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An Imidazolium-Modified Chiral Rhodium/diamine-Functionalized Periodic Mesoporous Organosilica for Asymmetric Transfer Hydrogenation of α–Haloketones and Benzils in Aqueous Medium

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Use of a hydrophobic, imidazolium-functionalized periodic mesoporous organosilica for immobilizations of chiral organometallic complexes as a heterogeneous catalyst is a highly desirable as this catalyst can promote greatly an aqueous organic transformation due to its hydrophobic function and phase-transfer feature in an aqueous medium. Herein, by utilizing a three-component co-condensation strategy, we incorporate conveniently 1 2bis(triethoxysilyl)ethane, (R, R)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylenediamine and 1,3-bis(3-(triethoxysilyl)propyl)-1H-imidazol-3-ium iodide within its silicate network, which is coordinated with (Cp*RhCl₂)₂ to lead to an imidazolium-modified chiral rhodium/diamine-functionalized periodic mesoporous organosilica. Solid-state carbon spectrum discloses its well-defined chiral rhodium/diamine active species, and its X-ray diffraction, nitrogen adsorption-desorption measurement and transmission electron microscopy image reveal its ordered dimensional-hexagonal mesostructure. As a bifunctional heterogeneous catalyst, this periodic mesoporous organosilica boosts significiently asymmetric transfer hydrogenation of α -haloketones and benzils in water, where the hydrophobic periodic mesoporous organosilica, phase-transferfeatured imidazolium-functionality, and confined chiral organorhodium catalytic nature are responsible for its catalytic performance. Furthermore, catalyst can be recovered and recycled for seven times without loss of its catalytic activity, making it an attracting heterogeneous catalyst for asymmetric transfer hydrogenation in an environmentally friendly manner.

1. Introduction

Asymmetric transfer hydrogenation as a powerful methodology has been studied extensively in enantioselective reduction of ketones and imines, where chiral N-sulfonylated diamine-based organometallic complexes, such as η^5 -Cp*Mseries (Cp* = pentamethyl cyclopentadiene) and η^6 -arene-Mseries (η^6 -arene = aromatic ring; M = Ru, Rh and Ir), are wellknown as efficiently homogeneous catalysts.^[1] Recently, some of them have been expanded successfully to various enantioselective reactions in an environmentally friendly medium.^[2] In spite of great efforts have been made on asymmetric transfer hydrogenation, contributions from industrial fields are much lower than expected. Main limitations are due to the expensive transition-metal recycling and product contamination arising from metal leaching. Therefore, exploration of an immobilization strategy to overcome these limitations and development of a practical approach to realize an green catalysis are still an unmet challenge in asymmetric catalysis.

Recent developments through use of periodic mesoporous

organosilicas (PMOs) as supports for immobilizations of chiral organometallic complexes have led to many efficient, reusable heterogeneous catalysts.^[3] Prominent feature of these heterogeneous catalysts possesses PMO-supported organosilicate networks, which ensures a high reaction rate in an aqueous reaction system relative to an SiO₂-supported inorganosilicate networks.^[4] This superiority is due to the hydrophobic nature of PMO-support, which can concentrate greatly organic substrate into pore channels and reach a highly catalytic performance.^[5] In particular, some imidazolium-functionalized PMOs can offer additional contributions for catalytic reactions. These imidazolium-functionalities within PMOs can function as a phase-transfer-featured catalyst to promote catalytic performance in an aqueous medium.^[6] Although lots of imidazoliumfunctionalized PMOs have been reported,^[7] immobilization of chiral organometallic complex within an imidazoliumfunctionalized PMO for asymmetric catalysis is still not explored yet. Accordingly, taking advantage of imidazolium-functionality, together with benefit of hydrophobic organosilicate network, it is reasonable to expect that an imidazolium-modified chiral rhodium/diamine-functionalized PMO has an efficiently enantioselective reaction in an aqueous medium.

