Ligand-Controlled Cobalt-Catalyzed Transfer Hydrogenation of Alkynes: Stereodivergent Synthesis of Z- and E-Alkenes

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S *Supporting Information*

ABSTRACT: Herein, we report a novel cobalt-catalyzed stereo-divergent transfer hydrogenation of alkynes to Z- and E-alkenes. Effective selectivity control is achieved based on a rational catalyst design. Moreover, this mild system allows for the transfer hydrogenation of alkynes bearing a wide range of functional groups in good yields using catalyst loadings as low as 0.2 mol %. The general applicability of this procedure is highlighted by the synthesis of more than 50 alkenes with good chemo- and stereoselectivity. A preliminary mechanistic study revealed that E-alkene product was generated via sequential alkyne hydrogenation to give Z-alkene intermediate, followed by a Z to E alkene isomerization process.
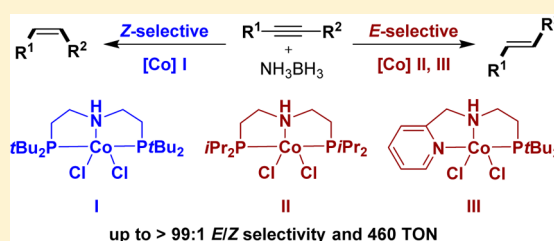
INTRODUCTION

Catalytic hydrogenation of unsaturated compounds is one of the most impactful reactions in organic synthesis.[1] For decades, these reactions relied on the use of rare and expensive late transition metals. It is highly desirable to replace noble metal catalysts by nonprecious base metals in catalytic hydrogenation reactions. The unique properties of such base metals like cobalt not only offer environmental and economic advantages but also provide new opportunities to uncover unusual reactivity and selectivity.[2] In this context, although several remarkable homogeneous cobalt catalysts have been developed for the hydrogenation of C=C,[3] C=O,[3c,4] and C=N[3c,4a] bonds, heterocycles,[5] as well as nitriles,[6] a general cobalt-catalyzed semihydrogenation of alkynes has not been revealed. Moreover, reports pertaining to Co-catalyzed transfer hydrogenation reactions are also scarce.[7]

Semihydrogenation of alkynes using the Lindlar catalyst[8] and various modern improvements of heterogeneous catalysts[9] have proven to be efficient ways to generate Z-alkenes. In contrast, few studies focusing on the corresponding E-selective (transfer) hydrogenation of alkynes have been reported. Most pioneering examples to actualize this transformation used precious metal catalysts,[10] such as Ru,[11] bimetallic [Ag–Ru],[12] Ir,[13] as well as Pd[14] complexes. Nevertheless, with respect to base-metal catalysis, very few catalytic systems have been developed for this reaction. More specifically, Milstein and co-workers developed a novel imino borohydride iron complex, which was prepared using sodium borohydride, for the E-selective alkyne hydrogenation in 2013.[15] Very recently, a Ni-catalyzed transfer hydrogenation of alkynes at elevated temperature using high catalyst loadings along with stoichiometric amounts of zinc and formic acid as reductants was reported.[16] Another nickel-catalyzed reaction utilizing ammonia borane (NH₃–BH₃, AB)

as a practical hydrogen source[17] has also been studied;[18] however, limited scope of substrates was demonstrated along with variable E/Z ratios. To date, a base-metal-catalyzed stereodivergent (transfer) hydrogenation of alkynes to produce Z- and E-alkenes with great selectivity and efficiency has not been established. Herein, we report the first example of cobalt-catalyzed transfer hydrogenation of alkynes to synthesize both Z- and E-alkenes selectively promoted by different ligands (Scheme 1). These reactions use a series of well-defined cobalt catalysts with ammonia borane as the hydrogen donor under mild conditions.

