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BINAP-Copper Supported by Hydrotalcite as Efficient Catalyst for Borrowing Hydrogen Reaction and Dehydrogenation Cyclization under Water or Solvent-Free Conditions[†]

Zhaojun Xu,^a Xiaoli Yu,^a Xinxin Sang,^{*a} and Dawei Wang^{*a}

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A BINAP-Cu system supported by hydrotalcite has been developed and proved to be a highly efficient catalyst for the atom-efficient and green borrowing hydrogen reaction and dehydrogenative cyclization. This BINAP-Cu complex supported by hydrotalcite is highly air-stable and can be recycled at least five times under solvent-free conditions. Notably, 1-benzyl-2-aryl-1*H*-benzo[d]imidazole derivatives could be synthesized from alcohols in only one step with water as the solvent for the first time. This provided a much greener and efficient catalytic method towards the synthesis of functionalized amines, ketones and 1-benzyl-2-aryl-1H-benzo[d]imidazole derivatives with high yields in water or solvent-free conditions.

Keywords: heterogeneous; copper complex; solvent-free; borrowing hydrogen; dehydrogenation

Introduction

Borrowing hydrogen reactions and dehydrogenative cyclizations are of great importance due to their wide applications and utility as a convenient and efficient tool for the material science and pharmaceutical industry.^{1,2} Borrowing hydrogen reactions are usually involved in the following process: dehydrogenation of an alcohol to the corresponding carbonyl compound, followed by (dehydrogenation is the first step of a hydrogen borrowing reaction) condensation and reduction of the C-C or C-N double bond using the borrowed H₂ from the alcohol.³ Water is produced as the only byproduct for borrowing hydrogen reactions,⁴ while H₂ and H₂O are produced as the byproducts for dehydrogenation cyclizations. Given this outcome, the atom efficiency of this strategy (borrowing hydrogen reaction and dehydrogenation cyclization) is high.⁵ The most commonly used catalysts, such as palladium, ruthenium, iridium and rhodium, are often effective due to their efficiency in catalytic dehydrogenation and borrowing hydrogen reactions.^{6,7} Despite borrowing hydrogen

† Footnotes relating to the title and/or authors should appear here.

reactions and dehydrogenation cyclizations being an atom-efficient and green transformation, a much greener process under solvent-free or clear solvent conditions remains a challenging task, particularly with inexpensive metals as catalysts, such as Fe, Co, Cu, Mn.⁸

Recently, we have synthesized several iridium and ruthenium complexes and explored their catalytic activity for borrowing hydrogen reaction of alcohols with amines.⁹ However, these iridium and ruthenium catalysts are expensive and could not be recycled, which would be a great waste for modern organic chemistry. To enhance the recyclability and to develop the most economic and promising catalysts, we investigated a BINAP-Cu complex supported by hydrotalcite (HT), which proved to be an efficient catalyst for borrowing hydrogen reaction, giving products in high yields. This BINAP-Cu complex supported by hydrotalcite was a highly airstable catalyst with good recyclability for at least five times under solvent-free conditions or with water as the solvent.

Results and discussion

Catalyst characterization

A crystal of the $[Cu(binap)I]_2$ complex was grown from a saturated acetonitrile/*n*-hexane solution at ambient

^{a.} The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China. E-mail: wangdw@jiangnan.edu.cn, sangxx@jiangnan.edu.cn

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temperature (please see Supporting Information for the synthesis of $[Cu(binap)I]_2$ complex for details). In order to confirm the structure of the complex, single crystal X-ray diffraction analysis was performed (Figure 1). A summary of crystallographic data and important bond lengths or bond angles are listed in the SI (see Supporting Information for the cif file containing complete single crystal data).



Figure 1. The structure of [Cu(binap)I]₂ and ORTEP diagram with thermal ellipsoids shown at the 30% probability level.