We are interesting various heterogeneous catalysts for green asymmetric catalysis.^[8] Recently, we found that hydrophobic PMO-supported organosilicate network could enhance reaction rate in asymmetric reactions.^[8a-e] Meanwhile, we also found that some imidazolium-

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functionality materials could boost catalytic in performance.^[8f-g] Consideration both, in this contribution, we incorporate the imidazolium-functionality within а hydrophobic PMO network, developing an imidazoliummodified chiral rhodium/diamine-functionalized PMO. As we envisaged, this PMO material possesses bifunctionality of hydrophobic function and imidazolium-phase-transfered catalytic function in an aqueous reaction condition. As a heterogeneous catalyst, it displays excellent catalytic activity and high enantioselectivity in asymmetric transfer hydrogenation of α -haloketones and benzils in water, where its bifunctionality together with chiral rhodium/diamine catalytic nature promote synergistically its catalytic performance.

2. Experimental

2.1. Characterization

Rh loading amounts in the catalyst were analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (S_{BET}) of samples were determined from the linear parts of BET plots (p/p_0) = 0.05-1.00). Solid state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with ¹H frequency of 400.1 MHz, ¹³C frequency of 100.5 MHz and ²⁹Si frequency of 79.4 MHz with 4 mm rotor at two spinning frequency of 5.5 kHz and 8.0 kHz, TPPM decoupling is applied in the during acquisition period. ¹H cross polarization in all solid state NMR experiments was employed using a contact time of 2 ms and the pulse lengths of 4µs.

2.2. Preparation of catalyst 5

In a typical synthesis, 2.0 g of structure-directing agent, pluronic P123 (CH₂-CH₂O)₂₀(CH₂(CH₃)CH₂O)₇₀(CH₂CH₂O)₂₀), was completely dissolved in a mixture of 80 mL of hydrochloric acid (0.2 N) and 6.0 g of KCl. The mixture was stirred at room temperature for 1.0 h. Subsequently, 3.0 g (8.47 mmol) of the silica precursor 1,2-bis(triethoxysilyl)ethane was added at 40 °C. After a pre-hydrolysis period of 40 minute, 0.25 g (0.50 mmol) of (*R*,*R*)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-

diphenylethylene-diamine (1) and 0.25 g (0.27 mmol) of 1,3bis(3-(triethoxysilyl)propyl)-1H-imidazol-3-ium iodide (2) was added. The reaction mixture was stirred at 40 °C for 24 h and then aged at 100 °C for 24 h. The resulting solid was filtered, rinsed with excess ethanol, and then dried overnight on a filter. The surfactant template was removed by refluxing in acidic ethanol (400 mL per gram) for 24 h. The solid was filtered, rinsed with ethanol again, and then dried at 60 °C under reduced pressure overnight to afford Imidazolium@ArDPEN@PMO (3) (1.78 g) in the form of a yellow powder. The part of collected solids (1.0 g) was suspended in 20 mL of dry CH_2Cl_2 , and 145.0 mg (0.25 mmol) of $[CpRh*Cl_2]_2$ was added to the solution at ambient temperature. The resulting mixture was stirred for 12 h. The mixture was filtered through filter paper and then rinsed with excess water and CH₂Cl₂. After Soxhlet extraction for 24 h in CH₂Cl₂ to remove homogeneous and unreacted starting materials, the solid was dried at ambient temperature under vacuum overnight to afford catalyst 5 (1.02 g) as a light-yellow powder. ICP analysis showed that the Rh loading was 9.64 mg (0.093 mmol) per gram of catalyst. IR (KBr) cm⁻¹: 3430.7 (s), 3064.5 (w), 2977.7 (w), 2930.4(w), 2898.4(w), 1630.5 (m), 1566.5 (w), 1496.2 (w), 1464.2 (w), 1416.8 (w), 1329.9 (w), 1052.2 (s), 1194.2 (s), 1098.5 (s), 925.6 (m), 789.9 (m), 695.3 (m), 576.3 (m), 441.9 (m). ¹³C CP/MAS NMR (161.9 MHz): 147.1, 136.3, 128.1 (<u>C</u>H of imidazolium, and <u>C</u> of Ph or Ar), 94.7 (<u>C</u> of Cp ring), 70.8-75.2 (-N<u>C</u>HPh-), 59.1 (-O<u>C</u>H₂CH₃), 51.9 (-NCH₂CH₂CH₂Si-), 20.1-31.7 (-NCH₂CH₂CH₂Si-, and -<u>C</u>H₂Ar), 17.9 (-OCH₂<u>C</u>H₃), 9.6 (Cp<u>C</u>H₃), 12.3-0.5 (-<u>C</u>H₂Si) ppm. ²⁹Si MASNMR (79.4 MHz): T¹ (δ = -48.2 ppm), T² (δ = -57.4 ppm), T³ ($\delta = -65.5$ ppm.