Z-Selective alkyne hydrogenation is an intrinsic feature for most transition metal catalysts through a *cis*-hydrometalation of the C≡C bond. In spite of this, the unusual E-isomer is possible to be generated via a sequential Z-selective alkyne hydrogenation, followed by a Z- to E-alkene isomerization process (Scheme 2).[12,15] The isomerization process could be

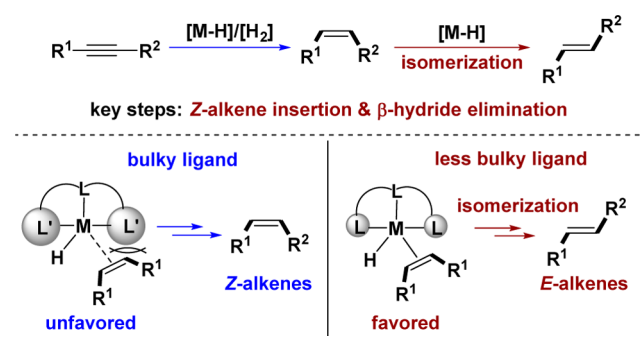**Scheme 1. Stereodivergent Cobalt-Catalyzed Transfer Hydrogenation of Alkynes**[a]
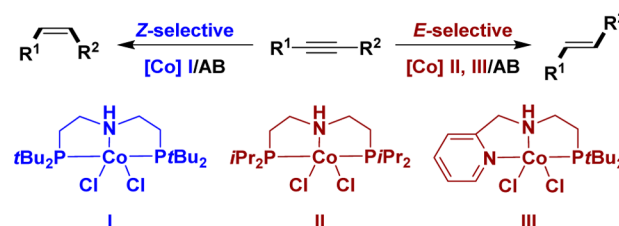

[a]AB = NH₃–BH₃.

Scheme 2. Steric Effect Controlled Stereodivergent Alkyne Reduction

rationalized by insertion of the Z-alkene intermediate into a metal hydride bond and a following β-hydride elimination step. In principle, the coordination and insertion of Z-alkene intermediate require a less steric hindered metal center with an open coordination site, which would also facilitate the following β-hydride elimination step.[19] Thus, this isomerization process should be promoted by a less bulky ligand, affording the E-alkene products. In this case, a nonignorable problem would be the undesired over reduction of alkenes to alkanes due to the prerequisite interaction of Z-alkene intermediates with the metal catalyst. Meanwhile, we proposed that this isomerization process could be suppressed by using an appropriate bulky ligand due to the sterically unfavored coordination and insertion of Z-alkenes. As a result, Z-alkene products would be selectively generated in this way. Therefore, a ligand-controlled stereodivergent transfer hydrogenation of alkynes is promising. Delightfully, the cobalt-based catalyst systems described here addressed these problems, providing access to both Z- and E-alkene products in good chemo- and stereoselectivity.

■ RESULTS AND DISCUSSION

Catalysts Development. Our study commenced with preparing the NH-based PNP and NNP[20] cobalt pincer complexes I−III (Scheme 1). These cobalt complexes were easily accessible by the treatment of CoCl$_2$ with 1.1 equiv of the corresponding ligands. The preparation and crystal structure of complex II were reported.[21] The structures of the other two cobalt complexes I[22] and III were characterized by X-ray diffraction analysis in this study (Scheme 3). The neutral pincer ligands coordinate to the Co center in a tridentate mode. Moreover, these complexes show a paramagnetic behavior and effective magnetic moments between 4.2 and 4.5 μ_B, which are consistent with a high spin state consisting of three unpaired electrons. P-$tert$-butyl and P-isopropyl PNP ligands could lead

Scheme 3. Molecular Structures of Cobalt Complexes I and III[a]
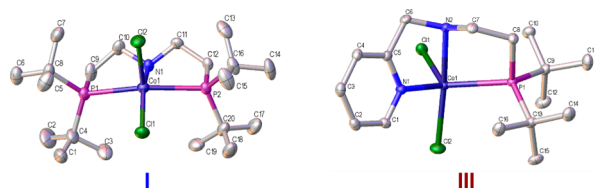
[a]The thermal ellipsoids set at 50% probability and hydrogen atoms were omitted for clarity.

to different levels of steric hindrance in the resulting cobalt pincer complexes I and II. Besides, it was envisioned that the modification of PNP to an NNP pincer ligand would give rise to a hemilabile cobalt catalyst III.[23] We considered it as an advantage over other catalysts to ultimately facilitate the formation of E-alkene product since the labile pyridine coordination would create a less sterically hindered metal center (vide supra).

