), $NaBHEt_3$ (15 mol%) and toluene (2 mL) at room temperature for 5 hours. Then the residue was treated with NaOH (3 N, 3 mL) and H_2O_2 (30%, 3 mL) in ether (6 mL), and stirred for overnight at room temperature.[b] Isolated yield of **5**.

Table 3. IP·$CoCl_2$-catalyzed hydroboration/cyclization of 1,6-enynes[a]



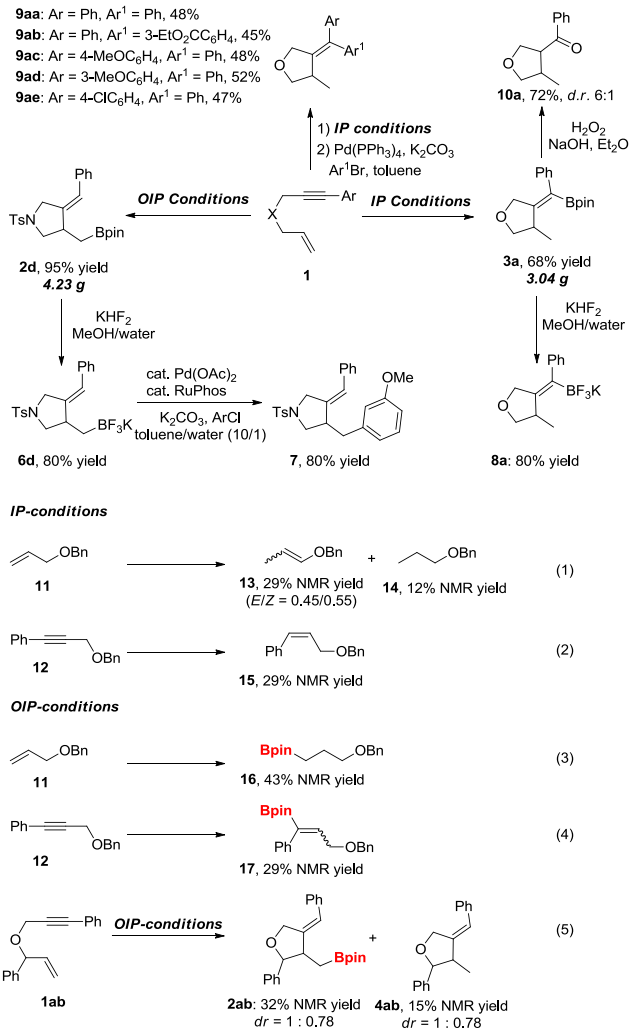
Entry	Enynes	Products	Yield (%)[b]
1	**1a**	**3a** : X = O, R = Ph	68
2	**1b**	**3b** : X = NMe, R = Ph	68
3	**1c**	**3c** : X = NBn, R = Ph	51
4	**1d**	**3d** : X = NTs, R = Ph	54
5	**1e**	**3e**: X=  , R = Ph	36
6	**1f**	**3f** : X = O, R = 2-MeC_6H_4	30/14[c]
7	**1g**	**3g** : X = O, R = 3-MeC_6H_4	65
8	**1h**	**3h** : X = O, R = 4-MeC_6H_4	64
9	**1i**	**3i** : X = O, R = 4-$MeOC_6H_4$	60
10	**1l**	**3l** : X = NTs, R = 4-MeC_6H_4	63
11	**1m**	**3m** : X = NTs, R = 4-PhC_6H_4	63
12	**1q**	**3q** : X = NTs, R = Me	56
13	**1r**	**3r** : X = NTs, R = nC_4H_9	19
14	**1t**	**3t** : X = O, R = 3-$MeOC_6H_4$	48
15	**1u**	**3u** : X = O, R = 4-ClC_6H_4	36
16	**1v**	**3v** : X = NTs, R = 4-NCC_6H_4	29
17	**1w**	**3w** : X = O, R = 2-thienyl	85
18	**1x**	**3x**: X = NTs, R = H	41
19	**1y**	**3y**: X = NTs, R = $SiMe_3$	0

[a] IP-conditions: 1 (5 mmol), HBPin (10 mmol), IP·$CoCl_2$ (5 mol%), NaBHEt3 (15 mol%) and toluene (10 mL) at room temperature for 5 hours; [b] Isolated yield of **3**. [c] Yield of the regioisomer **2f**.

It was worth to note that the gram-scale reaction of **1d** with HBPin under OIP-conditions afforded **2d** in 95% yield without decomposition (Scheme 2). The gram-scale reaction of **1a** catalyzed by IP·$CoCl_2$ was readily conducted to give **3a** in 68% yield. Oxidation of alkenyl-boronate **3a** with H_2O_2 can be performed to give the corresponding ketone **10a** in 72% yield with 6/1 *dr*.[5] The pinacol boronates could be easily converted to the corresponding organotrifluoroborates **6d** and **8a**, in 80% yield respectively.[8i] Additionally, the cyclization followed Suzuki-coupling reactions of **1a** afforded the corresponding tetra-substituted olefins **9aa-9ae** in 45-52% yields, and **6d** could be delivered to tri-substituted olefin **7** in 80% yield.

