Organic Letters

Cobalt-Catalyzed Migrational Isomerization of Styrenes

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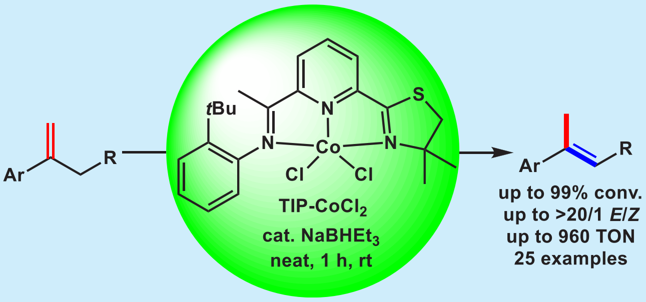
Cite This: https://dx.doi.org/10.1021/acs.orglett.9b04305

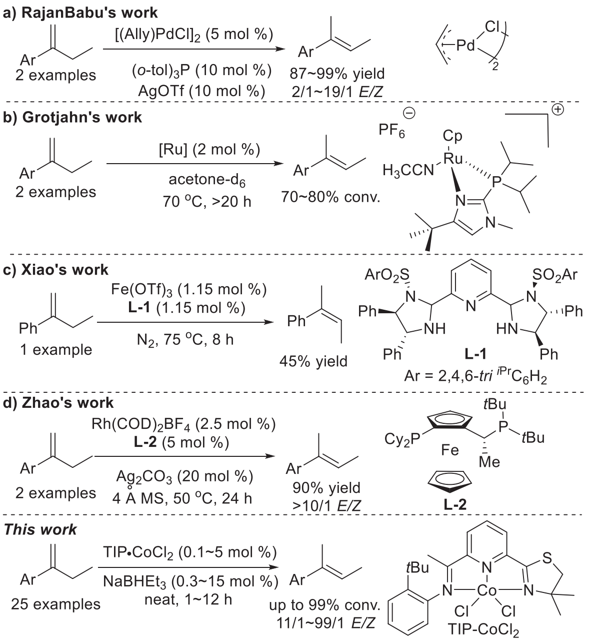
ABSTRACT: An efficient cobalt-catalyzed migrational isomerization of styrenes was developed using the thiazoline iminopyridine (TIP) ligand. This reaction is operationally simple and atom-economical using readily available starting materials to access trisubstituted alkenes. Even when using a 0.1 mol % catalyst loading, the reaction could be conducted in neat and completed in 1 h with excellent conversion and high *E* stereoselectivity.



Trisubstituted olefins are ubiquitous structural motifs found in many bioactive natural products, agrochemicals, and pharmaceuticals.[1] Notably, several classical approaches for the synthesis of trisubstituted alkenes have been well-defined, such as Wittig reaction, Horner−Wadsworth−Emmons reaction, Julia olefination, Peterson olefination, etc.[2] Furthermore, metal-catalyzed coupling reactions and olefin metathesis are also well-established methods for their synthesis.[3] Nevertheless, these approaches provided stoichiometric chemical waste and suffered from poor reactivity and *E*/*Z* selectivity.[2−4] Due to its great atom economy, migrational isomerization of easily accessible terminal olefins is an ideal method for the synthesis of trisubstituted olefin. A main feature of this method is migration of the original carbon−carbon double bond, which is driven by a thermodynamically favored termination step.[5]

