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Short Communication

# Highly selective reductive cleavage of aromatic carbon–oxygen bonds catalyzed by a cobalt compound

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ABSTRACT

A cobalt catalyst has been demonstrated, for the first time, to be effective for the reductive cleavage of inert aromatic C – O bonds with high selectivity. Compared with previous Ni catalysts, the cobalt catalyst reported here is more commercially available and air-stable.

## 1. Introduction

Transition-metal catalyzed selective activation of aromatic carbon–oxygen bonds is an important process for the conversion of readily available phenolic derivatives into various organic chemicals [1–4]. This process is challenging because the bond energy of the aryl carbon–oxygen bonds is quite high [5,6]. It has been reported that selective activation of aryl carbon–oxygen bonds can proceed smoothly in the presence of catalysts such as Pd and Ni compounds [1–4]. However, there is no example with Co species as the catalyst for this process. Thus our objective is set to develop a Co catalyst for the selective activation of aromatic carbon–oxygen bonds.

The selective reductive cleavage of aromatic carbon–oxygen bonds in aryl ethers is selected as an example to demonstrate our strategy. In literatures, the reductive cleavage of aromatic carbon–oxygen bonds has been reported to suffer from poor selectivity, and the competing cleavage of the π-bonds in aromatic rings is also a troubling problem [7–9]. Until the past few years, several effective homogeneous and heterogeneous catalyst systems based on Ni compounds were developed for the reductive cleavage of aromatic C – O bonds [10–18]. Recently, Rh and Fe compounds were demonstrated to be highly effective for the selectively reductive cleavage [19,20]. In this work, we describe an air-stable Co compound used to catalyze this transformation.

## 2. Experimental

### 2.1. Materials and instruments

All substituted diphenyl ethers were synthesized by the reaction between the corresponding substituted iodobenzenes and substituted phenols [18]. The other chemicals were obtained from commercial vendors and used without further purification.

$^1$H-NMR spectra were recorded on a Bruker 400 MHz instrument with chemical shifts reported in ppm relative to the internal standard of tetramethylsilane. Gas chromatography analyses were performed on a Varian CP-3800 instrument with a FID detector and a CP-WAX 57CB FS capillary chromatographic column (25 m × 0.32 mm). GC–MS spectra were recorded on an Agilent 6890/5973N gas chromatography–mass spectrometer, and data were reported in m/z, % relative intensity, and possible fragment.

### 2.2. General experimental procedure for the reductive cleavage of aromatic carbon–oxygen bonds

To a dried 40 mL tube equipped with a magnetic stirrer, 0.2 mmol of substrate, 0.5 mmol of $LiAlH_4$, 0.03 mmol of $Co(acac)_2$, 0.5 mmol of *t*-BuONa, and 2 or 1.5 mL of toluene were added under nitrogen atmosphere. The reaction tube was sealed and placed in a constant-temperature oil bath set at 140 °C to perform the reaction for 24 h (note: *the pressure tube was required* because the pressure of the reaction system was more than the standard atmospheric pressure). Once the reaction time was reached, the mixture was cooled to room temperature. The mixture was then acidified to pH 5–6 with 2 M hydrochloric

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acid. GC analysis of the mixture provided the GC yields of the products (note: in order to minimize the analysis error, the mixture after the reaction was not purified or concentrated). The reductive cleavage products were identified by GC–MS data. Some products were purified by column chromatography, and identified by $^1$H-NMR.

