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Homogeneous Catalysis **Very Important Paper**

Cobalt-Catalyzed Stereodivergent Semihydrogenation of Alkynes: Synthesis of *E*- and *Z*-Alkenes

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Abstract: Transition metal-catalyzed semihydrogenation of alkynes is one of the most efficient, sustainable, and environmental-friendly strategies for accessing stereoisomerically pure olefins. Herein, we report a tridentate nitrogen-containing ligand (8-OIQ) promoted cobalt-catalyzed stereodivergent semihydrogenation of internal alkynes; a series of *Z*- and *E*-alkenes could be synthesized with high stereoselectivity. Besides, this protocol exhibits excellent functional group tolerance and operates under mild reaction conditions (1 bar H_2, room temperature). A preliminary mechanistic study revealed that acetonitrile plays an important role in suppressing over-reduction and controlling the stereoselectivity in this transformation.

Introduction

Alkenes with defined stereochemical configurations are essential building blocks in organic production of pharmaceuticals, agrochemicals, and synthesis, finding widespread applications in the functional materials (Scheme 1a).[1–3] The development of efficient and stereoselective methods for synthesizing *Z*- and *E*-alkenes remains a highly desirable goal. Although traditional methods like Wittig,[4] Peterson,[5] Horner–Emmons–Wadsworth,[6] Julia–Kocienski olefination,[7] olefin metathesis,[8] and cross-coupling reactions[9] have been employed, they often produce mixtures of *E*/*Z* isomers or frequently substrate-dependent.

In recent years, transition metal–catalyzed stereoselective semihydrogenation of alkynes has emerged as a highly promising approach for constructing *Z*- and *E*-alkenes.[10–13] The pioneering work of the heterogeneous Lindlar catalyst[14] in 1952 paved the way for a broad range of applications in alkyne semihydrogenation. Since then, extensive research has focused on developing homogeneous[15–17] and heterogeneous noble metal[2,18] catalytic systems for this transformation. With increasing concerns about sustainability and resource scarcity, significant efforts have been devoted in the past decade to developing catalysts based on readily available and cost-effective non-noble metals, particularly first-row transition metals. [10–12,19–22] Cobalt, an earth-abundant and environmentally benign transition metal, is of particular interest. Cobalt-catalyzed stereoselective semihydrogenation of alkynes has emerged as a flourishing research area (Scheme 1b).[23–33] Liu[23] and Balaraman[26] separately reported the pincer ligand promoted cobalt catalyzed selective transfer semihydrogenation of internal alkynes, demonstrating the potential for both *Z*- and *E*-selectivity through ligand variation. However, this approach suffers from limitations in atom economy and environmental impact due to the use of ammonia borane as a hydrogen source. Meanwhile, Fout et al.[24] developed an NHC-cobalt catalyst capable of achieving *E*-selective semihydrogenation. Zhang et al.[25] demonstrated a cobalt catalyst derived from $Co(OAc)_2{\cdot}4H_2O$ and ethylenediamine for alkyne hydrogenation, predominantly yielding *Z*-alkenes with trace amounts of *E*-alkenes and alkanes. Recently, Khusnutdinova[30] and Ruiter[31] independently developed cobalt-catalyzed semihydrogenation of alkynes. However, overhydrogenation and limited selectivity restrict their application. As demonstrated, very few practical methods exist that allow for the direct and highly stereoselective semihydrogenation of internal alkynes under ambient conditions. The stereochemical outcome of alkene synthesis is highly dependent on the choice of ligands and catalysts. To the best of our knowledge, cobalt-catalyzed highly stereodivergent semihydrogenation with single type of ligand and catalyst has not yet been reported. The main challenges in achieving stereodivergent semihydrogenation include: 1) achieving differentiated recognition of both (*E*-) and (*Z*-) alkenes with one type of catalyst and 2) preventing the overhydrogenation of both isomers.

Here, we report an 8-oxazoline iminoquinoline (8-OIQ) ligand promoted cobalt-catalyzed highly stereodivergent semihydrogenation of alkynes using atmospheric hydrogen as reductant (Scheme 1c). By simply modifying the ligand structure and adjusting the amount of additive acetonitrile, a series of *E*- and *Z*-alkene isomers were synthesized with excellent activity and selectivity.

