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A simple and highly effective method for hydrogenation of arenes by $[Rh(COD)Cl]_2$

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ABSTRACT

Hydrogenation of arenes, including chiral BINOLs and the lignin model compounds, has been achieved efficiently by using the simple complex $[Rh(COD)Cl]_2$ as catalyst precursor.

The complete hydrogenation of arenes to non-aromatic cyclic compounds and that of phenols to alcohols represent important industrial catalytic transformation due to the increasing industrial demand for low aromatic diesel fuels.[1] Moreover, the hydrogenation of benzene to cyclohexane, which has been used primarily in the production of adipic acid, a precursor to nylon, is probably the most important industrially practiced arene hydrogenation reaction.[2] In most cases, arene hydrogenation has been performed with heterogeneous catalysts such as Rh/C, Rh/Al_2O_3, Pd/C and Raney nickel or others under drastic reaction conditions.[3] Recently, Roucoux et al. and Xu et al. have developed the liquid–liquid biphasic conditions for arene hydrogenation.[4] Finke et al. used the metal nanoparticles as catalysts for the hydrogenation of arenes and ketones.[5] Park and coworkers reported rhodium and iridium nanoparticles as the catalysts for the hydrogenation of arenes.[6] Other conditions for arene hydrogenation were also developed, such as supercritical CO_2 conditions,[7] ionic liquid condition,[8] and others.[9]

Recently, we developed a method for the highly enantioselective hydrogenation of quinoline derivatives using chiral iridium complexes.[10] As a test case, we attempted the hydrogenation of substituted phenols, but the almost racemic products were obtained in all tried conditions using chiral rhodium or ruthenium complexes as catalysts. Further studies found that the hydrogenation reaction can still occur in air using the $[Rh(COD)Cl]_2$ as catalyst in the absence of chiral ligands and bases. In this Letter, we reported the hydrogenation of arenes, including phenols, especially enantiopure BINOL in air using $[Rh(COD)Cl]_2$.

In our initial investigation, we found that the $[Rh(COD)Cl]_2$ could catalyze the hydrogenation of phenol in air with moderate activity. In order to obtain high selectivity of the main product, the effect of solvents was evaluated (Table 1). This reaction was strongly solvent dependent. For CH_2Cl_2, the reactivity is high, and the selectivity is moderate. Low reactivity were obtained in THF, EtOAc, and EtOH, good reactivity with moderate selectivity was obtained in MeOH, and high reactivity and selectivity of compound **2a** were obtained in *i*-PrOH (Table 1, entry 6). Excitingly, we found that the reactions performed in air revealed high catalytic activity than those in nitrogen (Table 1, entries 6 and 7). The results revealed that the hydrogenation was oxygen promoted by using this method.[11] Subsequently, when the catalyst loading was reduced to 0.01 mol %, only 33% of conversion was obtained. Next, some commercially available stabilizers were also investigated for the hydrogenation of phenol. The results were summarized in Table 1 and 4 Å MS gave the best result.

In the presence of 0.25 mol % of $[Rh(COD)Cl]_2$ and 50 mg of 4 Å MS, a variety of substituted phenols have been tested to examine the reaction scope (Table 2). The hydrogenation of phenol was completed, and cyclohexanol was the sole product (Table 2, entry 1). The substituted monocyclic phenols were hydrogenated smoothly with excellent reactivities and selectivities to give the substituted cyclohexanols (Table 2, entries 2–6). However, the hydrogenation of 2-hydroxybiphenyl was not complete under the standard conditions, which might be attributed to steric effect. When the catalyst loading was enhanced to 0.50 mol %, full conversion and 95% selectivity were obtained (Table 2, entry 3). This hydrogenation system could tolerate a big *t*-butyl group, and gave high yield of 4-*t*-butyl cyclohexanol, which was an useful intermediate in the fragrance and perfume industries (Table 2, entry 6).

