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Chemoselective transfer hydrodechlorination of aryl chlorides catalyzed by Cp*Rh complexes

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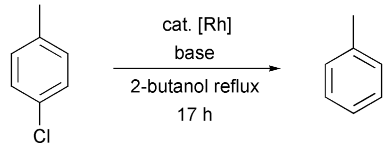
An effective Cp*Rh catalyzed transfer hydrodechlorination of aryl chlorides was achieved with high tolerance towards a variety of functional groups using 2-butanol as a hydrogen source.

The dechlorination of aryl chlorides is an extremely important chemical transformation from the preparative and environmental point of view.[1] Recently, much attention has focused on the transition metal catalyzed dechlorination of aryl chlorides. A large number of dechlorination systems have been developed, but these systems are mainly applicable to the dechlorination of aryl chlorides without a functional group. These dechlorination systems involve the use of metal hydrides,[2] metal alkoxide,[3] hydrosilanes,[4] molecular hydrogen,[5] Grignard reagents,[6] and sodium formate[7] as the hydrogen source. Dechlorination systems with alcohols as the hydrogen source have been relatively unexplored[8] in spite of their usefulness in other hydrogen transfer reactions as a mild hydrogen donor. In this paper we report a new system for transfer hydrodechlorination of a variety of aryl chlorides catalyzed by Cp*Rh complexes with 2-butanol as a hydrogen source.

Initially, we investigated the rhodium-catalyzed dechlorination of 4-chlorotoluene under various conditions. The reactions were carried out in the presence of a catalytic amount of a rhodium complex together with base in 2-butanol under reflux for 17 h to afford toluene (eqn. (1)). The results are



(1)

summarized in Table 1. At first we examined the catalytic activities of several rhodium complexes. The complexes with η^5-pentamethylcyclopentadienyl (Cp*) ligands, $[Cp^*RhCl_2]_2$ (**1**) and $Cp^*Rh(OAc)_2\cdot H_2O$ (**2**) showed high catalytic activity to give toluene in yields of 92 and 96%, respectively (entries 1, 2). On the other hand, rhodium complexes without Cp* ligands were less active (entries 3, 4). Next, the effect of various bases was examined with $[Cp^*RhCl_2]_2$ (**1**) as a catalyst. The catalytic activity was closely related to the base. Among inorganic bases, KOH and Cs_2CO_3 were highly effective for the present reaction

Table 1 Dechlorination of 4-chlorotoluene by various catalytic systems[a]

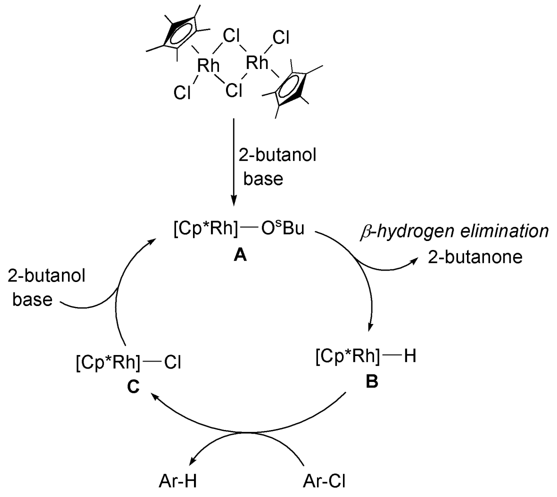
Entry	Catalyst (mol% Rh)	Base (eq.)	Yield[b] (%)
1	$[Cp^*RhCl_2]_2$ (**1**) (2.5)	KOH (2.0)	92
2	$Cp^*Rh(OAc)_2\cdot H_2O$ (**2**) (2.5)	KOH (2.0)	96
3	$RhCl(PPh_3)_3$ (2.5)	KOH (2.0)	63
4	$[RhCl(CO)_2]_2$ (2.5)	KOH (2.0)	15
5	None	KOH (2.0)	0
6	**1** (5.0)	NaOH (2.0)	50
7	**1** (5.0)	K_2CO_3 (1.0)	61
8	**1** (5.0)	Cs_2CO_3 (1.0)	85
9	**1** (5.0)	Et_3N (2.0)	66
10	**1** (5.0)	Cy_2NMe (2.0)	84
11	**1** (5.0)	KOH (1.0)	64
12[c]	**1** (5.0)	KOH (2.0)	60
13[d]	**1** (5.0)	KOH (2.0)	2

[a] The reaction was carried out under reflux with 4-chlorotoluene (2.0 mmol), catalyst, and base in 2-butanol (6 cm^3) for 17 h. [b] Determined by GC. [c] The reaction was carried out in 2-propanol. [d] The reaction was performed in ethanol.

