Heterogeneous Catalysis

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Heterogeneous Enantioselective Hydrogenation of Aromatic Ketones Catalyzed by Cinchona- and Phosphine-Modified Iridium Catalysts[**]

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Dedicated to the Catalysis Society of Japan on the occasion of the 50th anniversary

Heterogeneous catalytic systems for asymmetric reactions are fascinating because of their potential in synthetic applications.[1] However, because of the high substrate specificity of these catalysts, the complexity of the task at hand, and the difficulties in understanding and designing the catalytic reactions, there have been just three established systems reported.[1a] One system identified for asymmetric hydrogenation is the cinchona-modified Pt/Al_2O_3 for asymmetric hydrogenation of α-keto esters, which was developed by Orito et al. in 1979.[2] Baiker et al. successfully used this catalyst in the asymmetric hydrogenation of activated aromatic ketones.[3] However, when considering the asymmetric hydrogenation of simple aromatic ketones and derivatives, which are among the most fundamental subjects in modern synthetic chemistry, few successful heterogeneous catalytic examples are reported.

Chiral modifiers are the origin of the enantioselectivity in most heterogeneous catalytic reactions, and natural cinchona alkaloids and their derivatives have been widely used as versatile chiral catalysts, ligands, column packing, and chiral shift reagents.[4] Two of the three most well-known heterogeneous catalytic systems in asymmetric reactions are based on natural cinchona alkaloids and their derivatives as the chiral modifiers.[2,5] Stabilizers, which are widely used in preparing nanometal catalysts, including amines,[6] phosphines,[7] and thiols,[8] have been gradually introduced into supported catalysts in recent years. We previously reported polyvinylpyrrolidone (PVP) and cinchona-stabilized Rh in the asymmetric hydrogenation of α-keto esters, in which moderate to good enantioselectivities were obtained.[9] Meanwhile, little attention has been paid to the preparation of supported metal catalysts stabilized by phosphines. Reported herein is a Ph_3P-stabilized Ir/SiO_2 catalyst system modified by a chiral diamine, derived from cinchona alkaloids, for the asymmetric hydrogenation of simple aromatic ketones and their derivatives; the results are compared to known homogeneous catalysts.[10] To the best of our knowledge, this is the first report of the asymmetric hydrogenation of simple aromatic ketones with a greater than 95% *ee* by using a new heterogeneous catalyst. This report is also the first successful example of the asymmetric hydrogenation of simple aromatic ketones employing Ir and H_2.

The high-resolution transmission electron microscopy (HRTEM) picture (Figure 1 in the Supporting Information) of $3\%\,Ir/SiO_2/2tpp$ (tpp = triphenylphosphine) showed that Ir is highly dispersed on the SiO_2 as an amorphous agglomerate. The X-ray photoelectron spectroscopy (XPS) analysis indicated that the metal component is present in a reduced state (Ir $4f_{7/2}$ core level centered at 61.6 eV) compared to Ir^0 (Ir $4f_{7/2}$ core level centered at 60.8 eV),[11] and the binding energy (103.5 eV) of Si_{2p} is similar to the expected value (103.4 eV) for the corresponding SiO_2.[12] The full range XPS spectra indicated that the amount of Ir supported on the SiO_2 is 3% wt/wt. The catalysts are remarkably stable in the solid state and can be stored open to air.

IR and ^{31}P solid state NMR (^{31}PMAS NMR) spectra are effective for the investigation of the mutual ligand–metal–support interactions of solid catalysts.[13] Information on the interaction between the metal and the phosphine was first confirmed by FTIR methods in which the red shift of the $P{-}C_6H_5$ deformation around 1434 cm^{-1} in $3\%\,Ir/SiO_2/2tpp$ is an indication of the coordination of PPh_3 to the metal. Interaction between the cinchona alkaloid and the metal was also confirmed by FTIR analysis in which the blue shift of the N−H deformation around 3366 cm^{-1} in $3\%\,Ir/SiO_2/2tpp$/diamine **2** is an indication of the coordination of the amine with the metal. Furthermore, the interactions between PPh_3, Ir, **2**, and SiO_2 were detected by ^{31}PMAS NMR spectroscopy (Figure 1); the broad signal at $\delta = -5.4$ ppm in Figure 1a was assigned to the PPh_3 supported on the SiO_2 on the basis of literature reports.[13a] The broad signal at $\delta = 37.4$ ppm may be attributed to a strong P···Si interaction on acidic SiO_2 (Figure 1a), which is similar to phenomena observed in previous reports.[13] The broad signals at $\delta = 8.2$ ppm and $\delta = 26.0$ ppm in Figure 1c are new, and appear during the catalyst ($3\%\,Ir/SiO_2/2tpp$) preparation, whereas the signal for the PPh_3 supported on SiO_2 disappeared and the signal for the P···Si interaction was enhanced. When diamine **2** was added to the $3\%\,Ir/SiO_2/2tpp$ catalyst (Figure 1d), two new signals appeared ($\delta = 13.5$ and 30.3 ppm) and the signal of the P···Si