2.3. General procedure for the asymmetric transfer hydrogenation.

A typical procedure was as follows. Catalyst **5** (21.50 mg, 2.0 μ mol of Rh, based on ICP analysis), HCO₂Na (0.68 mg, 1.0 mmol), α -haloketones or benzils (0.20 mmol), and 2.0 mL of water were added sequentially to a 10.0 mL round-bottom flask. The mixture was then stirred at 40 °C for 1–12 h. During this period, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was separated by centrifugation (10,000 rpm) for the recycling experiment. The aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with brine twice and then dehydrated with Na₂SO₄. After evaporation of ethyl ether, the residue was purified by silica gel flash column chromatography to afford the desired products. The *ee* values were determined by a HPLC analysis using a UV-Vis detector and a Daicel chiralcel column (Φ 0.46 × 25 cm).

3. Results and discussion

3.1. Synthesis and structural characterization of the heterogeneous catalyst



Scheme 1. Preparation of catalyst 5.

Cp*RhArDPEN-functionalized Imidazolium-modified chiral periodic mesoporous organosilica, abbreviated as (Cp*RhArDPEN:[9] Imidazolium@Cp*RhArDPEN@PMO (5) Cp^* = pentamethylcyclopentadiene and ArDPEN = N-4ethylenephenylsulfonyl-1,2-diphenylethylenediamine), was synthesized as outlined in Scheme 1. Three-component cocondensation of 1,2-bis(triethoxysilyl)ethane, (R,R)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylene-

diamine (1) and 1,3-bis(3-(triethoxysilyl)propyl)-1*H*-imidazol-3ium iodide (2),^[10] led to chiral diamine-functionalized PMO (Imidazolium@ArDPEN@PMO (3)) in the form of a white powder. Direct complexation of 3 with (Cp*RhCl₂)₂ afforded then the crude heterogeneous catalyst. This crude one was treated with a strict Soxhlet extraction to give its pure catalyst 5 as a lightyellow powder (see SI in experimental part and Figure S1).



Figure 1. Solid-state ¹³C CP/MAS NMR spectra of 3 and catalyst 5.



Figure 2. Solid-state ²⁹Si CP/MAS NMR spectra of 3 and catalyst 5.

Assembly of three-component siloxanes, especially welldefined chiral rhodium/diamine species, within its silicate network of 5 could be proven by solid-state ¹³C cross-polarization (CP)/magic angle spinning (MAS) NMR spectroscopy. As shown in Figure 1, both 3 and 5 produced carbon signals of Si<u>CH₂CH₂Si</u> groups at ~5 ppm and of imidazolium moiety at ~147 and ~136 ppm, corresponding to the imidazolium-modified, ethylenebridged organosilica. In the part of chiral rhodium/diamine complex, signals between 70 and 75 ppm were attributed to the carbon atoms of N<u>C</u>H groups in the TsDPEN moiety, whilst peaks at 94.7 and 9.6 ppm in the spectrum of **5** ascribed the carbon atoms of the Cp ring and to the carbon atoms of the <u>C</u>H₃ groups attached to Cp ring (in contrast, no carbon signals in the latter case in the spectrum of **3** demonstrates the formation of the Cp*RhArDPEN complexes in **5**). Their chemical shifts in catalyst **5** were similar to those of its homogeneous counterpart (Cp*RhTsDPEN),^[11] disclosing that both had the similar welldefined chiral rhodium/diamine species.