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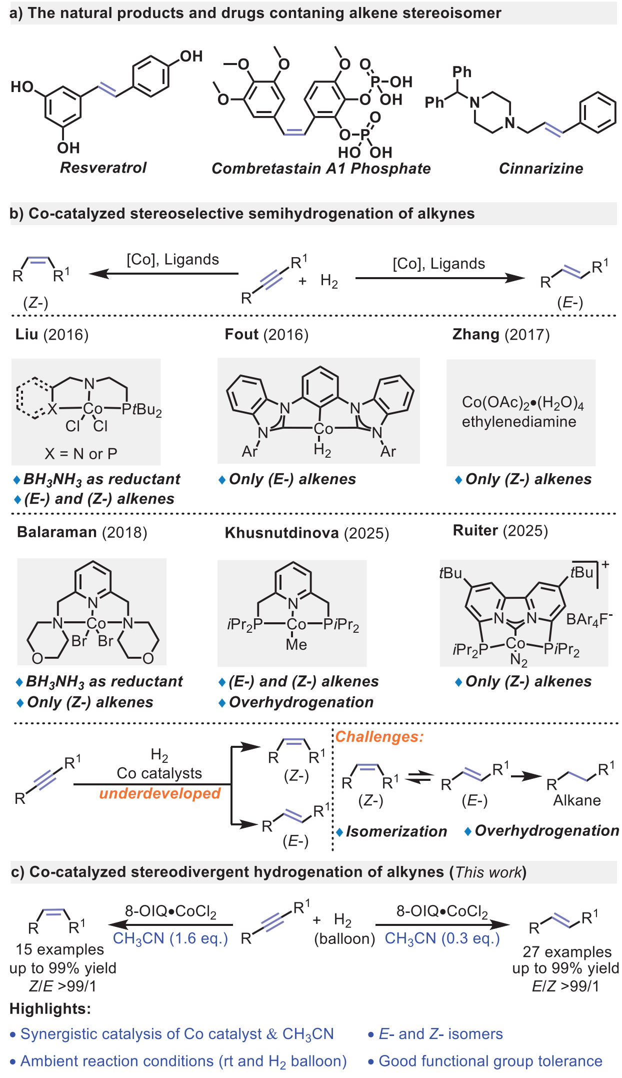
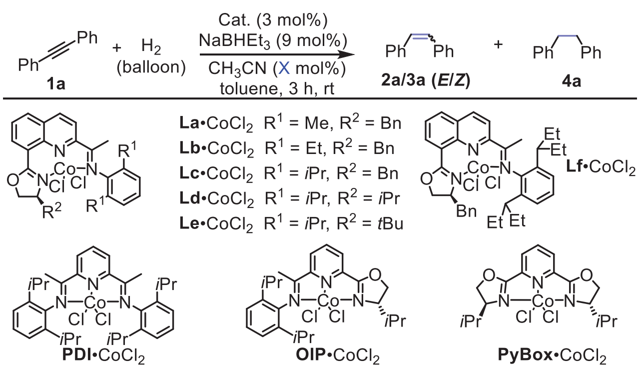


Scheme 1. Transition metal-catalyzed semihydrogenation of alkynes.

Table 1: Optimization of the stereodivergent semihydrogenation conditions.[a)]

