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Chemoselective Transfer Hydrogenation of α,β-Unsaturated Ketones Catalyzed by Pincer-Pd Complexes Using Alcohol as a Hydrogen Source

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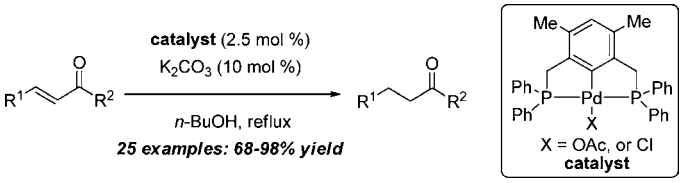
ABSTRACT



A pincer-Pd complex was utilized in the chemoselective transfer hydrogenation of α,β-unsaturated ketones using *n*-BuOH as a hydrogen source and solvent. Good to excellent yields were obtained for various substrates even with reducible groups. Based on deuterium-labeling experiments, the reaction mechanism is proposed to occur via a pincer-Pd-hydride intermediate.

The chemoselective transfer hydrogenation of α,β-unsaturated ketones is an important tactic in organic synthesis. A great amount of progress has been made in this area, especially concerning transition-metal-catalyzed transfer hydrogenations.[1−3] Unlike the wide use of silicon hydride in this reaction, which is efficient but has problems associated with safety, cost, and purification, other cheaper and greener hydrogen sources have not been fully investigated.[2,3] Use of alcohol as a cost-effective and environmental-friendly hydrogen source represents an attractive alternative. A few examples using alcohol as a hydrogen source in this type of reaction catalyzed by transition metal complexes of

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monodentate and bidentate phosphine ligands have been reported.[3] Among them, Sodeoka reported impressive work on the stereoselective conjugate reduction of β,β-disubstituted α,β-unsaturated ketones utilizing the complexes of Pd-BINAP and Pd-DUPHOS.[3f,g] However, the research in this field is inadequate and a more efficient catalytic system is still greatly desired to achieve higher chemoselectivity and activity.

Compared with the transition metal complexes of monodentate and bidentate ligands, individual tridentate pincer-metal complexes[4] (**I** in Figure 1) are considered to be more structurally stable and to possess fewer catalytic intermediate conformations. This usually improves selectivity and activity leading to excellent catalytic behavior in reactions involving metal-hydride intermediates[5] and others.[6] Pd-hydride mediated transfer hydrogenations have been extensively studied for the reduction of various unsaturated compounds.[7] Recently, pincer-Pd-hydride complexes have attracted increasing attention for their application in O_2 and CO_2 insertion reactions.[8] However, there are no reports concerning the insertion of other unsaturated compounds into pincer-Pd-hydride complexes.

Herein we present the first example of chemoselective transfer hydrogenations of α,β-unsaturated ketones catalyzed by PCP pincer-Pd complexes (**II** in Figure 1), employing the easily accessible and inexpensive *n*-BuOH as a hydrogen donor and solvent.[9] We envisioned that the pincer-Pd-hydride complex generated in this reaction system may act as a key intermediate in the catalytic cycle.

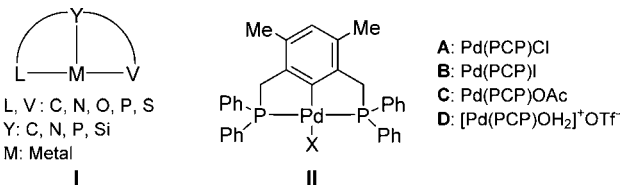

Figure 1. Pincer-metal complexes and PCP pincer-Pd complexes.

The PCP pincer ligand in **II** was readily synthesized from 1,5-bis(chloromethyl)-2,4-dimethylbenzene using a modified procedure[10] involving nucleophilic substitution by diphenylphosphine oxide and reduction by $HSiCl_3$. The ligand was coordinated with Pd salts to form the PCP pincer-Pd complexes **II** possessing different anions, and the structures of complexes **A** and **C** were confirmed by single crystal X-ray diffraction (for the details, see Supporting Information (SI)).

The prepared PCP pincer-Pd complex **A** was tested in the conjugate reduction of chalcone **1a** to investigate the

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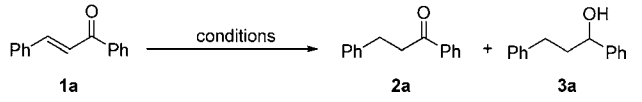
influence that commercially available, inexpensive alcohols had on the reaction (Table 1). When the reaction was conducted in primary alcohols and *i*-PrOH in the presence of NaOH (25 mol %), the reduced product **2a** was obtained predominantly with none or a trace amount (<1%) of the over-reduced product **3a** (entries 1−9). Compared to other alcohols bearing β-H atoms adjacent to the hydroxyl group, the use of MeOH gave a relatively lower yield (entry 1). While using the acidic alcohol TFE, almost no product was detected (entry 8). When the reaction was performed in *s*-BuOH and 2-pentanol, over-reduced product **3a** was obtained in 8% and 11% yields, respectively (entries 10−11). It was found that *n*-BuOH was the most suitable solvent for the conjugate reduction of **1a**, giving the desired product in the highest yield (entry 4).