Figure 3. Small-angle powder XRD patterns of 3 and catalyst 5.



Figure 4. Nitrogen adsorption-desorption isotherms of 3 and catalyst 5.

Figure 2 showed the silicate compositions of catalyst **5** in its solid-state ²⁹Si MAS NMR spectroscopy. It was found that both **3** and **5** only presented one group of characteristic T signals for organosilica, suggesting that all Si species were bonded covalently to carbon atoms.^[12] In constrast these values with those isomer values reported in the literature (-48.5, -58.5, and -67.5 ppm for T¹, T², and T³ of R(HO)₂SiOSi, R(HO)Si(OSi)₂, and RSi(OSi)₃, respectively),^[13] the observed strong T²-T³ signals at -57.4, and -65.5 ppm in the spectrum of **5** demonstrated that R–Si(OSi)₂(OH) and R–Si(OSi)₃ species (R = propyl-linked imidazolium or ethyl-linked chiral functionality or

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ethylene-bridged group) were its main silicate compositions in catalyst 5. It is noteworthy that there were not Q signals from -90 to -120 ppm, indicating that the carbon–silicon bond was not cleaved during the co–condensation process.

Meanwhile, X-ray diffraction (XRD), nitrogen adsorptiondesorption measurement, and transmission electron microscopy (TEM), further demonstrated the ordered mesostructure and welldefined pore arrangement of catalyst 5. As shown in Figure 3, the small-angle XRD patterns revealed that both 3 and 5 produced an intense d_{100} diffraction peak along with two similar weak diffraction peaks (d_{110}, d_{200}) , indicating their dimensionalhexagonal pore structures (p6mm).[8a-b] Nitrogen adsorptiondesorption isotherms (Figure 4) suggested their mesoporous structures due to the presence of typical type IV isotherms with an H₁ hysteresis loop and visible step at $P/P_0 = 0.50-0.80$. Their structural parameters were listed in a Table that was an inset in Figure 3. TEM images further confirmed above judgement (Figure 5), where the highly ordered mesostructure with dimensional-hexagonal arrangements of catalyst 5 would be observed clearly.



Figure 5. TEM images of catalyst 5 viewed along [100] (a) and [001] (b) directions.

3.2. Catalytic performance of the heterogeneous catalyst

3.2.1. Catalytic properties

Chiral N-sulfonylated diamine-based organometallic complexes as a type of highly efficient catalysts are well-documented in various asymmetric reactions.^[2, 9] Some applications in the asymmetric transfer hydrogenation of a-haloketones have also been explored.^[14] In the present study, we first examined the catalytic and enantioselective performance of catalyst 5 in the asymmetric transfer hydrogenation of 2-bromo-phenylethanone in water. Because this asymmetric reaction in water is a typical two-phase reaction system, it often needs surfactant as phase transfer catalyst, such as sodium dodecyl sulfate or cetyltrimethylammonium bromide, promote its catalytic performance in a homogeneous catalysis.^[14a] In this case, due to the designed heterogeneous catalyst 5 containing the hydrophobic PMO silicate network and phase-transfer-featured imidazoliumfunctionality, this enantioselective reaction catalyzed by 5 was carried out in the absence of surfactant system, where the HCO₂Na worked as a hydrogen source and 1.0% mol **5** acted as a catalyst according to the reported method.^[14a] It was found that the asymmetric transfer hydrogenation of 2-bromophenylethanone catalyzed by **5** gave (*S*)-2-bromophenylethanol with 95% yield and 99% *ee* value. Such a result was comparable to that attained with its homogenous counterpart of Cp*RhTsDPEN in the presence of sodium dodecyl sulfate as phase transfer catalyst,^[14a] better than that in the absence of sodium dodecyl sulfate as phase transfer catalyst. This finding suggested the superiority of catalyst **5**. Furthermore, the asymmetric reaction could also be run at much higher substrate-to-catalyst mole ratio without affecting its *ee* value, as exemplified by the asymmetric transfer hydrogenation of 2-bromophenylethanone at substrate-to-catalyst mole ratio of 200 (Table 1, entry 2).