Hydrotalcite (HT) has a potential use for the dispersion of small nanoparticles as a catalyst support. Herein, we utilized HT as a support for the [Cu(binap)I]₂ complex. The detailed synthetic procedure for [Cu(binap)I]₂@HT is presented in the experimental section. It was clear that the [Cu(binap)I]₂ complex was successfully loaded on HT following several modes of characterization. [Cu(binap)I]₂@HT was characterized by FT-IR (Fig. S2, see Supporting Information for details), SEM and TEM (images of [Cu(binap)I]₂@HT were shown in Fig 2; small particles irregularly dispersed on the surface of flaky hydrotalcite, see Fig. S7 for enlarged EDX image), TGA and N₂ adsorption-desorption isotherms (Figs. S4-S5). The powder XRD pattern of the synthesized catalyst was shown in Fig. S6.



Figure 2. (a) SEM images of [Cu(binap)I]₂@HT (b) TEM micrographs of [Cu(binap)I]₂@HT.

Catalytic activity for borrowing hydrogen reaction

Initially, the borrowing hydrogen reaction between aniline with benzyl alcohol was selected as the model to examine this newly supported heterogeneous $[Cu(binap)I]_2@HT$ catalyst under solvent-free conditions. It was very pleasing to find that N-benzylaniline was obtained in low yield (Table 1, entry 1). In order to achieve a high yield, a series of screening experiments were explored by varying bases for the representative reaction. KOH produced the best result, while other bases such as Cs₂CO₃, K₂CO₃, NEt₃, K₃PO₄, KOH and

*t*BuOK offered lower efficiency. Moreover, it was observed that the reaction did not proceed efficiently in the absence of catalyst (Table 1, entry 8). In addition, we conducted a series of control experiments for the behavior of the free catalyst in the absence of carrier HT (see Table S4 in Supporting Information). The results revealed that the reaction only produce moderate yield even after reaction screening.

 Table 1. Screening of reaction conditions ^a

NH ₂ + () OH (M], Base					
1a	2a	3a			
Entry	Catalyst	Base	Yield[%] ^b		
1	[Cu(binap)I]2 @HT	Na ₂ CO ₃	42		
2	[Cu(binap)I] ₂ @HT	Cs ₂ CO ₃	53		
3	[Cu(binap)I]2 @HT	K_2CO_3	68		
4	[Cu(binap)I]2 @HT	<i>t</i> BuOK	37-		
5	[Cu(binap)I]2 @HT	NEt ₃	7		
6	[Cu(binap)I]2 @HT	K ₃ PO ₄	30		
7	[Cu(binap)I]2 @HT	КОН	82		
8	-	KOH	<5		

^aReagents and conditions: **1a** (2.0 mmol), **2a** (4.0 mmol), catalyst (2 mol%Cu, 5 % loading, w/w), base (1.0 mmol), 100 °C, 12 h, under solvent-free conditions.^b Isolated yield.



Figure 3. Effect of temperature on the model reaction process.

In order to study the influence of temperature, the reaction profiles were explored. As illustrated in Figure 3, Only 53% yield of the corresponding product was achieved in the presence of $[Cu(binap)I]_2@HT$ (5% loading, w/w) under grinding condition at room temperature. Whereas by increasing the temperature to 60 °C and then 80 °C, significant improvement was observed and yield of the product increased significantly (Figure 3). Furthermore, an increase in temperature to 100 °C and 120 °C had nearly no significant change in the yield of the product. Thus, 80 °C

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was chosen as the optimal reaction temperature for future investigations.

After extensive screening, the effect of catalyst loading was also studied (Table 2). Increasing the catalyst loading to 10% showed 85% yield of the desired product could be obtained, whereas the yield decreased slightly by increasing the amount of the catalyst to 20%. Thus, the optimal reaction conditions are as follows: [Cu(binap)I]2@HT (5% loading, w/w) as the catalyst, KOH as the base under solvent-free conditions at 80 °C for 12 h.

Table 2. Effect of catalyst loading on the model reaction.^a

Entry	Catalyst loading [%, w/w]	Temp. [[°] C]	Time [h]	Yield[%] ^b
1	5	80	12	84
2	10	80	12	85
3	20	80	12	81
4	2	80	12	70
5	1	80	12	56
6	0	80	12	<5
7	5	80	6	77
8	5	80	24	85

^aReagents and conditions: 1a (2.0 mmol), 2a (4.0 mmol), catalyst ([Cu(binap)I]2@HT, 2 mol%Cu), base (1.0 mmol), under solventfree conditions.^b Isolated yield.