We also conducted the hydrogenation of benzene and some of its classical derivatives under optimal conditions (Table 3). The results showed that the hydrogenation was complete (Table 3, entries 1–4). For the heteroaromatic compounds such as 2-methylfuran, good reactivity and selectivity of **4e** could also be obtained. Similar results were also obtained in the hydrogenation of **3f** and **3g** (Table 3, entries 6 and 7). Two products were obtained (72% of **4h** and 28% of **4i**) in the hydrogenation of benzalacetone. For methyl 4-hydrobenzoate, **4j** was obtained as the desired and sole product. From these results, it might be inferred that this

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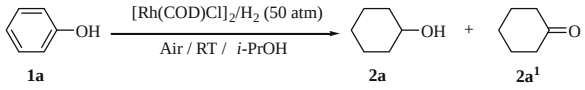
Table 1
Optimization of the reaction conditions for the hydrogenation of phenol[a]

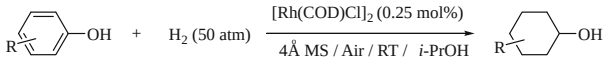


1a 2a 2a[1]

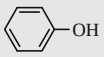
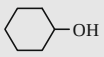
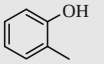
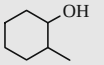
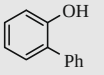
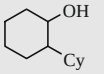
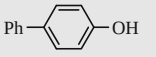
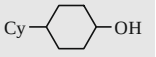
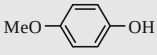
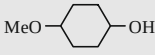
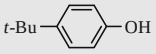
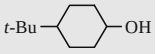
Entry	Solvent	Stabilizer	Convn.(%)[c]	**2a**(%)	**2a**[1](%)
1	THF	None	24	12	12
2	CH_2Cl_2	None	97	35	56
3	EtOAc	None	36	19	17
4	MeOH	None	93	62	26
5	EtOH	None	45	22	20
6	*i*-PrOH	None	>99	98	0
7	*i*-PrOH	None	52[d]	22	24
8	*i*-PrOH	None	33[b]	17	6
9	*i*-PrOH	4 Å MS	>99[b]	99	0
10	*i*-PrOH	Al_2O_3	87[b]	62	25
11	*i*-PrOH	Aliquat 336	66[b]	46	20
12	*i*-PrOH	PVP	56[b]	27	26
13	*i*-PrOH	TBAB	32[b]	18	14

[a] Conditions: 10 mmol substrate, $[Rh(COD)Cl]_2$ (1.3 mg, 0.0025 mol, 0.025 mol %), 10 mL solvent, 50 atm H_2, H_2/air = 50:1, rt, 14–16 h.
[b] 25 mmol substrate, $[Rh(COD)Cl]_2$ (1.3 mg, 0.0025 mol, 0.01 mol %), 20 mL solvent.
[c] Determined by GC analysis of the crude product.
[d] The reaction was carried out in N_2.

Table 2
Hydrogenation of phenol derivatives[a]



1 2

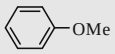
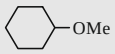
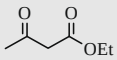
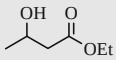
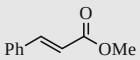
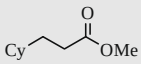
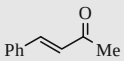
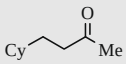
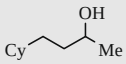
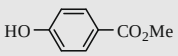
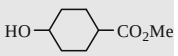
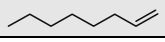
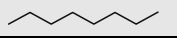
Entry	Substrate	Selectivity (%)[b]	*cis*/*trans* [c]	Product
1		99 (**2a**)	–	
2		97 (**2b**)	82:18	
3		95 (**2c**) [d]	81:19	
4		99 (**2d**)	69:31	
5		92 (**2e**)	81:19	
6		92 (**2f**)	63:37	

[a] Conditions: 1 mmol substrate, $[Rh(COD)Cl]_2$ (0.25 mol %), 6 mL *i*-PrOH, 50 mg 4 Å MS, 50 atm H_2, H_2/air = 50:1, rt, 14–16 h.
[b] Determined by GC analysis of the crude product, 100% convn.
[c] Determined by ^1H NMR analysis of the crude product.
[d] $[Rh(COD)Cl]_2$ (0.5 mol %) was used.

hydrogenation system is more effective for the hydrogenation of alkenes and arenes than that of ketones. It is well known that the hydrogenation of higher olefins is far less effective. Here, this system was successfully used in the hydrogenation of 1-octene (Table 3, entry 10).

