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Iridium Supported on Phosphorus-Doped Porous Organic Polymers: Active and Recyclable Catalyst for Acceptorless Dehydrogenation and Borrowing Hydrogen Reaction

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Abstract: Iridium-on-phosphorus-doped porous organic polymers (POP-Ir) were developed by anchoring simple iridium onto the skeleton of porous organic polymers through coordination bonds. This POP-Ir catalyst, which was thoroughly characterized by means of EDS, SEM, TEM, XRD, XPS, and FT-IR, revealed excellent catalytic activity for the reaction of diphenyl phosphinamide with benzyl alcohols through borrowing hydrogen strategy and acceptorless dehydrogenation with wide functional group tolerance. Moreover, this POP-Ir catalyst could be simply recovered and reused for at least five times without a significant loss of activity, and revealed considerable application prospects. The mechanism was investigated to further understand this POP-Ir catalytic system and transformations. Overall, the POP-Ir catalytic system has shown high activity and reusability in the borrowing hydrogen reaction between diphenyl phosphinamides and benzyl alcohols.

Keywords: porous organic polymer, iridium complexes, borrowing hydrogen, acceptorless dehydrogenation

Over the past decades, porous organic polymers (POPs) have attracted much attention of scientists.^[1] In general, POPs are composed of one or several organic building blocks by stable covalent organic bonds.^[2] Therefore, POPs possess high specific surface areas, thus enabling their excellent thermal and chemical stability, and the ability to endure harsh reaction conditions. On the other hand, PPh₃ has been known as a good ligand to improve the catalytic activity of coordination metals.^[3] It was observed that introducing PPh₃ could create high density of ligand sites in the POPs, which led to increased loading stability and capability of the active metals and enhanced capability of catalyst recovery. In some cases, it also produced higher catalytic activity and selectivity than homogeneous catalysts, which further demonstrates the great application potential of POPs. In the recent

years, a series of metals that were supported on POP-PPh₃ or other derivatives, have been reported,^[3] including rhodium,^[4] platinum,^[5] cobalt,^[6] iron,^[7] molvbdenum,^[7] zinc^[8] and gold.^[9] Recently, Zhang and Zhuang described a synthesis of novel hyper-crosslinked porous phosphorus-containing polymer (HC-TVP) from tris(4-vinylphenyl) phosphane through radical polymerization. The HC-TVP was successfully ionized when treated with hydrogen iodide to form an ionic porous polymer.^[7] Later, Shi and Ma discovered that triazole-gold(I complex could be anchored into porous organic polymer to enhance the stability and reactivity of gold(I) catalyst.^[9] In 2016, Ding and co-workers synthesized a multifunctional copolymer (PyPPh₂-SO₃H@porous organic polymers, POPs) through the reaction copolymerization under solvothermal conditions and the corresponding copolymersupported Pd-PyPPh2-SO3H@POPs catalyst showed higher activities.^[10] In 2017, Ding and Yan demonstrated that a series of zinc salts and triphenylphosphine integrated porous organic polymers which contained multifunctional sites and were able to show high catalytic performance in the cycloaddition of CO₂ with epoxides.^[8] In 2017, Zhan and Ding developed a P-doped porous organic polymer and employed it as support and ligand te achieve a novel Pd complex which has shown high efficiency in catalyzing hydrogenation reactions and resulted in high chemoselectivity.^[11]

Hydrogen auto-transfer methodology, also named borrowing hydrogen reaction, has attracted increasing attention during the past decade, as this method provides a mild, green and economical pathway to achieve alkylation of ketones and amines.^[12,13] With this borrowing hydrogen strategy, alcohols (or amines) are simply converted *in situ* into the corresponding carbonyl compounds, which are much more reactive than alcohols (or amines) and could react with coupling reagents.^[14] This method provides an environmentally friendly strategy to achieve the goal of sustainable and green chemistry.^[15] Recently, we designed and synthesized several iridium, copper and ruthenium catalysts and explored their catalytic activity through borrowing hydrogen strategy.^[16] However, these metal complexes are costly and exhibited low reusability, thereby, creating massive waste during organic synthesis process.^[17] As a part of our continuing work on borrowing hydrogen reactions,^[18] herein, we reported an innovative heterogeneous iridium catalyst (POP-Ir) which was supported on phosphorus- doped porous organic polymers (Figure 1). The POP-Ir catalyst has revealed excellent catalytic activity in the reaction of diphenyl phosphinamide with benzyl alcohol through borrowing hydrogen strategy and acceptorless dehydrogenation with wide tolerance of functional group.



