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Letter

Cobalt-Catalyzed *Z* to *E* Isomerization of Alkenes: An Approach to (*E*)-β-Substituted Styrenes

Hongmei Liu,[†] Man Xu,[†] Cheng Cai, Jianhui Chen,* Yugui Gu, and Yuanzhi Xia*

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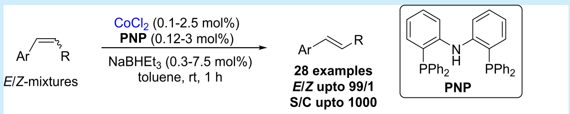
ABSTRACT: An efficient cobalt-catalyzed *Z* to *E* isomerization of β-substituted styrenes using the amido-diphosphine ligand was developed, delivering the (*E*)-isomers with good functional tolerance and high stereoselectivity. The reaction could be scaled up to gram-scale with a catalyst loading of 0.1 mol %, using a mixture of (*Z*)- and (*E*)-alkene as the starting material. Preliminary mechanistic studies indicated that cobalt(I)-hydride and a benzylic-cobalt species were probably involved in the reaction, as supported by experiments and DFT calculations.



An efficient method for geometrical Z to E isomerisation
an alternative approach to access (*E*)-alkenes
easily obtained starting materials and catalyst

The 1-propenylbenzenes are important building blocks in synthetic organic chemistry,[1] as such structural motifs are generally contained in many naturally occurring compounds,[2] having wide applications in the pharmaceutical chemistry,[3] pesticide,[4] flavor and fragrance industry[5] (Figure 1). A number of elegant methods have been established for the preparation of alkenes, including Wittig reaction,[6] Julia olefination,[7] olefin metathesis,[8] cross-coupling reaction[9] and alkyne semihydrogenation.[10] However, these protocols are always suffered from poor *E*/*Z* selectivity. The two isomers are difficult to separate from mixtures, and may lead to different reactivity,[11] regio-[12] or diastereoselectivity[13] in the functionalization reactions. Hence, the development of efficient and convenient method for geometrical isomerization between *E*/*Z* mixtures of alkenes is highly valuable.[14]

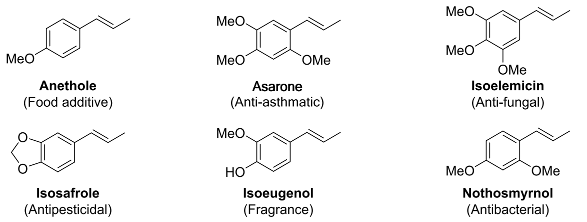
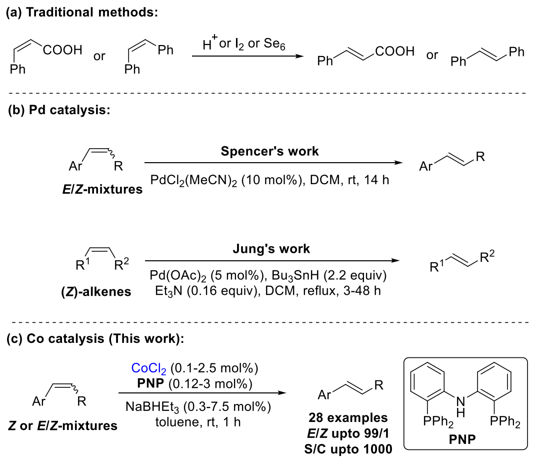


Figure 1. Selected industrially relevant targets containing 1-propenylbenzenes scaffold.