To show the effectiveness of the catalyst further, we studied the hydrogenation of some arenes under solvent-free conditions. Benzene was hydrogenated using $[Rh(COD)Cl]_2$ (0.05 mol %) in full conversion, and **4a** was obtained as the sole product (Table 4, entry 1). Toluene and anisole were also completely converted to the corresponding **4b** and **4c**, respectively. Importantly, the hydrogenation of 2-methylfuran and 1-octene was also complete with high selectivities; **4e** and **4k** were found as the sole products. However,

Table 3
Hydrogenation of benzene derivatives and others[a]

Entry	Substrate	Selectivity (%) [b]	Product
1		97 (**4a**)	
2		96 (**4b**)	
3		92 (**4c**)	
4		99 (**4d**)	
5		93 (**4e**)	
6		>95 (**4f**)[c]	
7		>95 (**4g**)[c]	
8		72 (**4h**)[c]	
		28 (**4i**)[c]	
9		>95 (**4j**)[c]	
10		92 (**4k**)	

[a] Conditions: 1 mmol substrate, $[Rh(COD)Cl]_2$ (0.25 mol %), 6 mL *i*-PrOH, 50 mg 4 Å MS, 50 atm H_2, H_2/air = 50:1, rt, 14–16 h.
[b] Determined by GC analysis of the crude product, 100% convn.
[c] Determined by ^1H NMR analysis of the crude product.

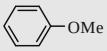
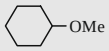
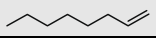
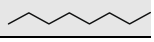
styrene gave a mixture of **4d** (72%) and **4l** (28%), which suggested that the hydrogenation of alkenes is easier than that of benzene ring (Table 4, entry 5).

At the same time, phenol was hydrogenated in a gram scale at room temperature (Table 5). We performed the reaction of 2.5 g of phenol with $[Rh(COD)Cl]_2$ (0.01 mol %, 1.3 mg) under 50 atm of H_2. **2a** was found as the sole product with full conversion, and the TON was up to 10,640 (Table 5, entry 4). When we added the substrate up to 5.0 g with the same quantity of $[Rh(COD)Cl]_2$ (0.005 mol %, 1.3 mg) under 50 atm of H_2, 84% of **2a** and 16% of cyclohexanone with 97% conversion were determined by GC analysis, and the TON was up to 20,642 (Table 5, entry 5). Importantly, the catalyst in situ from the complex $[Rh(COD)Cl]_2$ showed much higher reactivity than the commercial Rh/C as a catalyst in the hydrogenation reaction (Table 5, entries 4 and 6).

Optically active H_8-1,1′-bi-2-naphthol (H_8-BINOL) is a very useful starting material for the synthesis of relevant chiral ligands.[12] However, the literature about the synthesis of their derivatives is rare.[13] Gram et al. reported a widely used method for the synthesis of H_8-BINOL using PtO_2 as a catalyst; however, the catalyst is very expensive and the reaction time was too long (7 days).[13a] Sugimura developed the hydrogenation of BINOL using Pd/C as a catalyst, and the yield was somewhat low (70%).[13b] Ding et al. reported the reduction of chiral BINOL using Raney Ni/Al alloy with 97% ee of product.[13c] Recently, Korostylev et al. developed the hydrogenation of BINOL using Pd/C and Ru/C as catalysts.[13d] Motoyama et al. reported the hydrogenation of BINOLs using carbon nanofiber-supported ruthenium nanoparticles as catalysts.[13e] Here, we report a new and efficient method for hydrogenation of BINOL using $[Rh(COD)Cl]_2$ in *i*-PrOH.

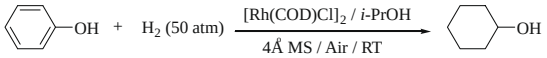
The hydrogenation of binaphthols was carried out with $[Rh(COD)Cl]_2$ in *i*-PrOH at 80 °C under 50 atm of H_2 pressure (Table 6). Under these conditions, the reaction proceeds well, and

Table 4
Hydrogenation of various arenes at room temperature without solvent[a]

Entry	Substrate	Convn.(%)[b]	Product
1		>95 (**4a**)	
2		>95 (**4b**)	
3		>95 (**4c**)	
4		>95 (**4e**)	
5		28 (**4d**)	
		72 (**4l**)	
6		>95 (**4k**)	

[a] Conditions: 20 mmol substrate, $[Rh(COD)Cl]_2$ (0.05 mol %), 100 mg 4 Å MS, 50 atm H_2, H_2/air = 50:1, rt, 14–16 h.
[b] Determined by ^1H NMR analysis of the crude product.