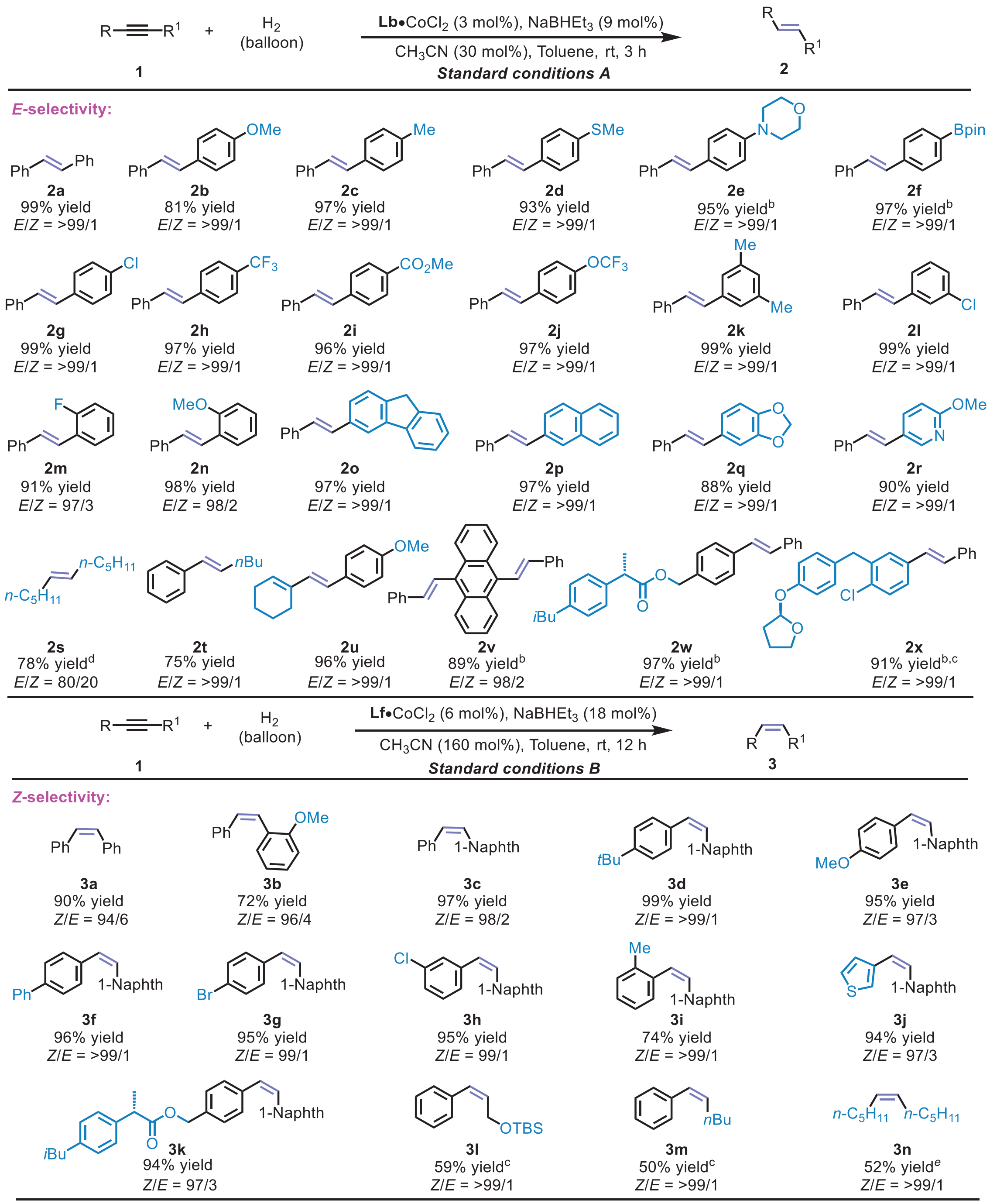


Entry	Cat.	X	Yield (%)[b)]	**2a**/**3a** (*E*/*Z*)	**4a** (%)[b)]
1	**La**·CoCl$_2$	30	98	>99:1	1
2	**Lb·CoCl$_2$**	**30**	**99**	**>99:1**	**0**
3	**Lc**·CoCl$_2$	30	98	37:63	0
4	**Ld**·CoCl$_2$	30	75	25:75	0
5	**Le**·CoCl$_2$	30	81	5:95	0
6	**Lf**·CoCl$_2$	30	68	4:96	0
7	**Lf**·CoCl$_2$[c)]	30	99	58:42	0
8	**Lf**·CoCl$_2$[c)]	120	92	13:87	0
9	**Lf·CoCl$_2$**[c),d)]	**160**	**90**	**6:94**	**0**
10	**Lf**·CoCl$_2$[c),d)]	200	92	7:93	0
11	**PDI**·CoCl$_2$	30	3	0:100	0
12	**OIP**·CoCl$_2$	30	19	0:100	0
13	**PyBox**·CoCl$_2$	30	19	0:100	0
14	**BINAP**·CoCl$_2$	30	99	32:68	5

[a)] Reactions were conducted using alkene (0.5 mmol), H_2 balloon, CH_3CN (30 mol%), cobalt cat. (3 mol%), NaBHEt$_3$ (9 mol%), and toluene (1 mL) at rt for 3 h. [b)] Yield and *E*/*Z* ratio were determined by ^{1}H NMR using TMSPh as an internal standard. [c)] 6 mol% **Lf**·CoCl$_2$, 18 mol% NaBHEt$_3$. [d)] 12 h.

Results and Discussion

Building upon our previously reported 8-OIQ ligand promoted earth-abundant metal-catalyzed functionalization of alkenes and ketones,[34–36] we initiated our investigation by examining the activity of readily available internal alkyne **1a** under 8-OIQ cobalt catalysis. It has been reported that acetonitrile accelerates the β-hydride elimination step in the dehydrogenative borylation of alkenes.[37] Our studies have further revealed its ability to inhibit isomerization in the Fe-catalyzed enantioselective hydrogenation of 1,1-disubstituted alkenes.[34] Consequently, we intend to investigate the use of acetonitrile as an inhibitor to mitigate overhydrogenation and control the *E*/*Z*-selectivity in the semihydrogenation of alkynes. Reactions were conducted under 1 atm of hydrogen with NaBHEt$_3$ as an activator, employing catalytic amounts of acetonitrile as an additive, and toluene as the solvent (Table 1). Using the **La**·CoCl$_2$ catalyst, the reaction proceeded smoothly, producing the *E*-alkene **2a** in 98% yield, with only 1% overhydrogenation product **4a** observed (Table 1, Entry 1). Increasing the steric bulk of the imine group in the **Lb**·CoCl$_2$ catalyst led to complete conversion of alkyne **1a** to **2a**, achieving a 98% yield (Table 1, Entry 2), as the standard conditions A. Further augmenting the steric hindrance of the 8-OIQ ligand resulted in a progressive increase in the yield of the *Z*-isomer **3a**, accompanied by a corresponding decrease in the yield of the *E*-isomer (Table 1, Entries 3–6). Encouragingly, the use of the sterically hindered imine ligand **Lf**·CoCl$_2$ give the good yield of alkene product **3a** with excellent selectivity ($Z/E = 96:4$, Table 1, Entry 6). Increasing the catalyst loading led to a higher conversion of **1a** but also resulted in an increased yield of the *E*-alkane **2a** ($Z/E = 42:58$, Table 1, Entry 7). Notably, increasing the concentration of the acetonitrile suppressed isomerization and overhydrogenation, leading to an enhanced yield of *Z*-alkane **3a** in 87% yield with 87:13 *Z*/*E*-selectivity (Entry 8). Finally, by extending the reaction time to 12 h, the yield of **2a** increased to 90% with excellent selectivity ($Z/E = 94:6$, Table 1, Entry 9), as the standard conditions B. Further increasing the amount of acetonitrile to 200 mol% did not significantly improve the yield or selectivity (Table 1, Entry 10). Common tridentate nitrogen-containing ligands (pyridine(diimine) (PDI), oxazoline iminopyridine (OIP),