Although contra-thermodynamic in nature, the *E* to *Z* isomerization of alkenes has been established via photochemical procedures.[15] Meanwhile, isomerizing of *cis*-alkene to *trans*-alkene could be achieved in the presence of strong acids, halogens, or elemental selenium, but these methods were not applicable to simple alkenes (Scheme 1a).[14b,16] In 2002, the Spencer group developed a systematic *Z* to *E* isomerization of *E*/*Z*-mixtures of β-substituted styrenes with the involvement of a π-allylic palladium catalyst; however, the catalytic system was not suitable for electron-deficient substrates and required a relatively high catalyst loading (10 mol %) (Scheme 1b).[17] In the presence of tributyltin hydride (2.2 equiv), Jung and coworkers described a *Z* to *E* isomerization of (*Z*)-alkenes employing a palladium-hydride catalysis under reflux conditions.[18]

Scheme 1. Methods for *Z* to *E* Isomerization of Alkenes



Owing to its high natural abundance, biocompatibility, and unique catalysis, earth-abundant transition metal catalysts such as iron, cobalt, nickel, and copper have attracted much attention in the past two decades.[1b−e,19] The earth-abundant transition metals[20] have been considered as an alternative to

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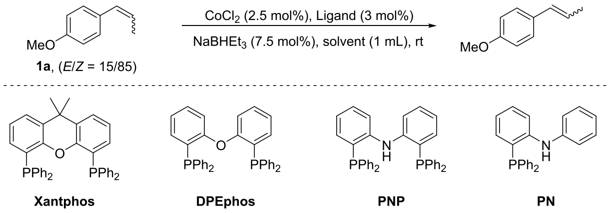
noble metals[21] for alkene isomerization. In combination with appropriate ligands, cobalt complexes have been demonstrated as efficient catalysts for position isomerization of alkenes.[22−30] In the 1970s, Orchin and co-workers found cobalt hydride complex [$CoH(Co)_4$] could catalyze isomerization of ally benzene and proposed a Co−H insertion/β-H elimination pathway based on deuterium-labeling experiments.[22] Subsequently, Satyanarayana and Periasamy disclosed migration isomerization of olefins over one position employing a $CoCl_2$/PPh_3/$NaBH_4$ system.[23] In 2009, Oshima and Yorimitsu developed a cobalt-catalyzed isomerization of 1-alkenes to (*E*)-2-alkenes with a NHC ligand in the presence of a Grignard reagent.[24] In 2014, Holland[25] and Hilt[26] independently reported cobalt-catalyzed (*Z*)-selective isomerization of terminal alkenes with bulky β-diketiminate and Ph_2PH as the ligand, respectively. Employing a radical based hydrogen atom transfer (HAT) mechanism, Shenvi and co-workers described a chemoselective isomerization of terminal alkenes with catalytic amounts of the Co-salen complex and organosilane.[27] Later, the Norton group found that $Co(dmgBF_2)_2(THF)_2$ could generate a low concentration of H· donor under H_2 pressure, which can promote radical isomerization of terminal alkenes.[28] In 2018, Liu and Jiao developed a regioselective olefin isomerization under kinetic control with designed pyridine-amine-phosphine cobalt complexes using ammonia borane as the reductant, delivering less hindered olefin products with high selectivity.[29] In combination of visible light with cobalt catalysis, König and co-workers reported a thermodynamic and kinetic isomerization of alkenes, in which the regioselectivity could be controlled by switching the ligand.[30] Very recently, Schoenebeck and co-workers developed an additive-free double bond migration of terminal alkenes via a nickel-catalyzed intramolecular 1,3-hydrogen atom relocation strategy.[31] However, geometrical isomerization of alkenes with earth abundant transition metal catalyst is still rarely reported.[32] In this current report, we present an efficient cobalt-catalyzed *Z* to *E* isomerization of *E*/*Z*-mixtures of alkenes, producing (*E*)-isomers with high stereoselectivity (Scheme 1c).

Table 1. Optimization of Conditions[a]



entry	solvent	time	ligand	product (*E*/*Z*)[b]
1	dioxane	1 h	–	16/84
2	dioxane	1 h	Xantphos	31/69
3	dioxane	1 h	DPEphos	27/73
4	dioxane	1 h	PNP	97/3
5	dioxane	1 h	PN	25/75
6	THF	1 h	PNP	50/50
7	DCM	1 h	PNP	97/3
8	toluene	1 h	PNP	98/2
9	toluene	12 h	PNP	98/2
10[c]	**toluene**	**1 h**	**PNP**	**98/2(99%)**[d]