Figure 1. The structure of POP-Ir.

The synthesis of supported iridium catalyst POP-Ir.

The synthetic method of polymers POP-PPh₃ was referred to the previous literatures and the steps of polymers synthesis were described in SI.^[9] Next, POP-PPh₃ and [Cp*IrCl₂]₂ were added to a dried Schlenk tube with MeOH as the solvent under N₂ atmosphere. The tube was closed and the resulting mixture was stirred at room temperature for 12 h. The desired heterogeneous iridium catalyst was obtained as a yellow solid (POP-Ir) by centrifugal suspension and washed with MeOH in ultrasonic vibration for several times (Scheme 1).



Scheme 1. The synthesis of supported iridium catalyst.

Characterization of POP-Ir.

After synthesis, the supported Ir catalyst (POP-Ir) was characterized through scanning electron microscope (SEM), energy dispersive spectrometer (EDS), X-ray power diffraction (XRD), X-ray photoelectron spectrometry (XPS) and transmission electron microscopy (TEM).



Figure 2. SEM images of (a) POP-PPh₃, TEM images of (b) POP-PPh₃, TEM images of (c), (d) POP-Ir.

The images of (a) and (b) were scanning electron microscope and transmission electron microscopy of POP-PPh₃ (Figure 2). It could be seen from the figure that the polymer had a reticulated spatial structure with large voids inside, which was beneficial to the formation of complexes. And the TEM images of (c), (d) obviously revealed that the iridium catalyst was supported on POP-PPh₃. The morphologies of the POP-Ir were clearly observed through the transmission electron microscopy (TEM). In the figure (d), characteristic structure and unit cell size of iridium complex after supported could be clearly observed. The measured average spacing of the crystal faces is 0.284 nm, which was within the normal range.



Figure 3. XRD pattern of (a) POP-Ir, (b) POP-PPh_{3.}

Next, X-ray power diffraction (XRD) was conducted to confirm the chemical structure of this catalyst. The steamed bun peaks at $2\theta = 22.80^{\circ}$ of XRD pattern (b) was characteristic peaks of polystyrene-like compounds, which was reported in previous studies. Meanwhile the peak at $2\theta = 12.67^{\circ}$ of XRD pattern (a) was the peaks of iridium. The results revealed that [Cp*IrCl₂]₂ were well loaded on the POP-PPh₃ (Figure 3). In addition, the EDS pattern showed peaks at 9.2 keV belonged to the characteristic peaks of iridium (Figure 4).



Figure 4. EDS pattern of POP-Ir.

The element compositions and surface chemical states of POP-Ir composite were also proved by X-ray photoelectron spectroscopy. The obvious and wide XPS spectra indicated the presence of C, P, Cl and Ir elements, and binding energy at 64.7 and 61.9 eV belonged to Ir³⁺ (Figure 5). More detailed data of XPS and analysis could be found in the SI.



Figure 5. XPS spectra of POP-Ir.

Figure S3 shows the XPS pattern of **1a**. After fitting the P spectral peaks, we found peaks at 132.18 eV, which belong to P-C bonds, and on the other hand the peaks at 130.75 eV, which belong to P-Ir bonds. This result is consistent with a previous report.^[9] In Figure S3c, the C1s peaks at 284.6 and 285.3 are attributed to C-C and C-P bonds, respectively. This observation is consistent with the proposed structure of $1a^{[10]}$. We also found peaks of binding energy at 64.7 eV and 61.9 eV, belonging to Ir^{3+} ,

which are consistent with the existing literature data.^[19] According to quantitative elemental analysis and calculations, the load of iridium is about 4.4% (Table S1).