Scheme 2. Substrate scope. [a] Standard conditions A: **1** (0.50 mmol), H_2 (balloon), **Lb**·$CoCl_2$ (0.015 mmol, 3 mol%), $NaBHEt_3$ (0.045 mmol, 9 mol%), and CH_3CN (0.15 mmol) in toluene (0.5 M) under rt for 3 h. Standard conditions B: **1** (0.50 mmol), H_2 (balloon), **Lf**·$CoCl_2$ (0.030 mmol, 6 mol%), $NaBHEt_3$ (0.090 mmol, 18 mol%), and CH_3CN (0.80 mmol) in toluene (0.5 M) under rt for 12 h. [b] 6 mol% of the cobalt catalyst. [c] 10 mol% **OIP**·$CoCl_2$ as the catalyst, 1.0 mL of THF was added; [d] a little of isomerized alkenes were obtained; [e] 12 mol% **OIP**·$CoCl_2$ were used as catalyst.

PyBox) and phosphine ligand, were also tested, but yielded unsatisfactory results (Table 1, Entries 11–14).

Having established optimized conditions, we explored the scope of the stereodivergent semihydrogenation of internal alkynes (Scheme 2). For *E*-selective transformations, a range of diphenylacetylenes bearing electron-donating (**1a**–**e**) and electron-withdrawing (**1f**-–**j**) substituents in the *para* position was successfully converted to their corresponding *E*-alkenes in 81%–97% yields with excellent *E*/*Z* selectivity (*E*/*Z* > 99:1). *Meta*-substituted (**1k** and **1l**) and *ortho*-substituted (**1m** and **1n**) diphenylacetylenes were also smoothly transformed into alkene products with high *E*/*Z* selectivity (97:3–99:1).

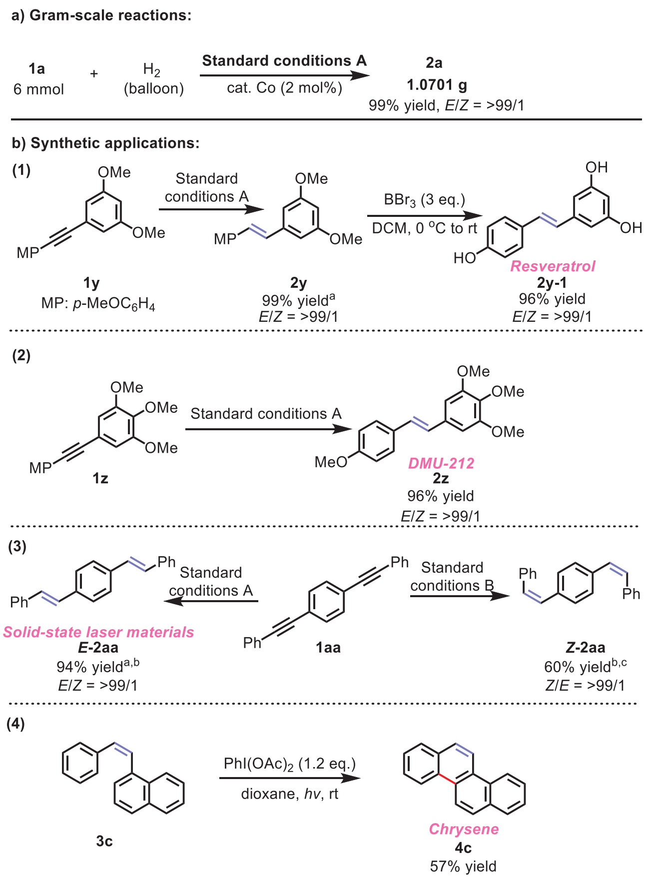
Furthermore, substrates featuring fluorene, naphthalene, piperonyl, and pyridine moieties (**1o**-–**r**) exhibited excellent yields and *E*/*Z* selectivity under standard reaction conditions.

Besides, the semihydrogenation of the nonfunctionalized alkyl-substituted alkyne **1s** also proceeded in the presence of catalyst **Lb**•$CoCl_2$ in high yield, albeit low *E*/*Z* selectivity was obtained. Alkynes bearing both aryl and alkyl substituents **1t** worked well and achieved >99:1 *E*/*Z* selectivity. Notably, the reaction of cyclohexenyl-substituted phenylacetylene **1u** also proceeded smoothly, affording a 96% yield with >99:1 *E*/*Z* selectivity. Next, we investigated the semihydrogenation of a substrate bearing two internal alkynes. Under optimized catalytic conditions, the reduction of **2v** resulted in excellent *E*/*Z* selectivity for both C=C bonds in good yield. Finally, reactions involving structurally complex alkynes derived from biorelevant molecules and pharmaceuticals proceeded without issue, yielding **2w–x** in 91%–97% yields with excellent *E*/*Z* selectivity.