Over the past decades, tremendous efforts have been dedicated to the development of efficient catalytic strategies based on noble metal complexes[6] including ruthenium,[7] rhodium,[7j,8] palladium,[9] iridium,[10] and others.[11] Recently, the earth-abundant metal catalysts also play an important role in this research area.[12] Although a wide range of efficient metal-catalyzed olefin migrational isomerization reactions have been developed, we find that the highly efficient and selective migrational isomerization of simple α-alkyl styrenes to trisubstituted styrenes is still a challenge and has not been well explored (Scheme 1). In 2009, the RajanBabu group described a palladium catalyst exhibits a high preference for the formation of the trisubstituted alkenes from a simple α-alkyl styrene (Scheme 1a).[9a] However, the *E*/*Z* selectivity (2/1−19/1 *E*/*Z*) and the scope of substrate (only 2 examples) need to be improved. In 2012, the Grotjahn group reported that using a ruthenium complex as a catalyst could catalyze the migrational isomerization of simple α-alkyl styrenes (Scheme 1b).[7c] In 2015, in the process of studying for the selective oxidation of aromatic olefins, the Xiao group found the isomerization of a simple α-alkyl styrene to trisubstituted alkenes with *Z*-selectivity (Scheme 1c).[13] Unfortunately, the yield of olefin isomerization could not exceed 80% and the scope of substrates was no more than two in both cases. In

Scheme 1. Isomerization of Simple α-Alkyl Styrene



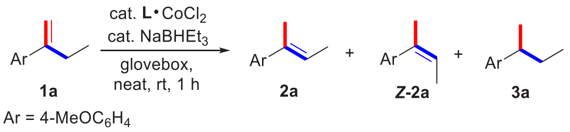
Received: November 30, 2019

2016, Norton and co-workers described an elegant radical isomerization reaction using $Co(dmgBF_2)_2(THF)_2$ under 6 atm of H_2 pressure in which seven examples on α-alkyl styrenes with functional groups were reported with 52−>95% yields. However, simple α-alkyl styrenes have not been mentioned.[12j] In 2018, the Zhao group presented an unprecedented enantioselective isomerization of homoallylic and bishomoallylic secondary alcohols (Scheme 1d).[8b] This catalytic system was also applied to the isomerization of simple α-alkyl styrenes with an excellent yield (80−90%) and *E*-selectivity (>10/1 *E*/*Z*). However, the recovery of starting materials was not mentioned and the scope of substrate has not been well explored.

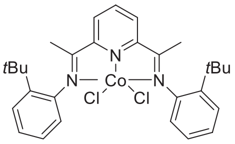
While studying cobalt-catalyzed alkene hydrofunctionalization,[14] we found that alkene isomerization occurred which is quite similar to results observed by other research groups.[12] Herein, we developed migrational isomerization of 1,1-disubstituted aromatic alkenes using a thiazoline iminopyridine (TIP) cobalt dichloride complex with high efficiency and stereoselectivity.

Results and Discussion. At the beginning of screening, 1-(but-1-en-2-yl)-4-methoxybenzene (**1a**) was chosen as a model substrate. The $NaBHEt_3$ was used as the activator. Since bis(imino)pyridine ligands and bis(oxazoline)pyridine ligands played an important role in cobalt-catalyzed alkene transformation,[14a] we first screened these two ligands. Only 66% and 24% yields of isomerization product were observed, respectively (entries 1 and 2, Table 1). The reaction of **1a** using an oxazoline iminopyridine (OIP) cobalt complex (**Lc**·$CoCl_2$, 5 mol %) as a catalyst in neat at room temperature for 1 h could be smoothly performed to afford the isomerized product *E*-**2a** in 88% yield and hydrogenation product **3a** in 6% yield, as well as with 6% recovery (entry 3). Then, the substitution on the OIP ligand was screened to enhance the reactivity and selectivity of isomerization. The use of the **Ld** ligand with the bulkier substitution 2,6-diisopropyl group on imine did slow down the isomerization reaction (entry 4). The use of **Le** with only one smaller methyl group on imine dramatically inhibited the hydrogenation product, however, slightly decreased the reactivity (entry 5). The use of **Lf** with a 2-*tert*-butyl group on imine did increase the reactivity (entry 6). Using the corresponding more electron-rich thiazoline iminopyridine ligand **Lg**[15] could dramatically improve the isomerization reaction which afforded **2a** in 96% yield with 2% yield of **3a** and 2% recovery (entry 7). The reaction using 1 mol % of catalyst could afford **2a** in 96% yield without loss of reactivity (entry 8). Due to the lack of the amount of reductant, the hydrogenation reaction was also inhibited. The reaction with a 0.1 mol % catalyst loading in 4 mmol scale could afford the desired product in 96% yield, and the turnover number was up to 960 (entry 9). So, the suitable stereochemical outcome on the ligand did affect the reactivity, and the side hydrogenation reaction could be inhibited by decreasing the amount of catalyst and reductant. The stereoscopic configuration was confirmed by NOE analysis. For operational simplicity, the standard conditions were chosen to be alkene (0.5 mmol), **Lg**·$CoCl_2$ (1 mol %), and $NaBHEt_3$ (3 mol %) in neat at room temperature for 1 h.