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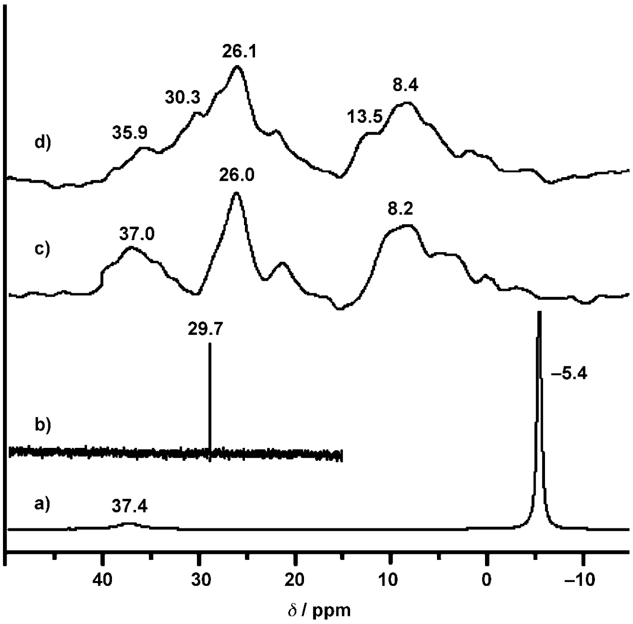
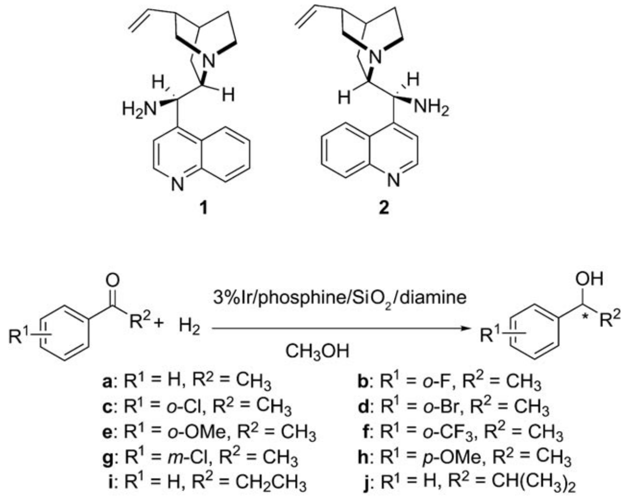


Figure 1. ^{31}PMAS NMR spectra of a) PPh_3/SiO_2, c) 3%Ir/SiO_2/2tpp, and d) 3%Ir/SiO_2/2tpp/diamine **2**; and ^{31}P NMR spectra of b) [{Ir(cod)Cl}$_2$]/2tpp/diamine **2**. cod = cycloocta-1,5-diene.

interaction weakened. The above results suggest that the broad signals at $\delta = 8.2$ ppm and 26.0 ppm in Figure 1c represent the coordination between PPh_3 and Ir on the SiO_2, and the new signals at $\delta = 13.5$ and 30.3 ppm in Figure 1d are valuable hints about the coordination between diamine **2** and Ir. In comparing these signals with those of the homogeneous [{Ir(cod)Cl}$_2$]/2tpp/diamine **2** catalyst (Figure 1b), the PPh_3–Ir coordination around 26.0 ppm in Figures 1c and d might be similar to the PPh_3–Ir coordination in homogeneous [{Ir(cod)Cl}$_2$]/2tpp/diamine **2** catalyst.