As mentioned above, *Z*-selective semihydrogenation poses a greater challenge due to the propensity for isomerization under cobalt catalysis. To demonstrate the versatility of cobalt-catalyzed semihydrogenation for the synthesis of *Z*-selective alkenes, a survey of substrate scope was conducted using the **Lf**•$CoCl_2$ catalyst. A series of *Z*-selective alkenes were obtained with excellent selectivity, regardless of whether the aromatic substituents were electron-donating (**3a–e, i**) or electron-withdrawing (**3f-h**). Substrates featuring a heteroaryl group also produced the desired product **3j** in 94% yield with excellent *Z*-selectivity. The substrate derived from pharmaceuticals was also well-tolerated, affording the *Z*-alkene **3k** with high *Z*-selectivity. It is worth noting that alkynes bearing both aryl and alkyl substituents still achieve high *Z*/*E* selectivity (*Z*/*E* = >99/1), despite moderate yields (**3l** and **3m**). Finally, the alkyl-substituted alkyne **1n** also proceeded well in *Z*-selective semihydrogenation with >99:1 *Z*/*E* selectivity.

To further demonstrate the utility of our methods, a gram-scale reaction in the presence of 2 mol% of the cobalt complex could be carried out smoothly to afford **2a** in 99% yield with >99% *E*-selectivity (Scheme 3a). A series of synthetic applications were conducted (Scheme 3b). Alkyne **1y** could be selectively transformed to the *E*-alkene **2y** in 99% yield. Following a literature method, compound **2y** was transformed to the natural polyphenolic phytoalexin resveratrol[38] with 96% yield through a deprotection reaction (Scheme 3b-1). Using readily available alkyne **1z**, our method provides a facile one-step route to the pharmaceutical molecule DMU-212[39] in 98% yield with >99:1 stereoselectivity (Scheme 3b-2). The 1,4-bis(phenylethynyl)benzene **1aa** could be converted to the diene *E*-**2aa** and *Z*-**2aa** in 96% and 60% yields, respectively (Scheme 3b-3). Notably, trans-distyrylbenzene (DSB, *E*-**2aa**)[40] is a widely studied model compound, particularly as a material for laser crystals. Finally, under irradiation conditions, the *Z*-alkene **3c** is smoothly transformed into chrysene **4c** with 57% yield (Scheme 3b-4).[41]

To gain insights into the reaction mechanism, a series of mechanistic experiments were performed (Scheme 4). To verify the reaction pathway involving the isomerization of a *Z*-alkene intermediate to the *E*-alkene product, two control experiments were conducted (Scheme 4a). The *Z*-alkene **3a** could be transformed into *E*-alkene **2a** with 96% yield under standard conditions A. When *E*-alkene **2a** was tested as a substrate under standard conditions B, no reaction was observed. Therefore, we propose that alkene isomerization is a key step in the *E*-selective semihydrogenation reaction.

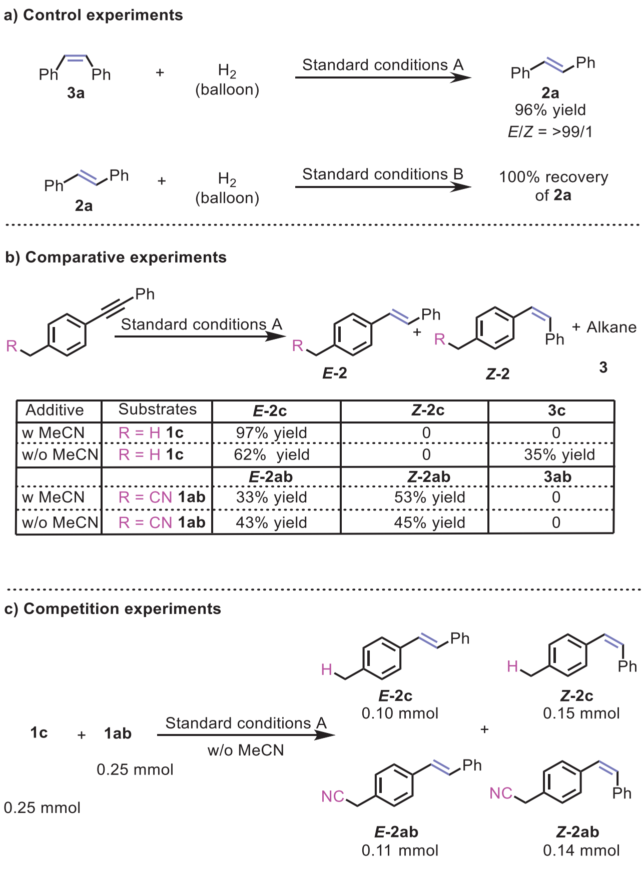


Scheme 3. Synthetic transformations: a) Gram-scale reaction and b) synthetic applications. [a]6 mol% of the **Lb**·$CoCl_2$ and 18 mol% $NaBHEt_3$ were used. [b]1.0 mL of THF was added. [c]10 mol% of **Lf**·$CoCl_2$ and 30 mol% of $NaBHEt_3$ were used.

To further explore the role of acetonitrile in reactions, a series of control experiments were conducted in standard conditions A (Scheme 4b,c).