The catalytic activities of these cobalt pincer complexes were then investigated in the transfer hydrogenation of diphenyle-thyne **1a** with 1 equiv of AB in methanol (Table 1). The use of

Table 1. Co-Catalyzed Transfer Hydrogenation of 1a[a]

Entry	[Co]	Conv. 1a (%)	Yield 2a (%)[b]	Yield 3a (%)[b]
1	CoCl$_2$	30	24	2
2[c]	I	99	94	5
3	II	100	8	92
4	III	100	ND	100
5[d]	III + Hg	100	ND	100
6	none	0	ND	ND

[a]Reaction conditions: Diphenylethyne **1a** (0.5 mmol), AB (0.5 mmol), and 1.0 mol % Co catalyst in 2 mL of MeOH at 50 °C for 16 h. [b]Yields were determined by GC analysis using biphenyl as the internal standard. ND means "not detected". [c]AB (0.6 mmol) was used. [d]One drop of mercury was added.

solely CoCl$_2$ as a catalyst afforded low conversion (30%) with the Z-isomer **2a** as the major product (Table 1, entry 1). When cobalt complex I was employed as the catalyst, the Z-alkene product **2a** was produced in 94% yield with 18:1 Z/E ratio (Table 1, entry 2), which revealed the crucial role of the supporting pincer ligand. Indeed, a slight change of PNP ligand structure from $tert$-butyl- to isopropyl-substituted phosphine resulted in a completely different stereoselectivity. The reaction catalyzed by complex II gave a high yield of the alkene products with 12:1 E/Z selectivity (Table 1, entry 3). Moreover, the NNP cobalt catalyst III led to an excellent yield of E-isomer **3a** with >99:1 E/Z selectivity highlighting the beneficial effect of the pyridine coordination site on NNP ligand (Table 1, entry 4). These results therefore support our initial hypothesis that the E/Z selectivity is well controlled by the levels of steric hindrance of cobalt catalysts. Furthermore, no impact was found when adding mercury to this reaction system, which suggests that the catalyst is homogeneous in nature under these reaction conditions (Table 1, entry 5). Notably, all of these cobalt catalyst precursors were readily activated in the presence of AB without any additional sensitive additives.[24] Moreover, no over-reduced alkane byproduct was detected in the presence of these cobalt pincer catalysts. Control experiment in the absence of cobalt gave no conversion (Table 1, entry 6).

In addition, the effects of several key reaction parameters (e.g., solvents and borohyrides effects) were investigated with cobalt complex III as the catalyst (Table S2). Among the solvents examined, only primary and secondary alcohols gave high yields for **3a** with high selectivity. In addition, no reaction

occurred in the absence of AB, which shows that methanol alone is not able to act as a reductant in this reaction.

Substrate Scope. After establishing the optimized reaction conditions for the stereodivergent transfer hydrogenation of **1a**, the substrate scope of this transformation was studied. In Table 2 we summarized the *Z*-selective semireduction of various

Table 2. Cobalt Complex I-Catalyzed *Z*-Selective Transfer Hydrogenation of Alkynes 1[a]

R = H	**2a**	94 (18:1)[b]	R = 4-CH$_3$	**2b**	86 (8:1)[c]
R = 2-CH$_3$	**2c**	91 (24:1)[c,d]	R = 3-CH$_3$	**2d**	94 (13:1)[c]
R = 4-OCH$_3$	**2e**	85 (8:1)	R = 4-F	**2f**	92 (23:1)[c,d]
R = 4-CF$_3$	**2g**	86 (15:1)[c,d]	R = 4-Cl	**2h**	95 (16:1)
R = 3-Cl	**2i**	93 (15:1)	R = 4-CN	**2j**	48 (16:1)[d,e]
R = 4-CO$_2$Me	**2k**	91 (14:1)[c]	R = 4-NH$_2$	**2m**	67 (4:1)[f]