Catalytic activity

Compared to the borrowing hydrogen reaction of amines, ketones and alcohols,^[20] the reaction of amides was much more challenging, especially for phosphinic amides.^[21] Substituted phosphinic amides, the special kind of phosphorus-containing compounds, have been widely used in pesticides, medicines, functional materials, etc. Although considerable efforts were made on synthesizing the substituted phosphinic amides through borrowing hydrogen strategy, no recoverable catalyst has been successful used in this transformation.[22]

With this POP-Ir (1a) in hand, the borrowing hydrogen reaction of diphenyl phosphinamide and benzyl alcohol was selected as the model reaction to test the catalytic activity. From the initial results, it was observed that iridium complex played a crucial role in catalyzing the reaction (Table 1, entries 1~3). Interestingly, it was found that KOH was the best base for this reaction (Table 1, entry 4). After screening the reaction time, we found that the reaction only took 4 hours to achieve a good yield (Table 1, entry 10). This catalyst greatly reduced the reaction time compared with previously reported conditions.^[22c] In summary, it was found that the optimal condition of this reaction was using KOH as the base with 10 mg catalyst loading (4% loading, w/w) and refluxing at 110 °C in toluene for 4 hours.

Table 1. Optimization of reaction conditions.^a

Ph ∖ II Ph ^{∕ P} ∖ 2	+ (ОН За	cat., tolu base, reflu	ene Ph∖ Jx, 4 h Ph́	O P N H 4a
Entry	Cat.	Base	Temp.	Time [h]	Yield [%]
1	-	KOH	120 °C	12	<5
2	POP	KOH	120 °C	12	<5
3	1a	KOH	120 °C	12	94
4	1a	KOH	110 °C	12	95
5	1a	KOH	100 °C	12	89
6	1a	K ₂ CO ₃	110 °C	12	76
7	1a	Cs ₂ CO ₃	110 °C	12	81
8	1a	NaOH	110 °C	12	83
9	1a	KOH	110 °C	8	94
10	1a	КОН	110 °C	4	95
11	1a	KOH	110 °C	2	83
12^{c}	1a	KOH	110 °C	4	87

^a Reagents and conditions: 2 (0.5 mmol), 3a (0.55 mmol), 1a (10 mg, 4% loading, w/w), base (0.2 eq.), toluene (1.0 mL), 4 h.^b Yields of isolated product. ^c 1,4-dioxane was used.

After optimizing the reaction conditions, the substrate expansion for the reaction of diphenyl phosphinamides and benzyl alcohols was examined (Table 2). It was obvious that there were relatively high yields for the benzyl alcohols with either electron withdrawing groups or electron donating groups which in different substitution positions of the aromatic ring

Table 2. Reaction of phosphinic amides and benzyl alcohols a,b



^{*a*} Reagents and conditions: **2** (0.5 mmol), **3** (0.55 mmol), POP-Ir (10 mg, 4% loading, w/w), KOH (0.2 eq.), toluene (1.0 mL), 4 h. ^{*b*} Isolated yields.

Functionalized triazine derivatives have revealed excellent biological activities for example anti-HIV activities, anti-HSV-1, antibacterial and anticancer activities. Traditionally, triazine derivatives are synthesized via nucleophilic displacement reaction of cyanuric chlorides, or substituted biguanides reaction with anhydrides, acid chlorides, carboxylates and or through cyclization reaction of acylamidines with guanidines or amidines.^[23] For example, Zhang and Cui have claimed that only 3,6-dihydro-1,3,5-triazine derivatives could be obtained through the reaction of biguanides with aldehydes and disclosed that benzyl alcohols were much more prospective and promising.^[24] In order to further verify the activity of the above catalyst 1a, we attempted to apply it to catalyse the dehydrogenation reaction of biguanides with benzyl alcohols (Scheme 2).



Scheme 2. The synthesis of triazine derivatives.

As shown in Table 3, many substrates are suitable for this dehydrogenation reaction resulting in high yields. Specifically, it was demonstrated that substrates with different functional groups such as methoxy, methyl and halide (Cl, Br, and F) at different substitution positions of the aryl groups were well tolerated. Furthermore, the substrates with aromatic ring structures such as pyridy, naphthyl and thienyl, also worked smoothly and afforded good yields. Several biguanide derivatives also reacted well and the corresponding 1,3,5-triazine derivatives were produced in good to excellent yields.