Table 3. Substrate expansion of the borrowing hydrogen reaction of amines with alcohols *a,b*





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Following the optimization conditions described above, we next examined the reaction scope in terms of other aromatic amines with alcohols and the results were summarized in Table 3. It was observed that a wide range of diverse substrates and functional groups could be tolerated, including fluoro, chloro, methyl, methoxy, bromine and ester substituents at the different positions of aromatic amines and alcohols. Nearly all amines were converted into the desired products in good yields under optimized conditions with the newly developed $[Cu(binap)I]_2@HT$ as the catalyst. Meanwhile, the racemic catalyst was also tested for this transformation and the result revealed that almost the same yield of 3a was achieved.

Additionally, we explored similar reaction conditions to the borrowing hydrogen reaction of ketones with alcohols. The results were summarized in Table 4. We were pleased to find that ketone derivatives were also achieved in good yields. In general, most of the substrates (ketones) were converted completely to produce the corresponding functionalized ketones. Moderate to good yields could be achieved regardless of the electron withdrawing or electron donating nature of the substituent groups. When two halogen atoms were introduced to this reaction, it was observed that this transformation could proceed well without the loss of the halogen atoms (5q, 5t, 5u). Moreover, iodine could be well tolerated with none of the dehalogenation products being observed (5m, 5q).

Table 4. Substrate expansion of the ketones with alcohol^{*a,b*}

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Table5.

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^aConditions: 4 (2.0 mmol), 2 (4.0 mmol), [Cu(binap)I]₂@HT (2 mol%Cu), K₂CO₃ (1.0 mmol), 8 h, 100 °C. ^bIsolated yields based on 4.

Catalytic activity for dehydrogenation cyclization

The 1H-benzo[d]imidazole skeletons are useful building blocks, which have been found in pharmaceuticals, natural products and plant alkaloids.¹⁰ Synthesis of these bioactive molecules is an interesting and promising venture in organic chemistry, especially under green conditions, which is a challenging task. Recently, we discovered that homogeneous catalysts couldn't promote the synthesis of 1Hbenzo[d]imidazole derivatives under water or solvent-free conditions and the catalyst couldn't be recovered yet.9b Herein, the synthesis of 1H-benzo[d]imidazole derivatives were carried out in the presence of [Cu(binap)I]2@HT in water for the first time and the experiments were summarized in Table5. Clearly, aromatic alcohols, including methylbenzyl alcohol, ethyl alcohol, tert-butyl alcohol, methoxybenzyl alcohol, chlorobenzyl alcohol, and furfuryl alcohol could be reacted smoothly, and different 1-benzyl-2-aryl-1Hbenzo[d]imidazole derivatives were obtained in moderate to good yields ranging from 71 % to 88 % using $[Cu(binap)I]_2$ @HT as a catalyst.



^aConditions: 6 (0.5 mmol), 2 (1.1 mmol), [Cu(binap)I]₂@HT (2 mol%Cu), K₂CO₃ (0.75 mmol), H₂O (2 mL), 12 h, 90 °C. ^bIsolated yields based on 6.

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Mechanism studies

Control experiments and activity exploration

For a better understanding of this catalyst system and these transformations, further exploration of the reaction mechanism is necessary. However, we expected that the supported heterogeneous [Cu(binap)I]2@HT catalyst could overcome the difficulties of recovery and reusability described earlier. As expected, the [Cu(binap)I]₂@HT was easily recovered. Importantly, it was found that this catalyst possessed good catalytic activity. This was attributed to synergistic effect of the BINAP ligand with carrier HT,¹¹ which was similar to the synergistic effect of phosphine and triazole.^{9b} Another possible reason is that the reaction occurs on the surface of the supported heterogeneous [Cu(binap)I]₂@HT catalyst, while homogeneous copper catalysts couldn't be dissolved in water (In fact, the dispersivity of homogeneous copper catalyst was extremely poor), thus homogeneous copper catalysts such as CuI or [Cu(binap)I]₂ only produced low yield or no conversion in water or solvent-free conditions (Scheme 1). As expected, the heterogeneous [Cu(binap)I]2@HT catalyst revealed much higher catalytic activity than the homogeneous homogeneous copper catalysts for these transformations described in this report.