## 3. Results and discussion

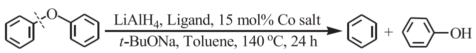
At the start of our investigations, the reductive cleavage of diphenyl ether was chosen as a model reaction to demonstrate the efficiency of various cobalt salts under the following conditions: 0.5 mmol of diphenyl ether, 1.25 mmol of $LiAlH_4$, 0.075 mmol of Co salt, 1.25 mmol of *t*-BuONa, 2 mL of toluene, reaction temperature of 140 °C and reaction time of 24 h. It was found that no conversion took place in the absence of Co salt even after prolonged reaction time (Table 1, entry 1). When $CoCl_2$ was used as the catalyst precursor, only a small amount of phenol and benzene products were obtained. $CoSO_4$ and $Co(NO_3)_2$ were also ineffective as the catalyst precursors. However, the reaction with $Co(CH_3CO_2)_2$ afforded phenol in 93% yield and benzene in 90% yield. Of the screened cobalt salts, $Co(acac)_2$ was optimal, and catalyzed the reaction to give the desired phenol and benzene products in very high yields (Table 1, entry 6). The SIPr·HCl as the ligand was indispensable for the homogeneous Ni-catalyzed reductive cleavage of aromatic C–O bonds [18], which prompted us to add the SIPr·HCl to increase the catalysis ability of the Co catalyst, but a similar result was obtained in case of combination of $Co(acac)_2$ with SIPr·HCl. Change of SIPr·HCl to other ligands such as DMEDA, 2,2′-bipyridine, 1,10-phenanthroline or $PPh_3$ led to a decrease in yields of phenol and benzene (Table 1, entries 8–11). It was noted that no product could be found in the absence of sodium *tert*-butoxide, suggesting that sodium *tert*-butoxide played a key role in the reaction. Although both sodium *tert*-butoxide and $LiAlH_4$ were sensitive to moisture, the removal of trace water in the solvent did not lead to an increase in the yields of the desired products. A high conversion of diphenyl ether was observed in the case of the use of the $Co(acac)_2$ that had been exposed to air for 24 h, revealing that the catalyst is air-stable. It is clear from economic perspectives that the use of $LiAlH_4$ may limit the applications, thus inexpensive hydrogen gas was chosen to replace $LiAlH_4$ as the hydrogen source. Unfortunately, such an attempt was unsuccessful. The reductive cleavages of diphenyl ether using poly(methylhydrosiloxane) or sodium borohydride as the reducing agent were also performed, but no conversion of the substrate was observed in all the cases.

Based on this optimized procedure, a series of diphenyl ethers were tested to evaluate the scope of this novel protocol for the reductive cleavage of aromatic C–O bonds. As shown in Table 2, aromatic C–O bonds in various diphenyl ethers underwent the reductive cleavage smoothly, while the competing cleavage of π-bonds in phenyl rings was not observed in most of the experiments. Steric hindrance was found to have an important effect on the reaction. For example, the C–O bonds of 4,4′-dimethyldiphenyl ether was cleaved to afford the products in high yields, whereas its more sterically hindered *o*-constitutional isomer was less reactive (Table 2, entries 2 and 3).

Alkyl C–O bonds in alkyl aryl ethers were less reactive under our conditions, and the reductive cleavage selectively occurred at the aromatic C–O bonds in the coexistence of aromatic C–O and alkyl C–O bonds (Table 2, entries 4,5,8,9). However, methylene C–O bonds in benzyl phenyl ethers were preferentially cleaved over the aromatic C–O bonds (Table 2, entry 12). In addition, it was noted that the aromatic C–O bonds in phenols were not reactive. Similar phenomenon was reported in previous investigations related to Ni and Rh-catalyzed reductive cleavage of aromatic C–O bonds [13,18].

When 4,4′-dimethoxydiphenyl ether was employed as the substrate, phenol was obtained in 64% yield, indicating that the aromatic C–O bond at the side of the phenylalkyl ether moiety was also cleaved (Table 2, entries 4 and 5). There was no equivalence in yields for the two products in the case of methoxy-substituted diphenyl ethers (Table 2, entries 4 and 5), which seemed to result from the formation of the by-products from the cleavage of the other aromatic C–O bonds besides the most reactive

**Table 1**
Selective reductive cleavage of aromatic C–O bonds in diphenyl ether catalyzed by Co catalysts.[a]

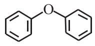
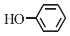
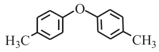
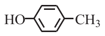
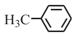
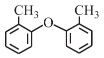
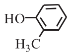
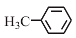
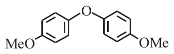
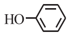
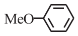
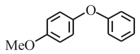
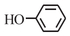
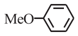
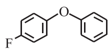
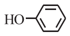
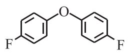
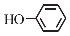
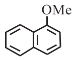
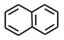
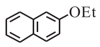
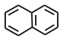
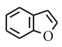
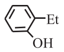
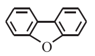
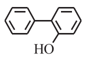
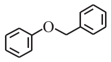
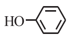
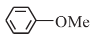