Table 1. Influence of Different Hydrogen Sources and Solvents[a]



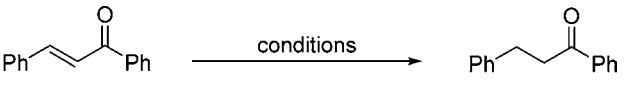
1a **2a** **3a**

		yield (%)[b]	
entry	solvent	**2a**	**3a**
1	MeOH	9[c]	0
2	EtOH	53	0
3	*n*-PrOH	62	<1
4	*n*-BuOH	72	<1
5	*i*-BuOH	44	0
6	*n*-pentanol	62	<1
7	3-methyl-1-butanol	66	<1
8	TFE	<1[c]	0
9	*i*-PrOH	22	0
10	*s*-BuOH	19	8[d]
11	2-pentanol	26	11[d]

[a] Reaction conditions: **1a** (0.50 mmol), **A** (5 mol %), NaOH (25 mol %), solvent (5 mL), 65 °C, 36 h. [b] Isolated yield. [c] GC yield based on recovered **1a**. [d] GC yield based on **2a**.

The yield could be further increased to 93% by using 10 mol % K_2CO_3 as a base and performing the reaction under reflux conditions in *n*-BuOH (for details concerning the screening of bases and temperatures, see SI). We next investigated the performance of different pincer-Pd complexes **A**−**D** (Table 2). Using **C** as the catalyst, the desired product was obtained in a better yield than that by using **A** (entry 3 vs 1), while **B** and **D** showed lower activity (entries 2, 4). No obvious decrease in yield was observed when 2.5 mol % of **C** was used to catalyze the reaction (entry 5). An excellent yield of 94% was still obtained with 1 mol % of **C** (entry 6). Further decreasing the amount of **C** to 0.5 mol % gave **2a** in 91% yield (entry 7). These results show the high catalytic activity of the pincer-Pd complex **C**. It is noteworthy that this reaction does not require Schlenck conditions or special equipment and that the procedure can even be performed under air.

Table 2. Influence of Catalysts with Different Anions[a]



1a **2a**

entry	catalyst (mol %)	time (h)	yield (%)[b]
1	**A** (5)	2.5	93
2	**B** (5)	18	10[c]
3	**C** (5)	1	96
4	**D** (5)	18	80
5	**C** (2.5)	2	96
6	**C** (1)	14	94
7	**C** (0.5)	36	91

[a] Reaction conditions: **1a** (0.50 mmol), catalyst, K_2CO_3 (10 mol %), *n*-BuOH (5 mL), at reflux. [b] Isolated yields. [c] GC yield based on recovered **1a**.

To demonstrate the general applicability of the pincer-Pd complex **C**, various α,β-unsaturated ketones were subjected to the optimized reaction conditions (Table 3). Both electron-donating and -withdrawing aromatic substituted α-enones were reduced to provide high yields of the desired products (entries 2−10, 12−20, 24). The position of the substituted groups did not significantly affect reactivity (entries 2−4, 12−14). Halogen-substituted chalcones also gave good to excellent yields of products (entries 6−8, 16−18). Additionally, we also studied the effect of pincer-Pd complex **C** on the transfer hydrogenation of heterocyclic α-enones. To our delight, it still exhibited high activity and selectivity to provide the desired products in excellent yield (entries 21, 22). These transformations represent the first synthesis of furyl or thienyl substituted saturated ketones via conjugate reduction. The high reactivity and selectivity of the pincer-Pd complex **C** to halogen or heterocyclic substituted α-enones provides an attractive alternative for the chemoselective transfer hydrogenation of α,β-unsaturated carbonyl compounds. Alkyl substituted α-enones were also reduced in good yields (entries 11, 23, and 25). A trisubstituted substrate 1,3-diphenylbut-2-en-1-one has been tested under the optimized conditions, but only about 15% conversion with trace product was obtained even after 12 h.

In order to ascertain a mechanistic understanding of the reaction, we carried out deuterium-labeling experiments for the transfer hydrogenation of **1a**. The use of CH_3OD as a hydrogen source and solvent afforded α-deuterated products **2aa** and **2ab** in the ratio 53/47. It should be noted that no β-deuterated product was detected in this reaction (Scheme 1, eq 1). Additionally, the reaction using CH_3CD_2OH as a hydrogen source provided exclusively **2ac** with deuterium at the β-position (eq 2).