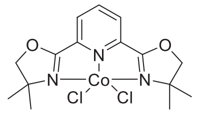
Table 1. Optimization for Isomerization of Alkenes[a]



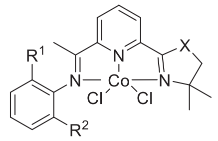
Entry	L•$CoCl_2$ (mol %)	Yield of **2a**/***Z*-2a**/**3a** (%)[b]	Recovery (%)[b]
1	**La** (5)	66/-/7	22
2	**Lb** (5)	22/2.3/6	69
3	**Lc** (5)	88/-/6	6
4	**Ld** (5)	64/-/8	28
5	**Le** (5)	79/-/-	16
6	**Lf** (5)	93/4/-	3
7	**Lg** (5)	96/-/2	2
8[c]	**Lg** (1)	96/-/-	4
9[d]	**Lg** (0.1)	96/-/-	4



La · $CoCl_2$



Lb · $CoCl_2$



Lc-g · $CoCl_2$

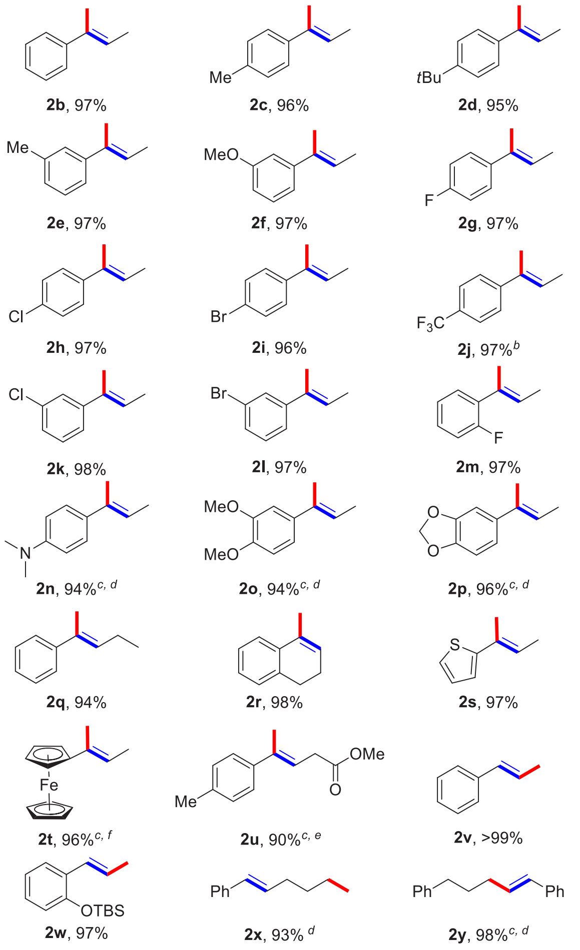
Lc: $R^1 = R^2$ = Me, X = O
Ld: $R^1 = R^2$ = *i*Pr, X = O
Le: R^1 = Me, R^2 = H, X = O
Lf: R^1 = *t*Bu, R^2 = H, X = O
Lg: R^1 = *t*Bu, R^2 = H, X = S

[a] The reaction was conducted using alkene (0.5 mmol), cobalt complex (*x* mmol %), and $NaBHEt_3$ (3*x* mol %) in neat at room temperature for 1 h in glovebox. [b] Determined by ^1H NMR using TMSPh or CH_2Br_2 as an internal standard. [c] Determined by GC and a calibration curve to achieve accurate integration/conversion. [d] 4 mmol scale.