Compared to other catalytic methodologies, Cu catalysis shows some interesting advantages over Pd, In, Ru or other metals. Firstly, Cu is cheaper than several other metals used in catalysis, and is a good choice in large- and industrial-scale applications. Secondly, Cu-based catalysts have proven to exhibit exceptional activity in the cleavage of C-O bonds and formation of C-N and C-C bonds.^{12a} Finally, Cu-catalyzed reactions work well with a variety of ligands, and the ligands required are usually structurally quite simple and inexpensive while ligands for Pd, In, Ru chemistry are often complicated, unstable in air and expensive. Copper(I) phosphine halide complexes are common precursors in catalysis.^{12b} However, there was still no research on the catalytic activity of copper(I) complexes in borrowing hydrogen reactions and dehydrogenative cyclizations in water and therefore [Cu(binap)I]₂ complex was prepared. Furthermore, to enhance the recyclability and to develop the most economic and promising heterogeneous catalysts, the BINAP-Cu complex supported by hydrotalcite (HT) was synthesized, which proved to be an efficient catalyst for borrowing hydrogen reaction, giving products in high yields.



Scheme 1. The control experiments for the synthesis of 1-benzyl-2-aryl-1H-benzo[d]imidazole.

Proposed reaction mechanism

The reaction mechanism of the borrowing hydrogen reaction between amine with alcohol or ketone with alcohol was clear, while dehydrogenative cyclization is more complicated. Therefore, it is necessary to account for this, giving way to the plausible mechanism for the synthesis of 1-benzyl-2-aryl-1*H*-benzo[d]imidazole as proposed and shown in Scheme 2. In the beginning, aldehyde was generated with the help of $[Cu(binap)I]_2@HT$, then imine **B** was formed via the condensation of amine and aldehyde **A**, and detected by MS analysis.^{9b,13} After the intermolecular electron transfer, intermediate **C** was formed. Finally, through cyclization and rearrangement, the desired product **7a** was released.



Scheme 2. The posible reaction pathway for synthesis of 7a.

The capture of intermediates

To unambiguously confirm this reaction mechanism, the separation of intermediates **A** and **B** were carried out. It was pleasing to see that intermediate **A** could be obtained in 65% yield when phenylmethanol was treated with $[Cu(binap)I]_2@HT$, while only 12% of intermediate **B** was isolated when the reaction was conducted with $[Cu(binap)I]_2@HT$ for 2 hours. The following observation has been supported by related results (Scheme 3).^{9b, 13}



Scheme 3. The posible reaction pathway for synthesis of 7a.

To validate the possibility of a radical pathway based on a single electron transfer (SET), control experiments with aniline and benzyl alcohol were carried out under the optimization conditions by using radical scavenger. As seen

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in Scheme 4, the results revealed that the yield of the desired product was generally unchanged when using 2,6-Di-*tert*butyl-4-methylphenol (BHT) (1.0 eq) and 2,2,6,6-tetramethyl piperidinyloxy (TEMPO) (1.0 eq) with $[Cu(binap)I]_2@HT$ as the catalyst. In order to explore the effect of inhibitor and its concentration on the reaction, we carried a series of contrast experiments (see Table S5 in Supporting Information). As the concentration of the inhibitor increased, the yields seemed to be not affected. As a result, a single electron transfer (SET) should be not involved in the process.



Scheme 4. Control experiments with radical scavengers.

Reusability of the catalyst

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The recycling test of [Cu(binap)I]₂@HT was investigated through the borrowing hydrogen reaction between aniline (1a) with benzyl alcohol (1b) under optimum conditions. The catalyst could be separated easily through high speed centrifugation, followed by washes with EtOH, deionized water and subsequent vacuum freeze-drying for 24 h. Then the new substrates and base were added for the next cycle. As shown in Figure 4, no significant decreases in yield could be seen with maintained reaction selectivity after five cycles.