Asymmetric hydrogenation of aromatic ketones was performed in a 20 mL stainless steel autoclave with a magnetic stirr bar, by using chiral diamine **1** (9-amino(9-deoxy)epicinchonine) and **2** (9-amino(9-deoxy)epicinchonidine) as modifiers, which are derived from natural cinchona alkaloids (Scheme 1). Chiral modifier **2** was used to test the effect of the different reaction factors on the asymmetric hydrogenation of acetophenone. The stabilizer (PPh_3) is very important in this system; without the stabilizer, the hydrogenation resulted in a conversion as low as 11% and an *ee* value of 9%. Classically modified 3% Ir/SiO_2 catalyst with tpp and chiral modifier **2** gave a 17% conversion and 52% enantioselectivity (40 °C, 20 h). These results indicate that phosphine not only stabilized the metal particles in the preparation of the catalyst, but also served to additionally modify the supported metal with diamine in the asymmetric hydrogenation. Since the properties of the stabilizers greatly influence the particle size and dispersion of the reduced metal in the catalyst,[5a] phosphines, such as tris(4-methoxyphenyl)phosphine (motpp), tris(4-trifluoromethylphenyl)phosphine (tftpp), tris(sodium-m-sulfonatophenyl)phosphine (tppts), 1,2-bis(diphenylphosphinomethyl)benzene (bdpx), (*S,S*)-(+)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (diop), 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl (bisbi) and (*S*)-2,2′-bis(di-4-tolylphosphino)-1,1′-binaphthyl (tolbinap), were tested, however, none of them were better than the simple achiral PPh_3. The highest activity and enantioselectivity was obtained when the initial molar ratio of PPh_3 to Ir used in the preparation of the catalyst was 2:1 (the actual PPh_3/Ir ratio on the SiO_2 support is 1.9:1, which was measured by ICP-AES methods). Increasing or decreasing the ratio of PPh_3 to Ir was unfavorable to both the activity and the enantioselectivity. Methanol is the best choice for a solvent as both low activity and poor enantioselectivity were observed in other solvents. Similar to homogeneous reactions[10] and some heterogeneous reactions,[9e,14a,15] a base is necessary to accelerate the reaction. The addition of different bases, such as *t*BuOK, LiOH, NaOH, or KOH, can enhance both the activity and the enantioselectivity. For the alkali metal hydroxides both the activity and the enantioselectivity decrease in the order of $Li^+ > Na^+ > K^+$. The addition of both modifier **2** and LiOH greatly enhanced the activity and enantioselectivity (Table 1, entry 2). A high concentration of the modifier is needed for simple aromatic ketone asymmetric hydrogenation; a similar observation was reported in recent work by Reyes and co-workers[16]. By using 1 mol% (compared to the supported Ir) of chiral diamine **2**, the enantioselectivity was maintained during the asymmetric hydrogenation at an elevated temperature and a prolonged reaction time (40 °C, 20 h, 36% conversion and 66% *ee*). Possibly, the sterically hindered diamine **2** prefers the base with the smaller metal cation to produce higher activity and enantioselectivity. In the absence of LiOH, the conversion was only 2% with 31% *ee* at 30 °C for three hours. By raising the reaction temperature and prolonging the reaction time (40 °C, 20 h), the reaction proceeds with 16% conversion and 54% *ee*. These results suggest that a proper stabilizer, molar ratio of P/Ir, solvent, and combination of chiral diamine and LiOH are helpful for the formation of the catalytic species and the resulting chiral induction.



Scheme 1. Modifiers used and the general reaction.

For the cinchona-modified Pt/Al_2O_3 system, it was found that a small change in the structure of modifier led to an interesting influence on the activity, the enantioselectivity,

Table 1: Enantioselective hydrogenation of aromatic ketones catalyzed by 3 %Ir/phosphine/SiO_2/diamine system (see Scheme 1).[a]