Using 1-methyl-4-(phenylethynyl)benzene (**1c**) as the substrate, the reaction without acetonitrile afforded the *E*-alkene product **2c** in only 62% yield, along with 35% of over-hydrogenated product. In contrast, the addition of acetonitrile resulted in a 97% yield of the **2c** as the sole product. When the cyano-substituted alkyne 2-(4-(phenylethynyl)phenyl)acetonitrile (**1ab**) was used as the substrate, over-hydrogenation and isomerization were suppressed regardless of whether acetonitrile was present or absent. These experiments showed that cyano group would inhabit the activity of catalyst (Scheme 4b). Moreover, competition experiments between **1c** and **1ab** in toluene without of MeCN has been conducted (Scheme 4c). The results indicated that the cyano group of **1ab** inhibited the semihydrogenation of both **1c** and **1ab**.

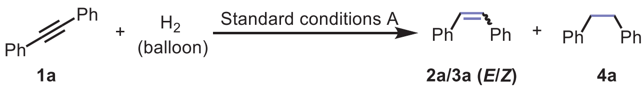
To further elucidate the influence of steric and electronic effects of nitriles in reaction. A series of alkyl and aryl nitriles were screened as additive for the reaction (Table 2). These



Additive	Substrates	*E*-2c	*Z*-2c	3c
w MeCN	R = H **1c**	97% yield	0	0
w/o MeCN	R = H **1c**	62% yield	0	35% yield
		***E*-2ab**	***Z*-2ab**	**3ab**
w MeCN	R = CN **1ab**	33% yield	53% yield	0
w/o MeCN	R = CN **1ab**	43% yield	45% yield	0

Scheme 4. Mechanistic studies.

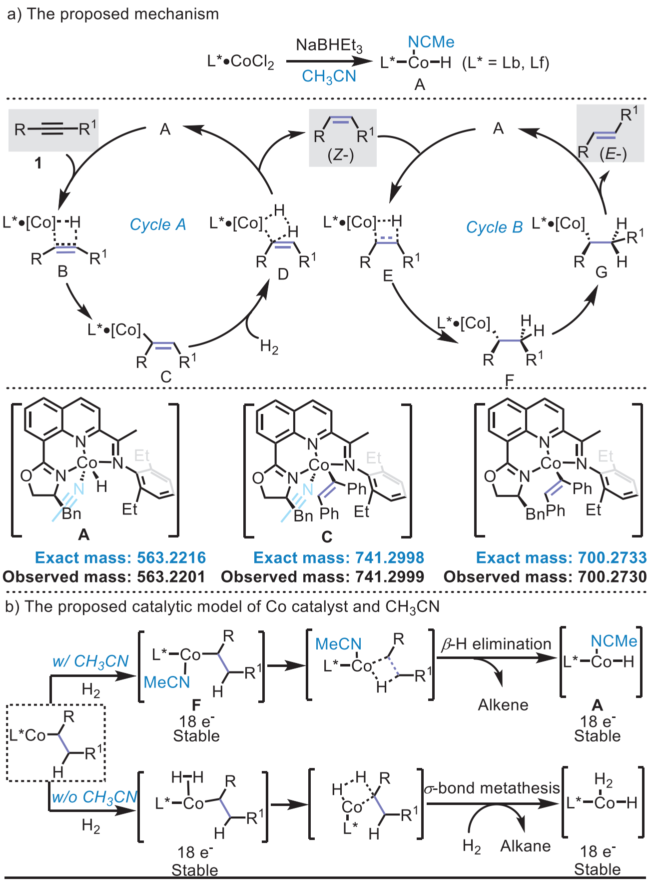
Table 2: Evaluation of sterically and electronically varied nitriles in reactions.[a)]



Entry	Nitrile	Yield (%)[b)]	2a/3a (%)[b)]	4a (%)[b)]
1	CH_3CN	99	>99:1	<1
2	*i*PrCN	99	>99:1	<1
3	*n*-$C_9H_{19}CN$	99	>99:1	<1
4	PhCN	62	13/87	0
5	*p*-$CF_3C_6H_4CN$	23	0/100	0
6	*p*-$MeOC_6H_4CN$	99	76/24	0

[a)] Standard conditions A: **1** (0.5 mmol), H_2 (balloon), **Lb**·$CoCl_2$ (0.015 mmol, 3 mol%), $NaBHEt_3$ (0.045 mmol, 9 mol%), and nitrile (0.15 mmol) in toluene (0.5 M) under rt for 3 h. [b)] Yield and *E*/*Z* ratio were determined by ^{1}H NMR using TMSPh as an internal standard.

experimental results revealed that the steric hindrance of the nitrile had a minimal effect (Table 2, Entries 1–3), whereas electronic effects had a pronounced influence on both the activity and selectivity (Table 2, Entries 4–6). In contrast to alkyl nitriles, aryl nitriles exhibit stronger coordination to the cobalt catalyst, which consequently decreases the catalyst's activity.[42] This observation aligns with our experimental results.



Scheme 5. Proposed mechanism.