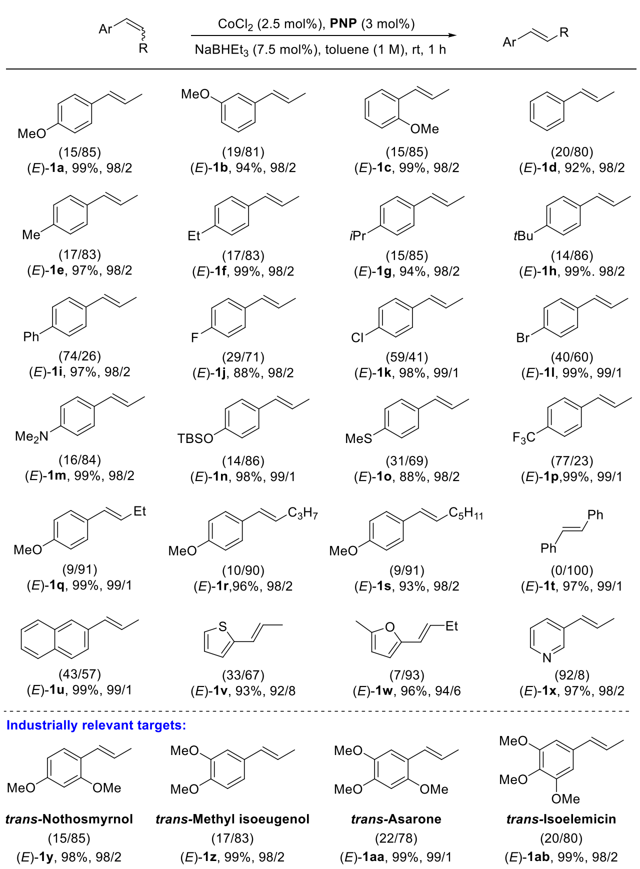
[a] Unless otherwise noted, the reaction was conducted with **1a** (0.5 mmol, *E*/*Z* 15/85), $CoCl_2$ (0.0125 mmol), ligand (0.015 mmol), and $NaBHEt_3$ (0.038 mmol) in solvent (1 mL) at room temperature for 1 h. [b] The *E*/*Z* ratio of product was determined by ^1H NMR analysis. [c] The reaction was conducted with **1a** (1 mmol, *E*/*Z* 15/85), $CoCl_2$ (0.025 mmol), **PNP** (0.03 mmol), and $NaBHEt_3$ (0.075 mmol) in toluene (1 mL) at room temperature for 1 h. [d] Isolated yield.

To initiate this study, the *E*/*Z*-mixture of anethole (**1a**) (*E*/*Z* 15/85) was subjected to the catalytic system of $CoCl_2$ and $NaBHEt_3$ in dioxane (0.5 M) (Table 1, entry 1). After stirring at room temperature for 1 h, the *E*/*Z* ratio of the alkene was almost unchanged (*E*/*Z* 16/84). A slight increase in *E*/*Z* selectivity was observed when Xantphos or DPEphos was used as the ligand in the reaction (entries 2−3). Interestingly, the use of the amido-diphosphine ligand (**PNP**) led to a significant raise in *E*/*Z* selectivity (entry 4, 97/3 *E*/*Z*), while bidentate amido-monophosphine ligand (**PN**) showed poor reactivity (entry 5). Screening of solvents (entries 6−8) showed that the *E*/*Z* selectivity could be slightly improved to 98/2 in toluene. Extending the reaction time to 12 h did not lead to further improvement in the stereoselectivity (entry 9). When increasing the concentration of **1a**, the reactivity was not effected and gave the desired (*E*)-antethole in 99% isolated yield with 98/2 stereoselectivity (entry 10).