	2n	72 (6:1)		**2o**	63 (2:1)[g]
	2p	63 (>99:1)[d]		**2q**	77 (37:1)[h]
	2r	90 (>99:1)[i]		**2s**	98 (6:1)[j]
	2t	94 (17:1)[d]		**2u**	99 (>99:1)

[a]Reaction conditions: **1** (0.5 mmol), AB (0.75 mmol), and 2.0 mol % Co catalyst **I** in 1 mL of MeOH at 50 °C for 20 h. Isolated yields of **2** along with *Z/E* ratios are shown. [b]AB (0.6 mmol) and 1.0 mol % Co catalyst **I**. [c]Reaction temperature is 60 °C. [d]GC yields of **2**. [e]AB (1.3 mmol), 75 °C. [f]AB (1.2 mmol), 3.0 mol % Co catalyst. [g]AB (0.5 mmol), 1.5 mol % Co catalyst **I**. [h]AB (1.2 mmol), 60 °C. [i]AB (0.5 mmol). [j]Isolated yield for a 76:13:11 mixture of **2s**, **3s** and over-reduced alkane byproduct.

alkynes **1** using Co complex **I** as the catalyst. Tested substrates in different steric and electronic natures all provided the corresponding *Z*-alkene products in good isolated yields with satisfying *Z/E* selectivity, revealing the general applicability of this protocol. Specifically, this reaction proceeded chemoselectively toward substituted diarylethynes bearing a range of electron-donating as well as electron-withdrawing substituents, **1e–m**. Functional groups, such as methoxyl, fluoro, trifluoromethyl, chloro, cyano, ester, amino, heterocycles, and hydroxyl groups were all well tolerated. However, the subtrates bearing amino- and pyridine-substitued groups, **1m** and **1o**, afforded lower *Z/E* selectivity probably due to the coordination of such functional groups. The reaction of dialkyl acetylene **1u** also proceeded smoothly in 99% yield with >99:1 *Z/E* selectivity.

As mentioned above, *E*-selective semireduction of alkynes is more challenging. A survey of the substrate scope was performed to demonstrate the versatility of this Co-catalyzed transfer hydrogenation of alkynes for the synthesis of *E*-alkenes using catalyst **III** (Table 3). The *E*-alkene products were obtained in good yields with high *E/Z* selectivity for most

Table 3. Cobalt Complex III-Catalyzed *E*-Selective Transfer Hydrogenation of Alkynes 1[a]

R = H	**3a**	92 (>99:1)[b]	R = 4-CH$_3$	**3b**	91 (>99:1)
R = 2-CH$_3$	**3c**	90 (>99:1)	R = 3-CH$_3$	**3d**	96 (>99:1)
R = 4-OCH$_3$	**3e**	98 (>99:1)	R = 4-F	**3f**	96 (>99:1)
R = 4-CF$_3$	**3g**	97 (>99:1)	R = 4-Cl	**3h**	95 (>99:1)
R = 3-Cl	**3i**	94 (>99:1)	R = 4-CN	**3j**	82 (>99:1)[c]
R = 4-CO$_2$Me	**3k**	90 (>99:1)[d]	R = 4-NO$_2$	**3l**	52 (4:1)[e]
R = 4-NH$_2$	**3m**	93 (>99:1)			

	3n	93 (>99:1)[f]		**3o**	70 (6:1)[g]
	3p	33 (>99:1)		**3q**	89 (>99:1)
	2r	70 (1:12)[h]		**2s**	94 (1:16)[i]
	3t	92 (23:1)[j]		**3u**	96 (1:1)[k]
	3v	90 (23:1)		**3w**	90 (>99:1)