Entry	Substrate	Diamine	*t* [h]	Yield [%]	*ee* [%]	Config.[b]
1	**a**	**1**	10	> 99	88	*S*
2	**a**	**2**	3	> 99	74	*R*
3	**a**	**1**[c]	6	> 99	86	*S*
4	**b**	**1**	10	44	86	*S*
5	**b**	**2**	3	96	77	*R*
6	**c**	**1**	10	80	96	*S*
7	**c**	**2**	3	> 99	86	*R*
8	**d**	**1**	10	83	92	*S*
9	**d**	**2**	3	> 99	90	*R*
10	**e**	**1**	10	55	94	*S*
11	**e**	**1**	20	> 99	95	*S*
12	**e**	**2**	3	99	86	*R*
13	**f**	**1**	10	60	81	*S*
14	**f**	**2**	3	96	83	*R*
15	**g**	**1**	10	33	75	*S*
16	**h**	**1**	10	75	87	*S*
17	**h**	**2**	3	97	76	*R*
18	**i**	**1**	10	21	86	*S*
19	**i**	**2**	3	97	75	*R*
20	**j**	**1**	10	48	52	*S*

[a] Reaction was carried out at 30 °C for modifier **2** and 40 °C for modifier **1**. Substrate: in a 2 mL methanol solution at [0.313 M], P_{H_2}:6.0MPa. Substrate/Ir/diamine = 200:1:2, [LiOH] = 0.125 mol L^{-1}. Products were analyzed by a GC instrument with an FID detector and β-DEX120 capillary column. [b] Determined by sign of rotation. [c] The double bond of modifier **1** was hydrogenated.

and the configuration of the product,[17] providing useful information for understanding the reaction mechanism; for example, when DHCD (10, 11-dihydrocinchonidine) is used as a modifier in the hydrogenation of α-keto esters, the catalyst activity and enantioselectivity are higher than those obtained with cinchonidine (CD). Modifiers containing a small alkoxy group (methoxy, ethoxy) gave the same enantiomer in similar excess to that obtained with CD. The enantioselectivity decreases rapidly with the increasing bulkiness of the ether group, and in some cases even the opposite enantiomer is formed with good *ee* values.[18] In our system, when the double bond in modifier **1** was hydrogenated, the reaction rate was enhanced for the hydrogenation of acetophenone, but the enantioselectivity was slightly decreased (Table 1, entries 1 and 3). This result is an indication that the double bond in modifier **1** is helpful in creating a favorable steric environment for enantioselectivity. To our surprise, when 9-amino(9-deoxy)epiquinine was used as a modifier in the hydrogenation of acetophenone, the reaction progressed very slowly with a low enantioselectivity even under elevated reaction temperatures and prolonged reaction times (30 °C, 20 h, 3 % conversion and 25 % *ee*; 40 °C, 20 h, 9 % conversion in 40 % *ee*). This indicates the high specific correlation between the modifier and substrate. Other modifiers, such as cinchonine, cinchonidine, and quinine, were tested, and the amine group in the nine-position of the modifier is essential (for details of different reaction parameters affecting the hydrogenation see the Supporting Information)

Because of the similarity of our Ir catalyst to the Ru/phosphine/diamine catalsyt in a homogeneous system, it is important to clarify whether the Ir leached into the reaction solution to from a soluble complex that has catalytic activity. There are few successful examples of homogeneous catalysts employing Ir with H_2 in the presence of both a phosphine and an amine are reported, but there are some successful examples reported for transfer hydrogenation.[19] For comparison to this work, homogeneous catalysts, formed in situ, were investigated for the hydrogenation and poor results were obtained. For example, the homogeneous Ir/2tpp/diamine **2** catalyst gave 100 % conversion and 45 % *ee* at 30 °C after 3 hours, the homogeneous Ir/2tppts/diamine **2** catalyst achieved 98 % conversion and 18 % *ee*, and the homogeneous Ir/bisbi/diamine **2** catalyst achieved 60 % conversion and 36 % *ee* (for details of the homogeneous catalytic experiment see the Supporting Information). The conventional filtering test[9e, 14] was employed to investigate the catalyst leaching. At the end of the hydrogenation reaction with chiral modifier **2**, the solution and the catalyst were separated by using high-speed centrifugation under an argon atmosphere, and both the solution and the catalyst were used for another hydrogenation reaction with acetophenone. The solution had no catalytic activity after when fresh substrate was introduced, and the leaching of Ir and PPh_3 from the 3 %Ir/SiO_2/2tpp catalyst into the solution was measured by ICP-AES methods to show that only 0.12 % Ir and 0.57 % PPh_3 were detected in the liquid phase after the first hydrogenation of acetophenone. This small amount of metal leaching is ascribed to an equilibrium between the soluble and the bound metal that commonly exists in supported heterogeneous catalyst.[20] Similar to the work reported by Bujoli and co-workers,[20a] the molar ratio of PPh_3/Ir leached into solution is large (9:1) , which poisoned the Ir which leached into the solution. A similar poisoning phenomenon was observed in other experiments (Figure 3 in the Supporting Information and a previous report).[20b] Both the small amount of metal leaching and the excess PPh_3 (PPh_3/Ir = 9:1) leached into the solution result in no observed catalytic activity upon addition of fresh substrate. However, the recovered catalyst maintained its activity, although the activity and enantioselectivity decreased in some content. Furthermore, mercury-poisoning experiments were run as they can selectively poison metal nanoparticles, by forming an amalgam with mercury, to help distinguish between homogeneous and heterogeneous catalysts.[21] In such an experiment for our system, the conversion in the presence of modifier **2** was 20 % after the initial 15 minutes; mercury was then added under argon atmosphere and the reaction was completely terminated as evidenced by no change in the conversion (20.7 %) after an additional reaction time of one hour. Additionally, according to the graph of the conversion versus time over the period of 0–30 minutes for the hydrogenation, the conversion of acetophenone increased linearly, showing no induction period for our system, proving that this catalyst does not convert into other catalytically active species. All the results above strongly support proposal that the reaction progresses under heterogeneous catalysis rather than homogeneous catalysis.