Table 1. Asymmetric transfer hydrogenation of aryl–substituted $\alpha\text{-}$ haloketones. a

Catalyst 5

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	Ar X = Br, Cl	HCOONa H ₂ O, 40 °C 6a-6l				
Entry	Ar (6)	X	Time (h)	%Yield ^b	%ee ^b	
1	Ph (6a)	Br	1.5 (1.5)	95(76)	99(92) °	
2	Ph (6a)	Br	5	88	98 ^d	
3	Ph (6a)	Br	2	93	98°	
4	Ph (6a)	Br	6	92	96 ^f	
5	4-FPh (6b)	Br	1.5	96	94	
6	3-FPh (6c)	Br	1.5	92	95	
7	4-ClPh (6d)	Br	1.5	93	94	
8	4-BrPh (6e)	Br	1.5	90	95	
9	3-BrPh (6f)	Br	1.5	88	93	
10	4-CF ₃ Ph (6g)	Br	1.5	91	97	
11	3,4-Cl ₂ Ph (6h)	Br	2	93	96	
12	4-NO ₂ Ph (6i)	Br	2	83	93	
13	4-CH ₃ Ph (6j)	Br	2	91	97	
14	4-OCH ₃ Ph (6k)	Br	3	92	98	
15	2-naphthyl (61)	Br	3	90	98	
16	4-FPh (6m)	Cl	1.5	96	94	
17	4-ClPh (6n)	Cl	1.5	93	97	

^a Reaction conditions: catalyst **5** (21.50 mg, 2.0 µmol of Rh based on the ICP analysis), HCO₂Na (1.0 mmol), α -haloketones (0.20 mmol) and 2.0 mL water, reaction temperature (40 °C). ^b Yield was determined by ¹H NMR analysis and the *ee* values were determined by chiral HPLC analysis (see SI in Figures S2). ^c Data in bracket were obtained using homogeneous Cp*RhTsDPEN as a catalyst. ^d Data were obtained at substrate-to-catalyst mole ratio of 200. ^e Data were obtained using the parallel PMO-supported analogue as a catalyst. ^fData were obtained using SBA-15-supported analogue as a catalyst.

On the basis of above excellent catalytic and enantioselective performance, catalyst **5** was further investigated with various aryl–substituted 2–bromoketones as substrates. As shown in Table 1, various 2–bromoketones could be smoothly converted to chiral products with high yields and enantioselectivities under the same reaction conditions. Also, it was found that the electronic properties of substituents at the Ar moiety did not affect enantioselectivities, that is, various electron-withdrawing and - donating substituents at the Ar moiety led to the same catalytic efficiency (Table 1, entries 5–14). In addition, α -chloroketones catalyzed by **5** could be smoothly converted to chiral products with high yields and enantioselectivities in aqueous medium (entries 16-17).