With the optimal set of conditions in hand, the substrate scope of *Z* to *E* isomerization was shown in Scheme 2. Except for (*Z*)-stilbene (**1t**), all alkene substrates were conveniently prepared by Wittig olefination, and the *E*/*Z* ratios of the starting materials were shown in the parentheses. A variety of β-methylstyrenes containing electron-rich or -deficient groups were suitable for this catalytic system, giving the (*E*)-products with *E*/*Z* selectivity equal to or greater than 98/2 (**1a**−**1p**). The methoxy substituent at the *meta*- or *ortho*-position of the phenyl ring have no influence on the stereoselectivity (**1b**−**1c**). The reaction of a mixture of (*E*)- and (*Z*)-β-methylstyrene delivered the (*E*)-isomer with 98/2 selectivity (**1d**). This catalytic system could tolerate alkyl, phenyl, fluoro, chloro, bromo, protected phenol, aniline, and thiophenol groups at the *para*-position of the phenyl ring, yielding the desired (*E*)-alkenes with 98/2 or even 99/1 selectivity (**1e**−**1o**). The introduction of a strongly electron-deficient substituent such as the trifluoromethyl group in the phenyl ring also led to excellent *E*/*Z* selectivity (**1p**, *E*/*Z* 99/1). The geometrical isomerization of β-alkyl styrenes proceeded smoothly to give the (*E*)-isomers with up to 99/1 selectivity (**1q**−**1s**). Pure (*Z*)-stilbene converted to (*E*)-stilbene under the standard conditions with 99/1 selectivity (**1t**). Other aryl alkenes, such as 2-naphthalene, thiophene, furan, and pyridine, were also tolerated to afford the corresponding (*E*)-isomers (**1u**−**1x**), while the reactions of five-membered aryl alkenes afforded the products with a slightly lower stereoselectivity. Furthermore, industrially relevant substrates, such as nothosmyrnol (**1y**), methyl eugenol (**1z**), asarone (**1aa**), and isoelemicin (**1ab**), were successfully converted to the corresponding *trans*-products in quantitative yields with high stereoselectivity (*E*/*Z* ≥ 98/2), respectively.

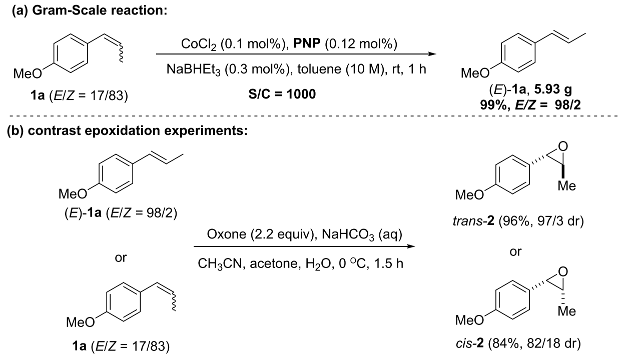
A gram-scale reaction was carried out with a catalyst loading of 0.1 mol % at room temperature for 1 h, producing the desired (*E*)-product in quantitative yields without compromising the stereoselectivity (Scheme 3a). This is much more efficient compared to other catalytic systems with noble metals for geometrical isomerization.[17,18] To further showcase the synthetic utility, contrast experiments of alkene epoxidation were performed (Scheme 3b). *trans*-Anethole [(*E*)-**1a**, 98/2 *E*/*Z*] could be converted to *trans*-β-methylstyrene oxide (*trans*-**2**,

Scheme 2. Substrate Scope for Co-Catalyzed *Z* to *E* Isomerization of Styrenes[a]



[a] The reaction was conducted with *E*/*Z*-mixtures of alkene (1 mmol, *E*/*Z* ratios were shown in the parentheses), $CoCl_2$ (0.025 mmol), **PNP** (0.030 mmol), and $NaHBEt_3$ (0.075 mmol) in toluene (1 M) at room temperature for 1 h. Isolated yields. The *E*/*Z* ratios were determined by ^{1}H NMR analysis.