[a]Reaction conditions: **1** (0.5 mmol), AB (0.5 mmol), and 1.0 mol % Co catalyst **III** in 2 mL of MeOH at 50 °C for 16 h. Isolated yields of **3** along with *E/Z* ratios are shown. [b]**1a** (5 mmol), AB (5 mmol) and 0.2 mol % Co catalyst **III** in 5 mL of MeOH at 50 °C for 16 h. [c]AB (0.35 mmol). [d]GC yield. [e]AB (0.4 mmol) and 3.0 mol % Co catalyst **III** in 1.5 mL of MeOH and 0.5 mL of THF for 36 h. [f]AB (0.75 mmol), 2.0 mol % Co catalyst **III**, 36 h. [g]AB (0.35 mmol), 36 h. [h]2.0 mol % Co catalyst **II**. [i]AB (0.75 mmol), 2.0 mol % Co catalyst **II** in 1 mL of MeOH for 20 h. Isolated yield for a 81:5:14 mixture of **2s**, **3s**, and over-reduced alkane byproduct. [j]AB (0.25 mmol), 2.0 mol % Co catalyst **III**. [k]AB (0.25 mmol), 4.0 mol % Co catalyst **II** in 1 mL of MeOH for 40 h. Isolated yield for a 45:45:10 mixture of **2s**, **3s**, and over-reduced byproduct.

tested substrates. A wide range of funtional groups were also well tolerated. In addition, catalyst **II** was found to be more reactive for the tranfer hydrogenation of dialkyl acetylenes. The *N*,*N*-dibenzyl propargyl amine and propargyl sulfamide **1r** and **1s** underwent this transfer hydrogenation reaction smoothly using catalyst **II**; however, *Z*-alkenes were isolated as the major products. The semireduction of nonfunctionlized dialkyl acetylene **1u** also proceeded in the presence of catalyst **II** in high yield, albeit low *E/Z* selectivity was obtained. The reaction of phenyltrimethylsilyl acetylene **1w** gave a 90% yield of the corresponding *E*-alkene **3w**. Unlike the known transfer hydrogenation of alkynes using formic acid as a reducing agent,[14] the near neutral reaction conditions used in the current study allowed for the tolerance of a trimethylsilyl group. A gram-scale synthesis of *trans*-stilbene **3a** was performed in the presence of 0.2 mol % cobalt catalyst **III**, which gave a 92%

yield of **3a** in high purity after a simple filtration. The turnover number (TON) of cobalt catalyst for this transformation reached as high as 460.

The semireduction of terminal alkynes **4** was also studied using these cobalt catalysts, and complex **II** was found to be more effective than cobalt catalysts **I** and **III** (Table 4). The

Table 4. Cobalt Complex II-Catalyzed Transfer Hydrogenation of Terminal Alkynes 4[a]

|					
R = H	**4a**	86/2	R = OCH$_3$	**4c**	70/4
R = H	**4a**	20/ND[b]	R = CN	**4d**	62/9[d]
R = H	**4a**	10/ND[c]	R = CF$_3$	**4e**	76/3[d]
R = tBu	**4b**	89/4		**4f**	77/3

[a]Reaction conditions: **4** (0.5 mmol), AB (0.25 mmol), and 2.0 mol % Co catalyst **II** in 2 mL of EtOH at 25 °C for 1 h. Yields of **5/6** were determined by GC analysis using biphenyl as the internal standard. [b]1.0 mol % Co catalyst **I**, 42% conversion. [c]1.0 mol % Co catalyst **III**, 58% conversion. [d]The reaction time was 5 h.

desired terminal alkenes **5** were formed in good yields with high chemoselectivity utilizing cobalt catalyst **II**. Very small amounts of the over-reduced byproducts **6** were detected in these cases.

Encouraged by high chemoselectivity for this cobalt-catalyzed semireduction of alkynes to alkenes, we believe the selective hydrogenation of a small fraction of alkyne impurities to alkenes is promising. As we know, steam cracking is a large-scale process that provides access to a mixture of important light alkenes. However, this process also leads to the formation of a small fraction (around 2%) of alkyne impurities. The development of an efficient method for the selective reduction of the alkyne impurities to alkenes is therefore significant, which would benifit the subsequent alkene functionalization processes. To demonstrate the feasibility, a 1:100 mixture of alkyne **1a** and *cis*-alkene **2a** was exposed to the optimized reaction conditions with 0.5 mol % cobalt catalyst **III** (Scheme 4). Notably, **1a** was selectively hydrogenated to *trans*-alkene **3a** along with the efficient *Z/E* isomerization of **2a** with 100% conversion.