Table 5
Hydrogenation of phenol in a gram scale[a]

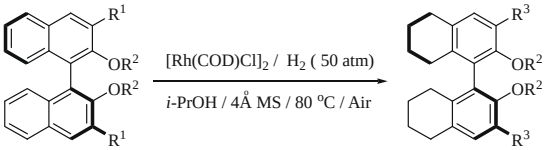


1a **2a**

Entry	Substrate (g)	Cat. (mol %)	Convn./**2a**(%)[b]	TON
1	1.0	0.1[c]	99/98	1064
2	1.0	0.05[d]	99/99	2128
3	1.0	0.02	99/99	4256
4	2.5	0.01	99/99	10,640
5	5.0	0.005	97/84[e]	20,642
6	2.5	0.02[f]	90/67[g]	4788

[a] Conditions: $[Rh(COD)Cl]_2$ (1.3 mg, 0.0025 mmol), *i*-PrOH, 100 mg 4 Å MS, 50 atm H_2, H_2/air = 50:1, rt, 14–16 h.
[b] Determined by GC analysis of the crude product.
[c] $[Rh(COD)Cl]_2$ (5.2 mg) was used.
[d] $[Rh(COD)Cl]_2$ (2.6 mg) was used.
[e] 16% of cyclohexanone was detected.
[f] Rh/C (20.6 mg, 0.0050 mmol) was used as a catalyst.
[g] 33% of cyclohexanone was detected.

Table 6
Hydrogenation of BINOL derivatives[a]



5 **6**

Entry	$R^1/R^2/R^3$	Yield (%)[b]	ee (%)[c]
1	H/H/H	99 (**6a**)	>99
2	Me/H/Me	97 (**6b**)	>99
3	Ph/H/Cy	99 (**6c**)	>99
4	H/MOM/H	95 (**6d**)	>99
5	H/Me/H	98 (**6e**)	>99

[a] Conditions: 0.25 mmol substrate, $[Rh(COD)Cl]_2$ (1 mol %), 50 mg 4 Å MS, 50 atm H_2, H_2/air = 50:1, rt, 14–16 h.
[b] Determined by ^1H NMR analysis of the crude product.
[c] Determined by HPLC.

the corresponding optically active **6a–e** were obtained with excellent yields.

To evaluate the applicability of the new technique to a multigram scale synthesis, we performed the hydrogenation of 10.0 g of BINOL with 0.1 mol % of $[Rh(COD)Cl]_2$ (80 °C, 50 atm of H_2, in air). Full conversion was achieved, and optically pure **6a** was obtained.

For the above catalytic system for hydrogenation of arenes using the simple complex $[Rh(COD)Cl]_2$, the active catalytic species may be rhodium nanoparticles or heterogeneous rhodium catalysts. It is well known that mercury is a good and accepted heterogeneous catalyst poison, due to its classical adsorption onto the catalyst surface.[4b,5a] Therefore, the behavior of the catalytic system was tested by using this method. Subsequently, phenol was selected as the reference substrate in the mercury poisoning experiment. A dark reaction solution, which was obtained from the complex $[Rh(COD)Cl]_2$, was stopped after about 50% conversion, and 300 equiv of mercury was added. After stirring for 1 h, the solution was reconnected to stainless steel autoclave, and the hydrogen was charged again. No further loss of phenol was detected, this result showed that Hg had completely poisoned the catalyst (see Supplementary data), which offer some evidences that rhodium(0) nanoparticles may be the catalytic active species.

In our catalytic system, air or oxygen is crucial for the reactivity and selectivity. Recently, Liu reported the oxygen-promoted Suzuki coupling reaction by the in situ-generated palladium nanoparticles under aerobic condition.[14] The report prompted us to suppose that the catalysts may be rhodium nanoparticles generated from the complex $[Rh(COD)Cl]_2$ in situ under aerobic condition in our reaction. As a result, the oxygen-promoted rhodium nanoparticles might be formed easily and maintained high catalytic activity (see Supplementary data).[2c,f,14]

In summary, we have developed a simple, highly effective hydrogenation of arenes, which provide direct access to saturated cyclic compounds. Furthermore, enantiopure H_8-BINOL derivatives could also be obtained easily by using this method. Further investigation on the mechanism and the range of substrates is currently in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.12.108.

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