Under the optimized conditions, the substrate scope was explored in Scheme 2. Various functional groups were well tolerated, such as ether, halide, protected alcohol, ester, and amine. Electron-donating substituents on the phenyl ring, such as methyl, methoxyl, and dimethylamino, could be well tolerated, and the conversions were all >94% (**2b−f**, **2n−p**). Electron-withdrawing substituents on the phenyl ring did not influence the conversion, but decreased the ratio of *E*/*Z* (**2g−m**). The *ortho*-, *meta*-, and *para*-substituents on benzene rings (**2c−m**) resulted in similarly remarkable conversion and an excellent *E*/*Z* ratio. The conversion and stereoselectivity were not obviously influenced by the length of the alkyl chain (**2q**). Intracyclic olefins (**2r**) could also be obtained with 98% conversion. Sulfur-containing heterocycles thiophene (**2s**) and ferrocene (**2t**) could be well tolerated to give the corresponding products in 97% and 96% conversion, respectively. Other than 1,1-disubstituted alkenes, monosubstituted alkenes could also be converted to internal alkenes (**2v−x**) with excellent benzylic selectivity. 1,2-Disubstituted alkenes could also be converted to a benzylic selective product (**2y**) with *E*-stereoselectivity.

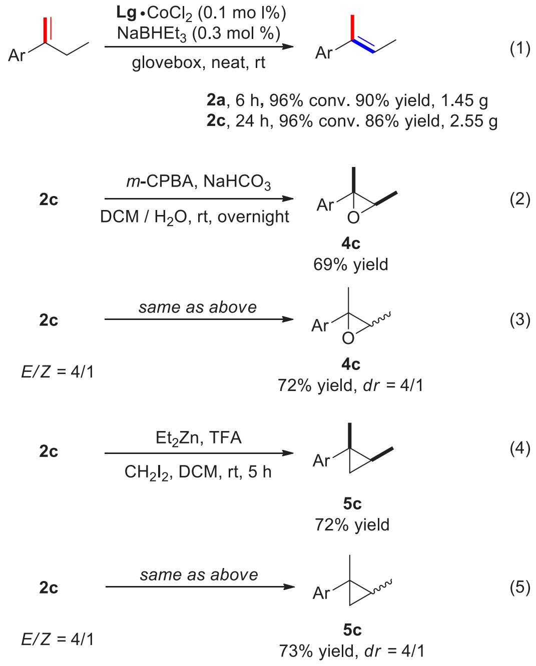
The gram-scale reaction could be smoothly carried out to afford **2a** and **2c** in 90% and 86% yield, respectively (eq 1, Scheme 3). The isomerization product could be further derivatized (eqs 2−5, Scheme 3). The trisubstituted alkenes *E*-**2c** could undergo epoxidation to afford epoxides **4c** in 69% yield with >99/1 dr, which is quite challenging to obtain. An analogous reaction using **2c** with a 4/1 *E*/*Z* ratio furnished **4c**

Scheme 2. Scope of Isomerized Alkenes[a]