Mechanistic Studies. To gain mechanistic insights, the kinetic behavior of this reaction was investigated using *in situ* IR (Figure 1). The *E*-selective semireduction of **1c** using catalyst

Scheme 4. Selective Semireduction and Isomerization of a 1:100 Mixture of 1a and 2a

1c + H$_3$N-BH$_3$ →(1 mol% **III**, MeOH, 50 °C) **3c** + **2c**
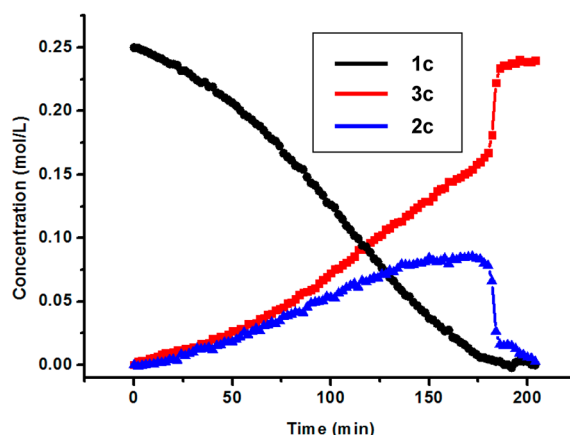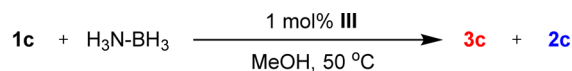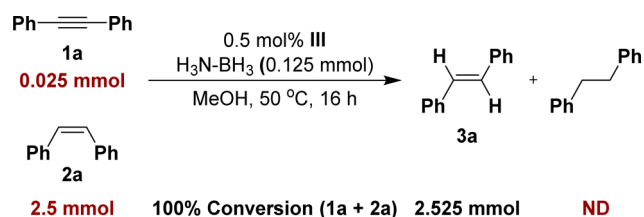
Figure 1. Kinetic profile of the *E*-selective semireduction of **1c**.

III was selected as a model reaction. The kinetic profile of this reaction clearly showed that the *Z*-alkene intermediate **2c** was generated in the first 3 h and that **2c** was further converted to the *E*-alkene **3c** via a *Z*- to *E*-isomerization process. It is noteworthy that a reduction in the concentration of **1c** led to a dramatic increase in the rate of the isomerization step illustrated by a sudden change at around 180 min on this kinetic profile. This result indicated that the isomerization process was inhibited by the alkyne substrate due to the higher affinity of alkyne with the cobalt catalyst compared with *Z*-alkene intermediate.

To further probe this isomerization process, *cis*-stilbene **2a** was exposed to the catalytic conditions (Table 5). It was

Table 5. Cobalt Complex III Catalyzed Isomerization of *cis*-Stilbene 2a to *trans*-Stilbene 3a[a]

| entry	time	AB (mmol)	conv. 2a (%)[b]	yield 3a (%)[b]
1	1 h	0.5	100	100
2	1 h	0.05	100	100
3	16 h	0	0	ND
4[c]	16 h	0.5		8

[a]Reaction conditions: **1a** (0.5 mmol), AB, and 1.0 mol % Co catalyst **III** in 2 mL of MeOH at 25 °C for 16 h. [b]GC yields. [c]**1a** (0.5 mmol) was added.

isomerized to *trans*-stilbene **3a** within 30 min at 25 °C with 1 mol % catalyst **III** and 1 or 0.1 equiv of AB (Table 5, entries 1 and 2). However, this isomerization process did not take place in the absence of AB, thereby highlighting the importance of AB for activating the cobalt catalyst precursors (Table 5, entry 3). The isomerization reaction was clearly inhibited by the addition of 1 equiv of alkyne **1a** into this reaction (Table 5, entry 4). This observation was in accordance with the results of the kinetic study described above. In contrast, the exposure of the *trans*-stilbene **3a** to the catalytic conditions resulted in no reaction. All taken together, these results indicate that the *E*-selectivity could be attributed to the transfer hydrogenation of alkyne to give *Z*-alkene intermediate followed by a fast *Z* to *E*

isomerization process, which is accorded with our initial hypothesis.