To further investigate the catalyst system and measure the extent of [Cu(binap)I]₂@HT leaching after the reactions, a hot filtration experiment was performed. The amounts of the [Cu(binap)I]₂@HT leaching into solution for the reaction of aniline with benzyl alcohol under solvent free conditions at 80 °C was detected by checking the Cu and P leaching amount before and after each reaction cycle through ICP analysis. The amount of Cu leaching after the first run was determined by ICP assessment and found to be only 0.64% (%, w/w). After 5 repeated cycles, the leaching was found to be 2.83%. Meanwhile, it was evident that less than 0.35% of the P species had leached into the reaction mixture even after five cycles. Thus, the ICP technique showed that the leaching of [Cu(binap)I]₂@HT was negligible. These experiments demonstrated [Cu(binap)I]2@HT had excellent stability and regenerating capability.



Figure 4. Catalytic reusability of [Cu(binap)I]₂@HT in the borrowing hydrogen reaction of aniline (1a) with benzyl alcohol (1b).

Conclusions

In summary, we established the synthesis, characterization, and catalytic activity of novel composite $[Cu(binap)I]_2@HT$ catalysts, which were demonstrably effective catalysts for borrowing hydrogen and dehydrogenation reactions under water or solvent-free conditions. This provided an efficient methodology for the synthesis of substituted amine derivatives, functionalized ketones and 1-benzyl-2-aryl-1*H*-benzo[d]imidazole derivatives under clear conditions.

Experimental Section

Materials

2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl (BINAP, 98%), Cuprous iodide (CuI, 98%), amines, alcohols and ketones were purchased from Energy Chemical and used without any treatment. $[Cu(binap)I]_2$ complex was synthesized according to the known procedure.¹⁴ Hydrotalcite (HT, Mg/Al = 3) were purchased from Makahi reagent and were used without further purification. Dimethyl sulfoxide, toluene, xylene, alcohols were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All other chemicals were of analytical grade. The used water was deionized water.

Preparation of [Cu(binap)I]2@HT

 $[Cu(binap)I]_2$ complex (50 mg) was dissolved in DMSO (10 mL) in a 100 mL Schlenk tube under a nitrogen atmosphere at 160 °C. After the complex completely dispersed and dissolved in solution, hydrotalcite (500 mg) was added to the solution with vigorous stirring. The mixture was continuously stirred for 24 h. Subsequently, deionized water (5 mL) was added to precipitate more solids. After cooling to ambient temperature, the precipitate was collected by centrifugation and washed with deionized water and

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ethanol for several times, followed by vacuum freeze-drying for 24 h.

Characterisation techniques

Single crystal X-ray diffraction analysis was conducted on Bruker Advance Smart 1000. The FTIR characterization of hydrotalcite (HT), [Cu(binap)I]₂ complex and hydrotalcite Supported [Cu(binap)I]₂ Catalysts were performed on Total reflection Fourier infrared spectrometer Nicolet 6700 (Thermo Fisher Scientific Co. Ltd., USA). X-ray diffraction (XRD) patterns of the sample powder were carried out by BRUKER-D8 Advance diffractometer with Cu Ka radiation $(\lambda = 0.154 \text{ nm})$ over a 2 θ range between 3 and 90°. The morphologies of hydrotalcite supported [Cu(binap)I]₂ complex was observed by scanning electron microscopy (SEM) Hitachi S-4800 (Hitachi Ltd., Japan). Energy dispersive X-ray (EDX) was obtained by scanning electron microscopy (SEM). The catalyst morphology structure was investigated by a JEOL JEM-2100 Transmission electron microscopy (TEM). The Brunauer-Emmett-Teller (BET) measurement of the sample was analyzed by the Full automatic specific surface area and micropore physical adsorption instrument ASAP2020 MP (micromeritics, USA). Thermogravimetic analysis (TGA) were measured on TG/DSC1/1100 Met-tler Toledo, the sample were heated from 25 to 800 °C at a heating rate of 10 °C min⁻¹ under flowing nitrogen.

Representative procedure for the preparation of 7a

The mixture of catalyst (2 mol%Cu), H₂O (2 mL), diamine (0.5 mmol), alcohol (1.1 mmol) and K₂CO₃ (0.75 mmol) was stirred in 20 mL colorimetric tube under 90 °C for 12 h. Then the reaction mixture was cooled down to the room temperature and the solvents was removed to give the residue. The residue was directly extracted by ethyl acetate and then purified by column chromatography with petroleum ether/ethyl acetate (petroleum ether /ethyl acetate = 10:1) as eluent to give the desired product (**7a**).

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