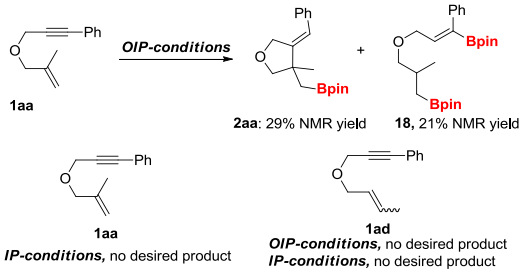
To demonstrate the details of transformations, control reactions of alkene **11** or alkyne **12** under IP-conditions were carried out to give isomerization products **13** in 29% yield and hydrogenation products **14** and **15** in 12% and 29% yields, respectively (eq. 1 and 2), which suggested that cobalt hydride might be the inital activated species.[13] Under OIP-conditions, the hydroboration products **16** and **17** were afforded in 29% and 43% yields, respectively (eq. 3 and 4). The observation of reductive cyclization product **4ab** suggested that the initial active species might also be Co-H species (eq 5). The poor diastereoselectivity observed decreased the possibility of cyclometallation pathway.[14] The reaction of α-substituted alkene **1aa** afforded **2aa** in 29% NMR yield and dihydroboration product **18** in 21% NMR yield (Scheme 3), which suggested that the alkyne insertion and alkene insertion underwent step by step. We proposed that the alkene-coordination to cobalt species could control the regioselectivity in the step of hydroboration of alkyne (see in SI). The reaction of **1aa** with HBpin did not give desired product under IP-conditions. The reaction of 1,2-disubstituted alkene **1ad** with HBpin did not give desired products either under OIP-conditions or IP-conditions (Scheme 3). Additionally, the deuterium experiments using DBpin[15] were conducted (Scheme 4). High deuterated ratios at the vinyl position under OIP-conditions and methyl position under IP-conditions were observed.

Scheme 2. Gram scale reactions and further applications.

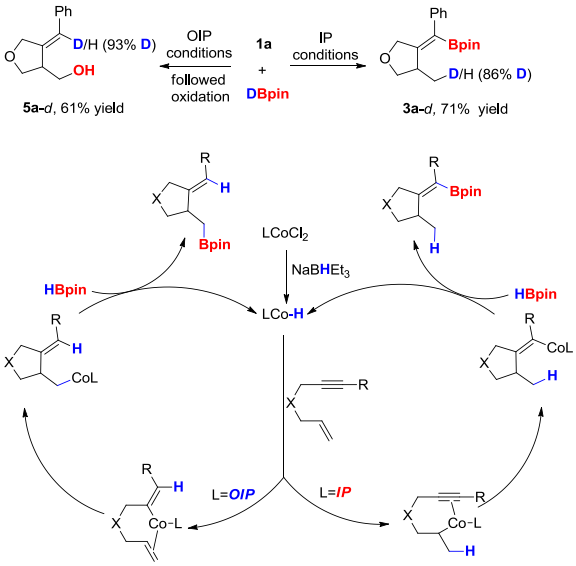


Based on above experimental and previously reported results,[8b,8h-i] cobalt complex could be reduced by $NaBHEt_3$ to generate cobalt hydride[8h-i] species (scheme 4). Using IP as a ligand, the alkene insertion to cobalt hydride bond might be the initial step to produce cobalt alkyl species which could be delivered to cobalt alkenyl species via alkyne insertion to cobalt carbon bond. The cobalt alkenyl species then underwent σ-bond metathesis with HBPin followed by reductive elimination to afford alkenylboronic ester and regenerate cobalt hydride species. Using the OIP ligand, the alkyne insertion to cobalt hydride bond might occur to afford cobalt carbon species which could undergo alkene insertion to give cobalt alkyl species. The cobalt alkyl species could react with HBPin via σ-bond metathesis followed by reductive elimination to afford alkylboronic ester and regenerate cobalt hydride species. However, the cyclometallation of enyne[16] could not be exclusively ruled out.

Scheme 3. Disubstituted alkene



Scheme 4. Deuterium experiments and plausible mechanism.



In summary, we have developed a ligand-controlled cobalt-catalyzed regioselective hydroboration/cyclization of 1,6-enynes to afford alkenylboronates and alkylboronates, respectively. The reactions could be easily scaled up and the boronate products could be derivatized to various useful compounds. A primary mechanism was proposed based on substrate-controlled experiments and deuterium experiments. This interesting side-arm-effect phenomenon will encourage us to explore more examples and mechanistic details on selectivity-controllable reactions by using multi-dentate ligands with non-precious transition metals.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal..

Procedures and analytical data (PDF)

X-ray diffraction of compound **3m** (cif)

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Notes

The authors declare no competing financial interest.

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