3.2.2. Investigation of the factors affecting catalytic performance

An important aim for incorporation of imidazolium-functionality within PMO network as a heterogeneous catalyst expects to enhance reaction rate in an aqueous medium because the hydrophobic benefit PMO network and phase-transfer-featured imidazolium-functionality is beneficial to an aqueous catalysis. As expected, the asymmetric transfer hydrogenation of 2-bromophenylethanone in water catalyzed by catalyst 5 could be completed within 1.5 h, which is slightly shorter than that attained with its homogeneous counterpart (2.0 hours). This phenomenon is rare since a general heterogeneous catalyst relative to its homogeneous counterpart often needs an obviously enlarged reaction time due to the common diffuse process of substrates during the catalysis process. This finding indicated that the high reaction rate obtained with catalyst 5 was attributed to the hydrophobic benefit and of phase-transfer-featured imidazolium-functionality in catalyst 5. In order to confirm their role, two analogues of catalyst 5, a parallel PMO-supported analogue (without imidazolium-functionality in PMO network) and a SBA-15-supported analogue (without hydrophobic silicate network in the similar dimensional-hexagonal pore arrangements), were employed to compare their catalytic performances in the asymmetric transfer hydrogenation of 2-bromo-phenylethanone. The results showed that the former case catalyzed by its parallel PMO-supported analogue could be reached to its catalytic completion in 2 hours, demonstrating a slightly slower reaction rate than that with catalyst 5 (Table 1, entry 3 versus entry 1). This finding proved the benefit of imidazolium-functionality in catalyst 5 because its parallel PMO-supported analogue has not imidazolium-functionality in the similar ethylene-bridged PMO organosilicate network. The latter case catalyzed by its SBA-15supported analogue needed an obviously long reaction time relative to that catalyzed by 5 (Table 1, entry 4 versus entry 1). This observation revealed the hydrophobic advantage of PMOsupported organosilicate network in catalyst 5 since this organosilicate network had a high hydrophobicity relative to the SiO₂-supported inorganosilicate network in the SBA-15supported analogue. Further evidence supports this judgment coming from a kinetic profile investigation, where the asymmetric transfer hydrogenation of 2-bromo-phenylethanone catalyzed by catalyst **5**, PMO-supported analogue and SBA-supported analogue were performed as shown in Figure 6. The results showed that the asymmetric reaction catalyzed by catalyst **5** resulted in an initial activity higher than that achieved with PMO-supported and SBA-15-supported analogues (the initial TOFs within 1.0 h were 83.7, 69.1 and 47.2 molmol⁻¹h⁻¹, respectively). Based on above these investigations, a conclusion could be drawn that the enhanced reaction rate of catalyst **5** relative to PMO-supported and SBA-15-supported analogues should be attributed to a synergistic result of the hydrophobic PMO silicate network and imidazolium-functionality in catalyst **5**.



Figure 6. Asymmetric transfer hydrogenation of 2-bromophenylethanone catalyzed by catalyst **5**, PMO-supported analogue and SBA-supported analogue. Reactions were carried out at 40 $^{\circ}$ C, using 10.0 μ mol of the catalyst, 5 equiv. HCOONa, and at an S/C ratio of 100 in 5.0 mL of water.

3.2.3. Catalyst's stability and recyclability

Another important consideration for design of the heterogeneous catalyst **5** is easy separation, where the recycled catalyst **5** can keep its catalytic activity and enantioselectivity after multiple cycles. As we envisaged, the heterogeneous catalyst **5** could be recovered easily through centrifugation and reused in the asymmetric transfer hydrogenation of 2-bromo-phenylethanone. As shown in Table 2, in eight consecutive reactions, the recycled catalyst **5** still afforded (*S*)-2-bromophenylethanol with 92% conversion and 93% *ee* (see SI in Figure S3). An inductively coupled plasma (ICP) optical emission spectrometer analysis found that the low leaching of Rh was responsible for its high recyclability, where the amounts of Rh in catalyst **5** after the eighth recycle was 9.31 milligrams per gram of catalyst and only 3.4 % of Rh loss.

Table 2. Reusability of catalyst 5 for transfer hydrogenation of 2-bromo-phenylethanone.^{a,b}

Run time	1	2	3	4	5	6	7	8	9
Conversion [%]	99	98	99	97	98	94	95	92	85

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10.0 mL water, reaction temperature (40 °C), reaction time (1.5 h). [b] The *ee* values were determined by chiral HPLC analysis (see SI in Figures S3).