Based on the experimental observations, a plausible reaction mechanism for this transformation is proposed (Scheme 5a). Building upon previous reports on cobalt-catalyzed hydrogenation of alkenes and semihydrogenation of alkynes,[29,43,44] an acetonitrile-coordinated cobalt-hydride species **A** is likely generated upon activation by $NaBHEt_3$.[45–47] The catalytic cycle for *Z*-selective semihydrogenation is depicted in Cycle A. Following migratory insertion of alkyne **1** to form complex **C**, reaction of the alkenyl complex **C** with H_2 via σ-bond metathesis liberates the (*Z*)-alkene and regenerates the cobalt hydride complex **A**. When the cobalt hydride species **A** bears a less sterically hindered ligand (**Lb**), the (*Z*)-alkene can re-enter the catalytic cycle, reacting with **A** to form a Co-alkyl intermediate **F**. The (*E*)-alkene product could be obtained via β-hydride elimination of Co-alkyl species **G**. The observed excellent selectivity suggests that the isomerization process occurs readily. The acetonitrile coordinated cobalt hydride species **A**, acetonitrile coordinated cobalt alkene species **C**, and cobalt alkene species has been detected by ESI-HRMS. The absence of over-hydrogenated alkane products suggests that β-hydride elimination in **F** is kinetically favored over the reaction of the alkyl complex with H_2 in the presence of acetonitrile (Scheme 5b).[37,48] This preference is likely due to acetonitrile's coordination to the cobalt catalyst, stabilizing it as 18 e$^-$ electron species.

Conclusion

In conclusion, we have developed a novel cobalt-catalyzed stereodivergent semihydrogenation of alkynes, enabling the synthesis of diverse *E*- and *Z*- alkenes with good functional group tolerance. This methodology operates under mild conditions, including room temperature, using 1 atm of H_2 as the reductant. Notably, the addition of acetonitrile plays a crucial role in controlling the *E*/*Z* selectivity and suppressing overhydrogenation of the alkene products. We believe that the synergistic catalysis of acetonitrile and the cobalt catalyst will provide a promising new avenue for the selective hydrogenation of other unsaturated compounds (Supporting Information).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: Cobalt • *E*- and *Z*-alkenes • Semihydrogenation • Stereodivergence • Synergetic catalysis

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[1] C. Oger, L. Balas, T. Durand, J.-M. Galano, *Chem. Rev.* **2013**, *113*, 1313–1350.

[2] R. C. Larock, in *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed., Wiley-VCH, New York **1999**.

[3] G. C. Tron, T. Pirali, G. Sorba, F. Pagliai, S. Busacca, *J. Med. Chem.* **2006**, *49*, 3033–3044.

[4] G. Wittig, U. Schöllkopf, *Chem. Ber.* **1954**, *87*, 1318–1330.

[5] D. J. Peterson, *J. Org. Chem.* **1968**, *33*, 780–784.

[6] W. S. Wadsworth, W. D. Emmons, *J. Am. Chem. Soc.* **1961**, *83*, 1733–1738.

[7] P. R. Blakemore, *J. Chem. Soc., Perkin Trans. 1* **2002**, 2563–2585.

[8] B. K. Keitz, K. Endo, P. R. Patel, M. B. Herbert, R. H. Grubbs, *J. Am. Chem. Soc.* **2012**, *134*, 693–699.

[9] *Metal-catalyzed cross-coupling reactions* (Eds: A. De Meijere, F. Diederich), Wiley-VCH, Weinheim **2004**.

[10] K. Rafał, G. Karol, *Chem. Rev.* **2025**, *125*, 4397–4527.

[11] W.-Y. Siau, Y. Zhang, Y. Zhao, in *Stereoselective Alkene Synthesis* (Ed.: J. Wang), Springer, Berlin, **2012**, pp. 33–58.

[12] B. J. Gregori, M. W. S. Schmotz, A. J. von Wangelin, *ChemCatChem* **2022**, *14*, e202200886.

[13] D. M. Sharma, B. Punji, *Chem. Asian. J.* **2020**, *15*, 690–708.

[14] H. Lindlar, R. Dubuis, *Org. Synth.* **1966**, *46*, 89–92.

[15] S. P. Desai, J. Ye, J. Zheng, M. S. Ferrandon, T. E. Webber, A. E. Platero-Prats, J. Duan, P. Garcia-Holley, D. M. Camaioni, K. W. Chapman, *J. Am. Chem. Soc.* **2018**, *140*, 15309–15318.

[16] Z. Huang, Y. Wang, X. Leng, Z. Huang, *J. Am. Chem. Soc.* **2021**, *143*, 4824–4836.

[17] V. Chugh, J. Wu, M. Leutzsch, H Randel, T.W., A. A. Auer, C. Farès, C. Werlé, *Chem Catalysis* **2024**, *4*, 101078.

[18] Z. Wang, Q. Luo, S. Mao, C. Wang, J. Xiong, Z. Chen, Y. Wang, *Nano Res.* **2022**, *15*, 10044–10062.

[19] G. J. Baker, A. J. P. White, I. J. Casely, D. Grainger, M. R. Crimmin, *J. Am. Chem. Soc.* **2023**, *145*, 7667–7674.