Table 2 Dechlorination of various aryl chlorides catalyzed by Cp*Rh complexes[a]

Entry	Aryl chloride	Catalyst (mol% Rh)	Base (eq.)	Yield[b] (%)
1	4-Chlorotoluene	**2** (2.5)	KOH (2.0)	(96)
2	3-Chlorotoluene	**1** (5.0)	KOH (2.0)	(92)
3	2-Chlorotoluene	**1** (5.0)	KOH (2.0)	(93)
4	2,6-Dichlorotoluene	**1** (5.0)	KOH (3.8)	(96)
5	3,4-Dichlorotoluene	**1** (5.0)	KOH (4.0)	(76)
6	2,3-Dichlorotoluene	**2** (5.0)	KOH (3.8)	(47)
7	1-Chloronaphthalene	**2** (1.0)	KOH (2.0)	98
8	2-Chloronaphthalene	**2** (1.0)	KOH (2.0)	96
9	4-Chlorobiphenyl	**2** (1.0)	KOH (2.0)	100
10	Methyl 4-chlorobenzoate	**2** (5.0)	Cy_2NMe (1.0)	95
11	4-Chlorobenzamide	**2** (5.0)	Cy_2NMe (1.0)	95
12	4-Chlorobenzoic acid	**2** (5.0)	Cy_2NMe (2.0)	96
13	4-Chloroacetophenone	**2** (5.0)	Cs_2CO_3 (1.0)	15 + 85[c]
14	4-Chloroanisole	**2** (5.0)	KOH (2.0)	(93)
15	1-Amino-4-chloronaphthalene	**2** (2.0)	KOH (2.0)	79
16	4-Chloro-1-naphthol	**2** (1.0)	KOH (3.1)	88

[a] The reaction was carried out under reflux with aryl chloride (2.0 mmol), catalyst and base in 2-butanol (6 cm^3) for 17 h. [b] Isolated yield. The values in parentheses are GC yields. [c] Yield of acetophenone (15%) and 1-phenylethanol (85%).



Scheme 1 Possible mechanism for the dechlorination of aryl chlorides catalyzed by Cp*Rh complexes.

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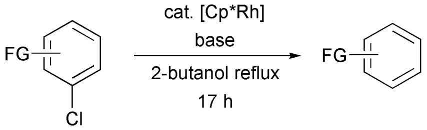
(entries 1, 6–8). An organic base, Cy_2NMe was also effective (entry 10), while Et_3N showed rather low activity (entry 9). The best result was obtained with two equivalents of KOH. The yield of toluene was reduced when an equimolar amount of KOH was employed (entry 11). When the reaction was carried out in 2-propanol or ethanol, the yield of toluene decreased (entries 12, 13), indicating that 2-butanol would be the best hydrogen donor for the present transfer hydrodechlorination system.

Under the optimal conditions determined above, dechlorination reactions of a variety of aryl chlorides were carried out (eqn. (2)). The results are summarized in Table 2. All the isomers of chlorotoluene were dechlorinated giving excellent yields of toluene (entries 1–3). The double dechlorination of dichlorotoluenes proceeded by use of 3.8–4.0 equivalents of KOH (entries 4–6). Chloronaphthalenes and 4-chlorobiphenyl were dechlorinated quite readily, requiring a smaller amount of catalyst (1.0 mol% Rh) (entries 7–9). Various electron-withdrawing (ester, amide, carboxylic acid and ketone) and electron-donating groups (alkoxy, amino and hydroxy) in aryl chlorides were well-tolerated for present catalytic dechlorination to give the corresponding aromatic products in excellent yields (entries 10–16). In the reactions of aryl chlorides with ester and amide substituents (entries 10 and 11), employment of Cy_2NMe as a base was appropriate to prevent hydrolysis. Dechlorination of 4-chloroacetophenone proceeded effectively with use of Cs_2CO_3 as a base, but reduction of the carbonyl group also occurred to give 1-phenylethanol (85%) as well as acetophenone (15%).



(2)

Although the mechanism for the present dechlorination reaction is not completely clear as of yet, a possible mechanism is shown in Scheme 1. The first step of the reaction would involve the formation of Cp*Rh alkoxide (**A**) by the reaction of Cp*Rh precursor with 2-butanol and base. Then the intermediate **A** would transform into Cp*Rh hydride (**B**) *via* β-hydrogen elimination from alkoxo ligand. Aryl chlorides would react with **B** to give dechlorinated arene and Cp*Rh chloride (**C**). The intermediate **C** would react with 2-butanol and base to regenerate the intermediate **A**.

In summary, we have shown a new catalytic system for transfer hydrodechlorination of a large variety of aryl chlorides with use of Cp*Rh catalysts and 2-butanol as a hydrogen source.

Notes and references

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