3.2.4. Expansion of asymmetric transfer hydrogenation

As a highly efficient PMO-supported heterogeneous catalyst, catalyst 5 was further explored in asymmetric transfer hydrogenation that is difficult to be transformed. In this case, the asymmetric transfer hydrogenation of benzils in water was investigated according to the reported methods,^[2a, 15] where the asymmetric reaction with the HCO₂Na as a hydrogen source and 1.0% mol 5 as a catalyst was performed. As shown in Table 3, it was found that catalyst 5 was still highly efficient in transformation of benzils to various chiral diols. Taking the asymmetric transfer hydrogenation of benzil as an example, the enantioselective reaction catalyzed by 5 gave (1S, 2S)-1,2diphenylethane-1,2-diol with 99% ee, where was comparable to that attained with its homogenous counterpart of Cp*RhTsDPEN.^[2a] Similarly, the synergistic advantages of hydrophobicity and phase-transfer-featured imidazoliumfunctionality in catlayt 5 could also be observed, where a kinetic profile in the asymmetric transfer hydrogenation of benzil catalyzed by catalyst 5, PMO-supported analogue, SBAsupported analogue confirmed this trends (see SI in Figure S4). Furthermore, catalyst 5 could be recovered easily and reused in the asymmetric transfer hydrogenation of benzils, where, the recycled catalyst 5 in eight consecutive reactions still afforded (S)-2-bromophenylethanol with 89% yield and 99% ee (see SI in Table S1 and Figure S6).

Table 3. Asymmetric transfer hydrogenation of benzils.^a

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	Ar O Ar -	Catalyst 5 HCOONa H ₂ O, 40 °C	OH Ar OH (<i>dl</i>)-7a-7g	OH Ar Ar OH (meso)-8a-8g	
ntry	Ar (7)	%Yield	Time (h)	dl/meso	%ee ^b
	Ph (7a)	94	2	87/13	99
	4-FPh (7b)	95	2	81/19	99
	3-FPh (7c)	92	2	75/25	95
	4-BrPh (7d)	93	2	65/35	99

^aReaction conditions: catalyst **5** (21.50 mg, 2.0 μ mol of Rh based on the ICP analysis), HCO₂Na (1.0 mmol), benzils (0.20 mmol) and 2.0 mL water, reaction temperature (40 °C). ^b The *ee* values were determined by chiral HPLC analysis (see SI in Figure S5).

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Conclusions

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In conclusions, by utilizing hydrophobic benefit and phasetransfer-featured imidazolium-functionality, we develop an imidazolium-modified chiral rhodium/diamine-functionalized periodic mesoporous organosilica. As a bifunctional heterogeneous catalyst, it displays high catalytic activity and enantioselectivity in the asymmetric transfer hydrogenation of α haloketones and benzils, where the hydrophobic organosilicate network, phase-transfer-featured imidazolium-functionality, and well-defined chiral organorhodium catalytic nature are responsible for highly catalytic performance. Moreover, the convenient recovery and high recyclability make this heterogeneous catalyst an attractive feature in practical organic transformations in an environmentally friendly manner.

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4-MePh (7e)

4-MeOPh (7f)

3-MeOPh (7g)

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Graphical Abstract :

An Imidazolium-Modified Chiral Rhodium/diamine-Functionalized Periodic Mesoporous Organosilica for Asymmetric Transfer Hydrogenation of α–Haloketones and Benzils in Aqueous Medium

Feng Zhou, Xiaoying Hu, Ming Gao, Tanyu Cheng*, Guohua Liu*



An imidazolium-modified chiral rhodium/diamine-functionalized periodic mesoporous organosilica is developed, which promotes greatly asymmetric transfer hydrogenation of α -haloketones and benzils in aqueous medium.