Some representative examples are listed in Table 1 for the asymmetric hydrogenation of aromatic ketones catalyzed by Ph_3P stabilized Ir/SiO_2 modified by diamine **1** or **2**. The extent of the enantioselectivity appears to be delicately influenced by the structure of the diamine auxiliary as well as the substituent in the substrate. In general, modifier **1** shows better enantioselectivity but lower activity than modifier **2**. The use of the *S* diamine affords the *R*-configurated alcohol product, whereas the *R* diamine gives the *S*-configured alcohol. *Ortho* substituents on acetophenone do not improve the activity of the asymmetric hydrogenation because of the steric bulk, but the activity increases with the decreasing electronegativity of the halogen (Table 1, entries 4–9). Our system is smilar to the cinchona-modified Pt/Al_2O_3 system[1] in that the enantioselectivitiy gradually increases as the reaction progresses (Table 1, entries 10 and 11). The highest enantiomeric excess was obtained for the hydrogenation of 2′-chloroacetophenone by using diamine **1** as the chiral modifier (Table 1, entry 6). Other substrates were also tested and it was found that when the substituent is in the *meta* or *para* position (Table 1, entry 15–17), the degree of the enantioselection was obviously decreased in comparison to the *ortho*-substituted counterparts. The enantioselectivity also decreased by increasing the bulkiness of the alkyl group from methyl or primary alkyl to isopropyl (Table 1, entries 1 and 2, and 18–20). The effect of the steric bulk and the electronic nature of the substrate influence the activity and the enantioselectivity of the reaction.

In conclusion we demonstrated the facile preparation of a supported iridium catalyst which is stabilized by PPh_3. When modified by a chiral diamine, derived from cinchona alkaloids, this catalyst exhibits a high activity and high enantioselectivity for the hydrogenation of simple aromatic ketones, especially for *ortho*-substituted aromatic ketones. The work reported herein provides a new direction for asymmetric synthesis. Additional work is currently in progress in this and related areas.

Experimental Section

Ph_3P stabilized Ir/SiO_2 catalyst was prepared with a slight modification to our previous reported method.[9] Under an argon atmosphere, a solution of SiO_2 (1.0 g, the average pore size is 4.5 nm, $S_{BET} = 135.9\,m^2g^{-1}$), H_2IrCl_6 (0.168 mmol) and PPh_3 (0.336 mmol) in *i*PrOH (30 mL) was stirred at room temperature for 24 h, after which formaldehyde (5 mL) was added and the mixture heated at 110 °C with stirring for 5 h. The mixture was then cooled to room temperature and the solid was then separated and dried under vacuum at room temperature for 6 h to give the catalyst 3 % Ir/SiO_2/2tpp (the average pore size is 3.9 nm, $S_{BET} = 125.6\,m^2g^{-1}$. The reduction of the average pore size and S_{BET} indicates the attachment of the Ir-tpp to SiO_2 surface). Similarly, other catalysts, with different stabilizers, were prepared by the same procedure.

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