Deuterium-labeling experiments were conducted to verify the hydrogen source of the alkene product. When CD_3OH was used as the solvent, the *cis*-reduction product was not deuterated in the presence of cobalt catalyst **I** (Scheme 5, eq

Scheme 5. Deuterium-Labeling Experiments
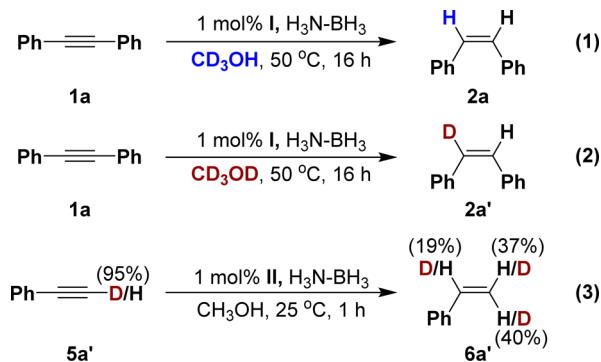
1). Conversely, the monodeuterated *trans*-product **2a′** was isolated when the reaction was carried out in the solvent of CD_3OD (Scheme 5, eq 2). These results therefore demonstrated that methanol mediates the protonation of the alkenyl cobalt intermediate. Moreover, 19% deuterium incorporation was observed at the C2 position of the deuterated product **6a′** for the transfer hydrogenation of deuterated phenylacetylene **5a′** (Scheme 5, eq 3). It indicates that the vinylidene-type[11b] and alkynyl-type mechanisms[25] are also possible minor reaction routes for the reaction of terminal alkynes.

The dehydrogenation product of the hydrogen donor AB was investigated (Scheme 6). Under the standard reaction

Scheme 6. Determination of the Dehydrogenation Product of AB
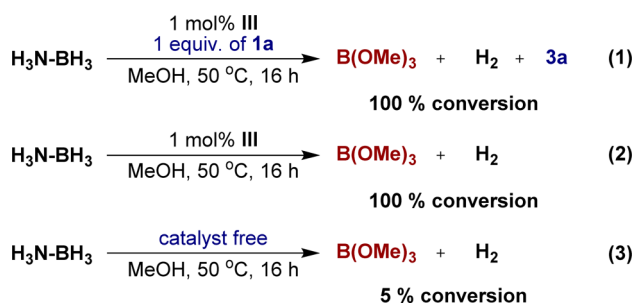
conditions, AB was completely converted to $B(OMe)_3$, which was the only boron-containing compound identified by ^{11}B NMR analysis, together with the formation of the hydrogenated product of **1a** and H_2 gas (Scheme 6, eq 1).[26] Two control experiments were then conducted without alkyne **1a** as a hydrogen acceptor. Under the optimized conditions, the dehydrogenation of AB delivered $B(OMe)_3$ and H_2 gas in full conversion (Scheme 6, eq 2). Moreover, AB is thermally stable in methanol at 50 °C, which revealed that the dehydrogenation of AB is a catalytic process (Scheme 6, eq 3).[27]