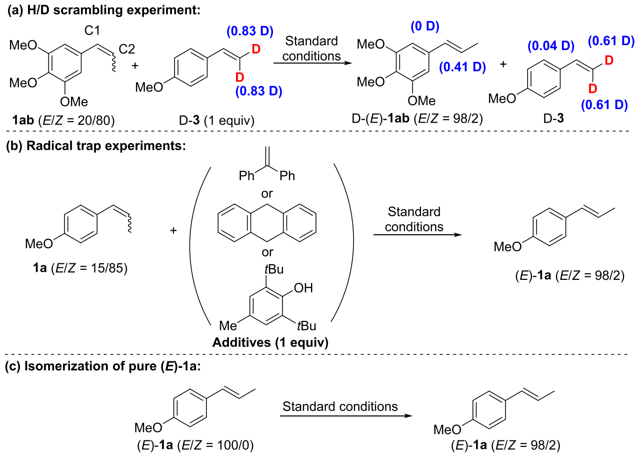
Scheme 3. Gram-Scale Reaction and Epoxidation of *E*/*Z*-Mixtures and (*E*)-Alkene



dr 97/3) smoothly, whereas the reaction of *E*/*Z* mixtures of **1a** gave a mixture of *cis*- and *trans*-epoxidation products.

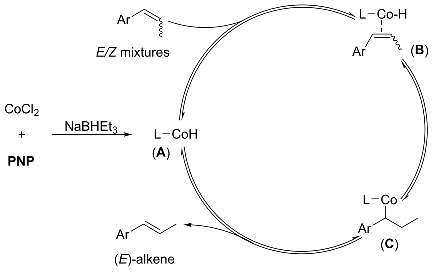
According to literature reports,[21d] the isomerization reaction could occur via a metal-hydride catalysis, HAT mechanism, or π-allyl metal intermediate. A series of preliminary experiments were conducted to gain insight into the catalytic cycle (Scheme 4). When 1 equiv of deuterated 4-methoxy styrene (**D-3**) was added to the reaction of **1ab**, a 41% proportion of the deuterium was incorporated at the C2 position of the isomerization product [D-(*E*)-**1ab**], while no deuterium was found at the C1 position (benzylic position), ruling out the formation of π-allyl metal intermediate. Interestingly, both C1 and C2 were deuterated in the recovered 4-methoxy styrene (Scheme 4a). When the reactions of **1a** were further performed in the presence of different radical initiators, 1,1-diphenyl ethene, di-*tert*-butylhydroxytoluene, and 9,10-dihydroanthracene, respectively (Scheme 4b), no influence on the results was found, indicating that the radical based HAT pathway is unlikely. Furthermore, the reaction of pure (*E*)-anethole yielded the product with 98/2 *E*/*Z* selectivity (the same as the reaction of *E*/*Z*-mixture of **1a**), which demonstrated that the *Z* to *E* isomerization process was reversible and controlled by thermodynamic properties (Scheme 4c).

Scheme 4. Preliminary Mechanistic Experiments



According to the above results, the plausible mechanism was proposed in Scheme 5. First, a ligated cobalt hydride species (**A**) is generated by treating $CoCl_2$ and **PNP** ligand with $NaBHEt_3$.[33] Then (*Z*)-alkene coordinates with species **A** to form complex **B** prior to its selective insertion into the Co−H bond to form a benzylic cobalt species **C**. Finally, the formation of an (*E*)-alkene and regeneration of cobalt hydride species **A** occur by β-H elimination.