| Entry | Co salt | Ligand | Yield of phenol (%)[b] | Yield of Benzene (%)[b] |
|---|---|---|---|---|
| 1 | – | – | 0 | 0 |
| 2 | $CoCl_2$ | – | 8 | 4 |
| 3 | $Co(NO_3)_2$ | – | trace | trace |
| 4 | $Co(CH_3CO_2)_2$ | – | 93 | 90 |
| 5 | $CoSO_4$ | – | 3 | 5 |
| 6 | $Co(acac)_2$ | – | 96 | 95 |
| 7 | $Co(acac)_2$ | SIPr·HCl[c] | 98 | 93 |
| 8 | $Co(acac)_2$ | DMEDA[c] | 7 | 8 |
| 9 | $Co(acac)_2$ | 2,2′-Bipyridine | 22 | 19 |
| 10 | $Co(acac)_2$ | 1,10-Phenanthroline | 33 | 31 |
| 11 | $Co(acac)_2$ | $PPh_3$ | 25 | 57 |

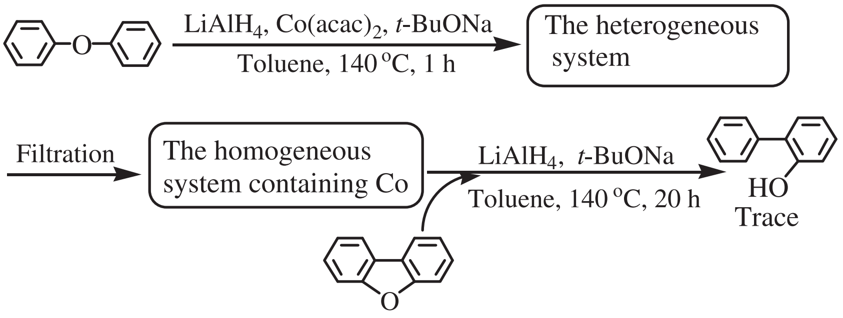
[a] Reaction conditions: diphenyl ether (0.5 mmol), $LiAlH_4$ (1.25 mmol), ligand (0.075 mmol), Co salt (0.075 mmol), toluene (2 mL), *t*-BuONa (1.25 mmol), 140 °C, 24 h.
[b] Determined by GC.
[c] DMEDA: *N*,*N*′-dimethyl ethylenediamine; for the configuration of SIPr·HCl, see Fig. S1.

**Table 2**
Co-catalyzed reductive cleavage of various aromatic C–O bonds.[a]

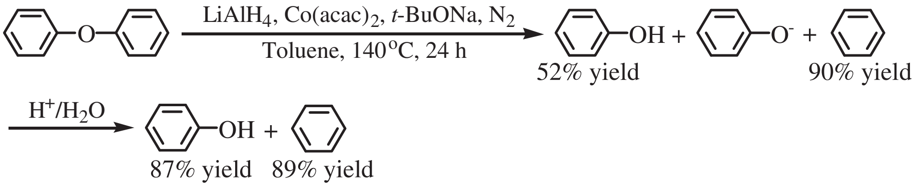
$$\text{R—O—R'} \xrightarrow[t\text{-BuONa, Toluene, } 140\,^{\circ}\text{C, 24 h}]{\text{LiAlH}_4\text{, 15 mol\% Co(acac)}_2} \text{R—OH} + \text{H—R'}$$

| Entry | Substrate | Product 1 | GC yield (%)[b] | Product 2 | GC yield (%)[b] |
|---|---|---|---|---|---|
| 1 |  |  | 93 |  | 92 |
| 2 |  |  | 98[c] |  | ~100 |
| 3 |  |  | 13 |  | 20 |
| 4 |  |  | 64 |  | 89 |
| 5 |  |  | 85 |  | 44 |
| 6 |  |  | 90 |  | 92 |
| 7 |  |  | 90 |  | 95 |
| 8 |  |  | 49 | – | – |
| 9 |  |  | 62 | – | – |
| 10 |  |  | 80 | – | – |
| 11 |  |  | 93[c] | – | – |
| 12 |  |  | 90 | – | – |
| 13 |  |  | Trace | – | – |

[a] Reaction conditions: substrate (0.2 mmol), $LiAlH_4$ (0.5 mmol), $Co(acac)_2$ (0.03 mmol), toluene (2 or 1.5 mL), *t*-BuONa (0.5 mmol), 140 °C, 24 h.
[b] Determined with an internal standard.
[c] The isolated yields were respectively 88% (entry 2) and 81% (entry 11).