On the basis of the above findings and according to literature data,[8i−l,11] a proposed catalytic cycle for the

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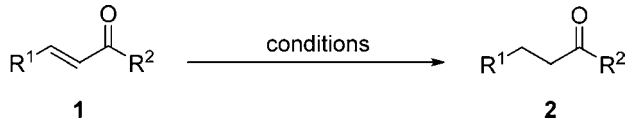
Table 3. Pincer Palladium Complex Catalyzed Chemoselective Transfer Hydrogenation of α,β-Unsaturated Ketones[a]



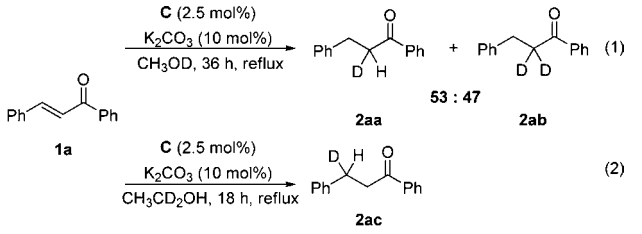
entry	1	R^1	R^2	time (h)	yield (%)[b]
1	**1a**	Ph	Ph	2	96
2	**1b**	*p*-MeC_6H_4	Ph	1.5	94
3	**1c**	*m*-MeC_6H_4	Ph	1.5	96
4	**1d**	*o*-MeC_6H_4	Ph	2	91
5	**1e**	*p*-$MeOC_6H_4$	Ph	1.5	94
6	**1f**	*p*-FC_6H_4	Ph	1	93
7	**1g**	*p*-ClC_6H_4	Ph	0.5	92
8	**1h**	*p*-BrC_6H_4	Ph	1	88
9	**1i**	*p*-$CF_3C_6H_4$	Ph	1	97
10	**1j**	2-naphthyl	Ph	1.5	95
11	**1k**	*i*-Pr	Ph	4.5	87
12	**1l**	Ph	*p*-MeC_6H_4	2	92
13	**1m**	Ph	*m*-MeC_6H_4	0.5	95
14	**1n**	Ph	*o*-MeC_6H_4	1	92
15	**1o**	Ph	*p*-$MeOC_6H_4$	0.5	97
16	**1p**	Ph	*p*-FC_6H_4	1	92
17	**1q**	Ph	*p*-ClC_6H_4	1	91
18	**1r**	Ph	*p*-BrC_6H_4	1	86
19	**1s**	Ph	*p*-$CF_3C_6H_4$	1	93
20	**1t**	Ph	2-naphthyl	0.5	98
21	**1u**	Ph	2-furyl	0.5	93
22	**1v**	Ph	2-thienyl	0.5	93
23	**1w**	Ph	*i*-Pr	32	81
24	**1x**	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	1.5	98
25[c]	**1y**	*n*-pentyl	Me	12	68[d]

[a] Reaction conditions: substrate (0.50 mmol), **C** (2.5 mol %), K_2CO_3 (10 mol %), *n*-BuOH (5 mL), at reflux. [b] Isolated yields. [c] **A** (2.5 mol %) was used instead of **C**. [d] GC yield based on *n*-dodecane as an internal standard.

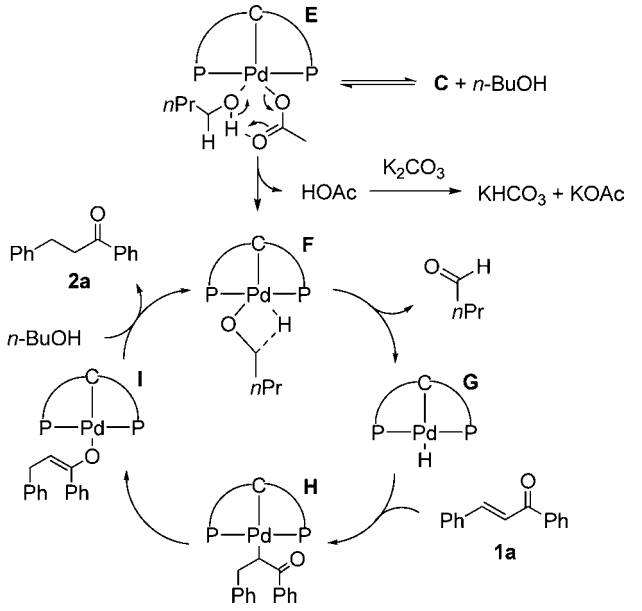
pincer-Pd-catalyzed conjugate reduction is illustrated in Scheme 2. The pincer-Pd complex **C** acts as a Brønsted base via the six-membered ring transition state **E** to generate the Pd-*n*-butoxide **F**, which through subsequent β-hydride elimination gives the key intermediate Pd-hydride **G**. The α-enone **1a** coordinates to the Pd-hydride and undergoes hydride transfer to give **H**. The resulting Pd enolate **I** produced via enolization of **H** is protonated by *n*-BuOH to give product **2a** and reproduced the Pd-*n*-butoxide **F** for use in the next catalytic cycle.

In summary, we have developed the first example of a chemoselective transfer hydrogenation of α,β-unsaturated ketones catalyzed by pincer-Pd complexes. The high reactivity and selectivity of the pincer-Pd complex **C** provide an attractive methodology for the

Scheme 1. Deuterium-Labeling Experiments



Scheme 2. Proposed Catalytic Cycle



preparation of saturated ketones from α-enones. Based on deuterium-labeling experiments, the reaction is considered to proceed via a pincer-Pd-hydride intermediate. Further investigations to utilize this newly developed methodology in asymmetric reactions are ongoing.

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Supporting Information Available. General experimental procedures and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.