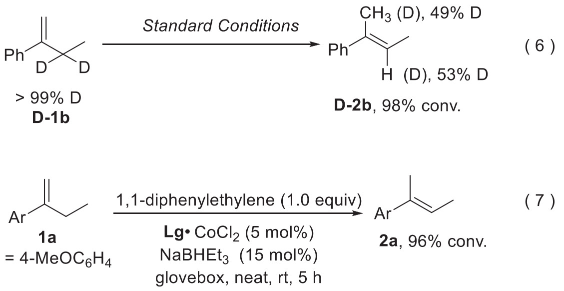


[a]The reaction was conducted using alkenes (0.5 mmol), Le·$CoCl_2$ (0.005 mmol) and $NaHBEt_3$ (0.015 mmol) in neat at room temperature for 1 h in glovebox. The conversions were determined by ^1H NMR using TMSPh or CH_2Br_2 as an internal standard or by GC analysis. Stereoscopic configuration was confirmed by NOE analysis. Without note, $E/Z > 20/1$. [b]$E/Z = 18/1$. [c]Using 5 mol % catalyst loading. [d]3 h. [e]5 h. [f]12 h.

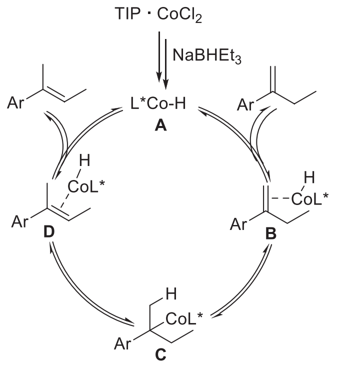
Scheme 3. Gram-Scale Reaction and Further Derivatizations



Scheme 4. Mechanistic Studies



Scheme 5. Proposed Mechanism



in 72% yield with 4/1 dr. The cyclopropane **5c** with high dr (99/1) could be obtained in 72% yield via cyclopropanation of trisubstituted alkenes *E*-**2c**. However, when the same reaction partners were studied using **2c** with an *E*/*Z* ratio of 4/1, **5c** was afforded in 73% yield with 4/1 dr.

To probe the possible mechanism of the migrational isomerization of simple α-alkyl styrene, the deuterium reaction of **D-1b** was performed under standard conditions to afford 98% conversion of **D-2b** with 49% D on the methyl group and 53% D on the vinyl group (eq 6, Scheme 4). The partial absence of deuterium at the vinyl group illustrated that alkene insertion and β-hydride elimination were reversible. The reaction of 1,1-diphenylethylene as a radical trap could be carried out smoothly which might exclude a radical pathway with hydrogen atom transfer (eq 7, Scheme 4).

Based on previous reports[16] and our experimental outcomes, an alkene insertion/β-hydride elimination pathway via a cobalt hydride intermediate for this protocol is shown in Scheme 5. The reduction of TIP·$CoCl_2$ by $NaHBEt_3$ could afford cobalt hydride species **A**, which underwent alkene insertion to deliver cobalt alkyl species **C**. This cobalt alkyl species **C** then underwent β-hydride elimination to regenerate cobalt hydride species and afford trisubstituted alkenes.

In summary, we have developed a cobalt-catalyzed isomerization of alkenes, which could convert 1,1-disubstituted aromatic alkenes to trisubstituted alkenes with high stereoselectivity. The thiazoline iminopyridine ligand was found as a suitable ligand for this efficient transformation. The monosubstituted and the 1,2-disubstituted alkenes could also be suitable under the same conditions to deliver benzylic selective products with excellent conversion and high stereoselectivity.

The reactions were carried out under neat conditions with an up to 960 TON. This operationally simple and atom-economical protocol offers an alternative method for the synthesis of highly stereoselective trisubstituted styrenes. Further studies on efficient and selective transformations based on alkene isomerization is underway 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.9b04305.

Experimental procedures, characterization data for all compounds (PDF)

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Author Contributions

†J.Z. and B.C. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support was provided by NSFC (21922107 and 21772171), Zhejiang Provincial Natural Science Foundation of China (LR19B020001), Center of Chemistry for Frontier Technologies, and the Fundamental Research Funds for the Central Universities.

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https://dx.doi.org/10.1021/acs.orglett.9b04305
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