[20] Y. Liang, U. K. Das, J. Luo, Y. Diskin-Posner, L. Avram, D. Milstein, *J. Am. Chem. Soc.* **2022**, *144*, 19115–19126.

[21] L. Ling, C. Hu, L. Long, X. Zhang, L. Zhao, L. L. Liu, H. Chen, M. Luo, X. Zeng, *Nat. Commun.* **2023**, *14*, 990.

[22] D. J. Hale, M. J. Ferguson, L. Turculet, *ACS Catal.* **2022**, *12*, 146–155.

[23] S. Fu, N. Y. Chen, X. Liu, Z. Shao, S. P. Luo, Q. Liu, *J. Am. Chem. Soc.* **2016**, *138*, 8588–8594.

[24] K. Tokmic, A. R. Fout, *J. Am. Chem. Soc.* **2016**, *138*, 13700–13705.

[25] C. Chen, Y. Huang, Z. Zhang, X. Q. Dong, X. Zhang, *Chem. Commun.* **2017**, *53*, 4612–4615.

[26] V. G. Landge, J. Pitchaimani, S. P. Midya, M. Subaramanian, V. Madhu, E. Balaraman, *Catal. Sci. Technol.* **2018**, *8*, 428–433.

[27] K. Li, R. Khan, X. Zhang, Y. Gao, Y. Zhou, H. Tan, J. Chen, B. Fan, *Chem. Commun.* **2019**, *55*, 5663–5666.

[28] X. Liu, B. Liu, Q. Liu, *Angew. Chem. Int. Ed.* **2020**, *59*, 6750–6755.

[29] H. Alawisi, H. D. Arman, Z. J. Tonzetich, *Organometallics* **2021**, *40*, 1062–1070.

[30] D. K. Pandey, J. R. Khusnutdinova, *ChemCatChem* **2025**, *17*, e202500041.

[31] M. T. Sheikh, P. Sakharov, S. Raje, G. de Ruiter, *ACS Catal.* **2025**, *15*, 5370–5377.

[32] K. Chen, H. Zhu, Y. Li, Q. Peng, Y. Guo, X. Wang, *ACS Catal.* **2021**, *11*, 13696–13705.

[33] W.-F. Tian, Y.-Q. He, X.-R. Song, H.-X. Ding, J. Ye, W.-J. Guo, Q. Xiao, *Adv. Synth. Catal.* **2020**, *362*, 1032–1038.

[34] P. Lu, X. Ren, H. Xu, D. Lu, Y. Sun, Z. Lu, *J. Am. Chem. Soc.* **2021**, *143*, 12433–12438.

[35] J. Zhao, G. Xu, X. Wang, J. Liu, X. Ren, X. Hong, Z. Lu, *Org. Lett.* **2022**, *24*, 4592–4597.

[36] X. Ren, Z. Lu, *Org. Lett.* **2021**, *23*, 8370–8374.

[37] I. A. Mkhalid, R. B. Coapes, S. N. Edes, D. N. CovEntry, F. E. Souza, R. L. Thomas, J. J. Hall, S. W. Bi, Z. Lin, T. B. Marder, *Dalton Trans.* **2008**, *8*, 1055–1064.

[38] A. P. Singh, R. Singh, S. S. Verma, V. Rai, C. H. Kaschula, P. Maiti, S. C. Gupta, *Med. Res. Rev.* **2019**, *39*, 1851–1891.

[39] A. Nowicki, P. Skupin-Mrugalska, M. Jozkowiak, M. Wierzchowski, M. Rucinski, P. Ramlau, V. Krajka-Kuzniak, J. Jodynis-Liebert, H. Piotrowska-Kempisty, *Int. J. Mol. Sci.* **2020**, *21*, 1100.

[40] Y. Jiang, Y. Y. Liu, X. Liu, H. Lin, K. Gao, W. Y. Lai, W. Huang, *Chem. Soc. Rev.* **2020**, *49*, 5885–5944.
[41] J. E. Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483.
[42] S. F. Rach, F. E. Kühn, *Chem. Rev.* **2009**, *109*, 2061–2080.
[43] P. Lu, H. Wang, Y. Mao, X. Hong, Z. Lu, *J. Am. Chem. Soc.* **2022**, *144*, 17359–17364.
[44] M. R. Friedfeld, M. Shevlin, G. W. Margulieux, L.-C. Campeau, P. J. Chirik, *J. Am. Chem. Soc.* **2016**, *138*, 3314–3324.
[45] T. Ouyang, C. Hou, J.-W. Wang, W.-J. Liu, D.-C. Zhong, Z.-F. Ke, T.-B. Lu, *Inorg. Chem.* **2017**, *56*, 7307–7311.
[46] W.-Y. Chu, R. Gilbert-Wilson, T. B. Rauchfuss, M. van Gastel, F. Neese, *Organometallics* **2016**, *35*, 2900–2914.
[47] J. Lee, J. Lee, J. Seo, *Nat. Commun.* **2024**, *15*, 8688.
[48] V. Aryal, S. Inaththappulige, A. Acharya, R. Giri, *J. Am. Chem. Soc.* **2025**, *147*, 1667–1676.

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