**Scheme 1.** The investigation on the catalytic activity of homogeneous species.



**Scheme 2.** The reductive cleavage of diphenyl ether.

C – O bond. Indeed, benzene and 4-methoxyphenol by-products were observed (Table 2, entry 5). The aromatic C – O bond in phenyl methyl ether without substitute group showed poor reactivity (Table 2, entry 13), and the introduction of methoxy or hydroxyl to the phenyl rings increased the reactivity of phenyl methyl ether, but it is confusing that the resulting experimental results from the reactions of methoxy or hydroxyl-substituted phenyl methyl ether were less reproducible.

Next, several control experiments were carried out to gain insight into the mechanism of the Co catalyst. It is possible that $Co^{2+}$ catalyst precursor can be effectively reduced by the highly reducing agents to low oxidation states [21], therefore the heterogeneous Co clusters or particles based on the reduction of $Co(acac)_2$ catalyst precursor may be the real catalytically active species. As expected, a certain amount of heterogeneous black clusters or particles was observed in the reaction system. After the heterogeneous species was filtered out when the reaction proceeded for 1 h, the obtained homogeneous system had less catalytic activity (see Scheme 1). This revealed that the heterogeneous Co species seemed to be the real active species. But the obtained heterogeneous species from the filtration of the reaction mixture had less catalytic activity. At the end of the reaction, 0.2 mmol diphenyl ether and 0.5 mmol $LiAlH_4$ were added into the mixture containing the catalyst to perform the reaction for another 24 h, and only 38% substrate was converted. These experimental results suggest that the catalytic species are easy to be deactivated and have a poor recyclability. Upon the basis of previous literatures [17,18,22] and our experimental results (see Scheme 2), we propose a plausible mechanistic pathway (Scheme 3), where the oxidative addition and the reductive elimination successively occur to give benzene and phenate products. Surprisingly, the phenol product was also observed before the acidification (Scheme 2), which is possibly rationalized by assuming that a part of phenate is converted to phenol via the transfer of the $H^+$ from the residual $H_2O$ in the solvent to phenate. It is worth noting that the formation of the reductive cleavage products does exist in the reaction medium before the hydrolysis (acidification) step based on the experimental results that the benzene and phenol products were observed in respectively 90% and 52% yield before the acidification (Scheme 2).

## 4. Conclusion

In summary, it is demonstrated for the first time that the reduced cobalt is an effective catalyst for the reductive cleavage of inert aryl C – O bonds under the conditions of the present study. The present approach allowed a series of aromatic C – O bonds in diphenyl ethers to be reductively cleaved into the corresponding products in moderate to high yields. It was suggested that the heterogeneous Co species from the reduction of $Co(acac)_2$ might be the real catalytically active species. The $Ni(COD)_2$ used in previous literatures is more expensive and easily decomposed [10–18]. Compared with the $Ni(COD)_2$ catalyst, the present Co catalyst is commercially available and air-stable. However, attempt to use inexpensive hydrogen gas to replace $LiAlH_4$ as the hydrogen source was unsuccessful. Investigation on improving the present method to be more economic is underway in our laboratory.

## Acknowledgments

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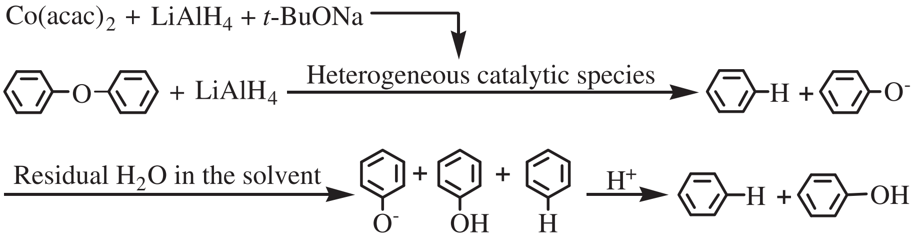

**Scheme 3.** Considerations on the mechanistic pathway.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.03.036.

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