On the basis of the above observations, a plausible reaction mechanism for this transformation was proposed (Figure 2). It was hypothesized that cobalt dichloride complexes **I**−**III** would be reduced by AB to generate catalytically active cobalt hydride
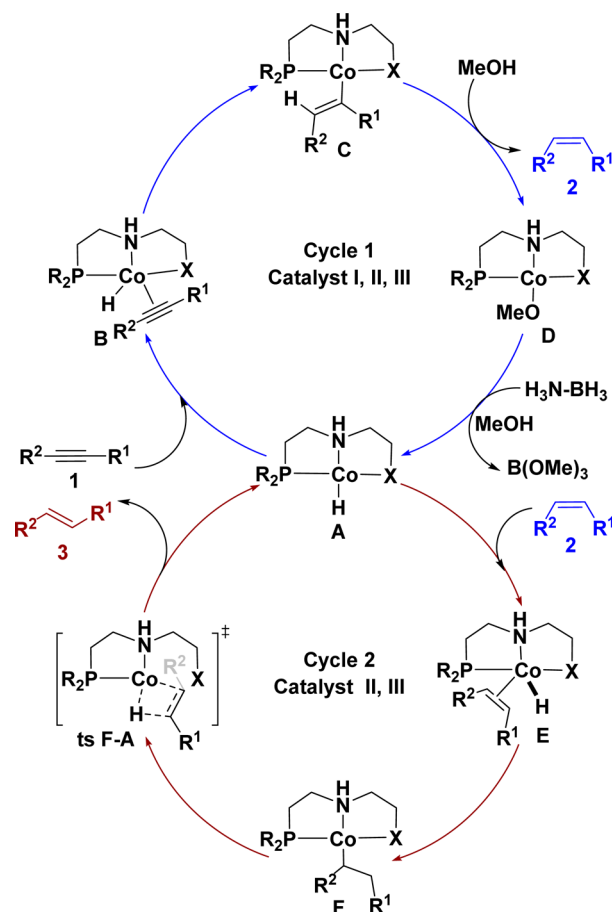

Figure 2. Plausible reaction mechanism.

complex **A**. Such species was previously proposed for the cobalt-catalyzed hydrogenation reactions[3d,6] as well as being reported for the hydroboration of alkenes.[28] Indeed, Chirik and co-workers recently proved that the treatment of $(PNP)CoCl_2$ complex with $NaHBEt_3$ furnished the $[(PNP)CoH]$ complex.[29] Catalytic cycle 1 would be responsible for the Z-selective hydrogenation of the alkynes. The coordination of alkyne substrate **1** to complex **A** followed by the insertion of the alkyne into the Co−H bond would lead to the formation of alkenyl cobalt complex **C**. The subsequent protonation of the Co−C bond by methanol would afford the Z-alkene intermediate **2** and methoxyl cobalt complex **D** verified by the deuterium-labeling experiments. Intermediate **D** would react with AB to regenerate complex **A** along with the production of $B(OMe)_3$ detected by ^{11}B NMR. The Z/E alkene isomerization process would then be accomplished by catalytic cycle 2. Specifically, the insertion of the Z-alkene intermediate into the Co−H bond followed by a β-hydride elimination finally would lead to the generation of thermodynamically more stable E-alkene product **3**.[30] The isomerization process could be promoted by the less sterically hindered cobalt complexes **II** and **III** to generated E-alkene products. In contrast, the more bulky cobalt catalyst **I** effectively prevented the occurrence of this isomerization process and afforded the Z-alkene products. The high chemoselectivity for the E-selective semireduction is caused by the much faster β-hydride elimination of the alkyl cobalt intermediate **F** compared with its protonation by methanol.[31]

CONCLUSIONS

We demonstrated a ligand-controlled stereodivergent transfer hydrogenation of alkynes to E-and Z-alkenes using cobalt catalysts. Ammonia borane was used as a bench-stable and practical hydrogen source[17] as well as a mild reagent for the activation of a series of readily accessible cobalt dichloride pincer catalysts. The current system operates under mild conditions and allows for the semireduction of various internal and terminal alkynes with good yields and selectivity in the absence of any sensitive additives. Notably, this Co-catalyzed reaction proceeds with high efficiency, and up to 460 turnovers has been realized. We believe this strategy for the selectivity control via rational catalyst design would provide useful insights for the development of other base-metal catalysis processes.

ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04271.

Experimental details and crystallographic data (PDF)

(ZIP)

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Notes
The authors declare no competing financial interest.

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