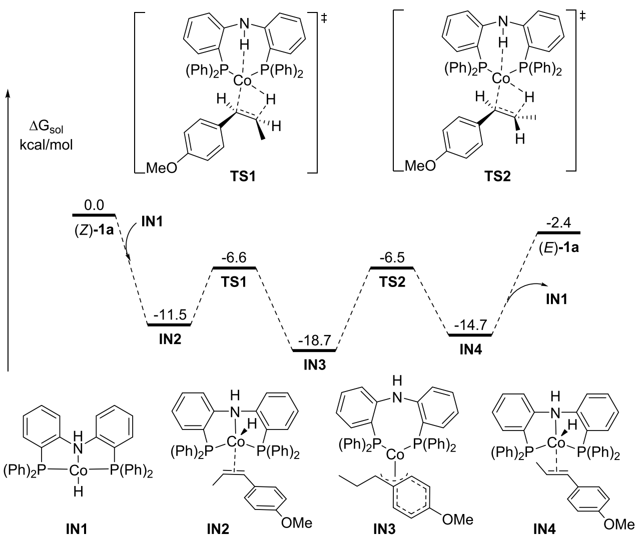
Scheme 5. Proposed Mechanism



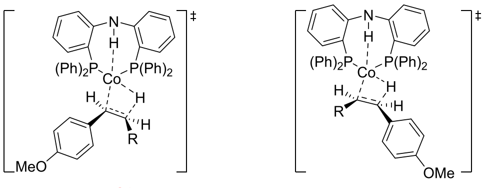
To better understand the experimental observations, DFT calculations were carried out to shed light on the details of the transformation (Scheme 6a).[34] It was found that when the cobalt(I)-hydride (**IN1**) is involved,[29] it complexes with (*Z*)-**1a** forming **IN2** favorably. The migratory insertion occurs very facilely via **TS1**, in which no N−Co coordination bond but interestingly a N−H → Co agostic interaction (Co−H = 2.28 Å; see SI for details) was found, affording intermediate **IN3**

Scheme 6. DFT Results (Relative Free Energies Are in kcal/mol)

(a) Calculated energy profile for the Co(I)-catalyzed isom-erization of 1a:



(b) Energies for explanation of the deuterium labeling experiments:



R = Me: ΔG(**TS1**) = -6.5
R = H: ΔG(**TS3**) = -8.4

R = Me: ΔG(**TS1'**) = -3.9
R = H: ΔG(**TS3'**) = -7.6

containing a delocalized benzylic anion moiety. From **IN3**, the barrier for β-H elimination via **TS2** is 12.2 kcal/mol and the product complex **IN4** is formed slightly endergonically. The dissociation step is endergonic by 12.3 kcal/mol, from which the (*E*)-**1a** is formed and **IN1** is regenerated. The calculated barriers in Scheme 6a are consistent with the mild conditions and fast transformation. The *E* isomer is thermodynamically more stable than the *Z* isomer by 2.4 kcal/mol, explaining well the distribution of the stereoisomers in reactions from the *Z*/*E* mixture and absolute *E* configuration. To understand the different deuterium incorporation in **1a** and **3** in Scheme 4a, the energies for alkene insertion into Co−H bond were compared. Calculations revealed that the insertion of substrate **1a** occurs more selectively via **TS1** than via **TS1′** by 2.6 kcal/mol (R = Me, Scheme 6b), as a more stable delocalized benzylic anion is formed via the former TS (see SI for details). However, when 4-methoxy-styrene is used (R = H), the energy of **TS3** is only 0.8 kcal/mol lower than that of **TS3′**. These energies are in good agreement with the deuterium labeling experiments.

In conclusion, we have developed an efficient and mild method for *Z* to *E* isomerization of a variety of β-substituted styrenes prepared from Wittig olefination. In a combination of $CoCl_2$, **PNP** ligand, and $NaBHEt_3$, the isomerization proceeded smoothly to give the desired (*E*)-isomers with high stereoselectivity at room temperature. This catalytic reaction could be scaled up easily with a low catalyst loading of 0.1 mol %, implying the potential practical application of the method. Preliminary mechanistic studies suggested that a cobalt(I)-hydride and a benzylic-cobalt species are involved in the catalytic cycle, which was supported by the experiments and DFT calculations. Further investigation of novel catalytic transformations mediated via β-elimination with an earth abundant transition metal catalyst are undergway in our laboratory.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00072.

Experimental and computational details, data, and spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Jianhui Chen − *Wenzhou University, Wenzhou, China;* orcid.org/0000-0002-5080-1880; Email: cjh@wzu.edu.cn
Yuanzhi Xia − *Wenzhou University, Wenzhou, China;* orcid.org/0000-0003-2459-3296; Email: xyz@wzu.edu.cn

Other Authors

Hongmei Liu − *Wenzhou University, Wenzhou, China*
Man Xu − *Wenzhou University, Wenzhou, China*
Cheng Cai − *Wenzhou University, Wenzhou, China*
Yugui Gu − *Wenzhou University, Wenzhou, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c00072

Author Contributions

†H.-M.L. and M.X. contributed equally.

Notes

The authors declare no competing financial interest.

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