Table 3. Substrate expansion of biguanides and benzyl alcohols.^{a,b}



^{*a*} Reagents and conditions: **5** (0.5 mmol), **3** (0.55 mmol), POP-Ir (10 mg, 4% loading, w/w), *t*-BuOK (1.5 eq.), 1,4-dioxane (1.0 mL), 10 h. ^{*b*} Isolated yields.

Unexpectedly, none of the desired products was detected in the reaction of halide-substituted benzyl alcohols with guanidines, but only dehalogenation product was achieved, which was observed. (Scheme 3)



Scheme 3. The reactions of dimethylbiguanide and halide substituted benzyl alcohols.

Catalyst investigation

The success of this heterogeneous POP-Ir catalytic system on borrowing hydrogen reaction promoted us to gain better insights into the possible mechanism. The control experiments of diphenyl phosphinamides and benzyl alcohols were conducted. If only the carrier POP was used to catalyze this reaction, it was observed that no desired product was obtained (Scheme 4). Furthermore, simple iridium salts couldn't catalyze this reaction and [Cp*IrCl₂]₂ only produced moderate yield. When phosphorus doped porous organic polymers were introduced into this system, high catalytic activity was obtained in the reaction of diphenyl phosphinamide and benzyl alcohol. This result surprising might be caused by phosphorus doped porous organic polymers, which should be the critical ligand in this transformation. On the other hand, the synergistic effect of the carrier POP and iridium shouldn't be ignored since it might be another reason for the high activity of POP-Ir catalyst. Meanwhile, the preliminary mechanism exploration experiments also ruled out the possibility of free radical pathway (Scheme 4).





Next, the Hammett plot equation was used in order to elucidate the electronic effects on the progress of the reaction. *para*-Substituted benzyl alcohols were used to construct the equation and the Hammett plot is shown in Scheme 5. The slope disclosed that the electronic effect of benzyl alcohols had some influence on the initial phase of this transformation and the rho-value was positive. In general, benzyl alcohols containing an electron-donating group at the *para*-position were relatively easier to be oxidized to afford the corresponding benzaldehydes. Deceleration by electron-donating groups on the benzyl alcohol in this reaction showed that electron-withdrawing groups on the reactant might be more favorable during this transition state. This resulting positive rho-value suggests that there would be a build-up of negative charge in the transition state.



Scheme 5. Hammett plot of *para*-substituted alcohols.

The intermolecular competition reaction on the kinetically relevant elementary steps was also conducted to fight out the rate determining step. The kinetic isotope effect value (KIE) of diphenyl phosphinamide and benzyl alcohol was obtained *vii* the first order reaction plot between $\ln[3a-d2]$ and $\ln[3a]$, suggesting an effective evidence that the dehydrogenation of 3a was the rate determining step for this borrowing hydrogen reaction (Scheme 6).



Scheme 6. Kinetic plot of benzyl alcohol and benzyl alcohold2. A₀: original concentration of substrate. A_t: concentration of substrate at time t. k: rate constant. $K_H/K_D = 2.03$.

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In addition, the kinetic investigations of N-benzyl-P, P-diphenylphosphinic amide synthesis (**4a**) was carried out to better explain the possible reaction pathway. The experiments revealed that benzaldehyde was the most convincing intermediate and suggested the formation and consumption of aldehyde were the key steps during the progress of this reaction. It was disclosed that the reaction needed only 4-5 hours to finish, and longer time was unnecessary (Figure 6).



Figure 6. Kinetic investigations for the synthesis of 4a.

After the reaction, the residue was completely dissolved in methanol and the catalyst POP-Ir (1a) was collected by centrifugation. The catalyst was washed and centrifuged several times with methanol, then dried under vacuum. Afterward, it was recycled in the aforementioned reactions. To out delight, it was found that good yields could be maintained in these two reactions when the catalyst was recycled up to five times (Scheme 7).

To further investigate the catalyst system of POP-Ir after the reactions, a leaching experiment was performed. POP-Ir was recycled in the 4 hour reaction of diphenylphosphonic amide and benzyl alcohol in toluene at 110 °C with KOH as the base. The amount of the Ir leaching into solution was determined after each reaction cycle through ICP-MS analysis. The result after the first three cycles showed that Ir was less than 1 ug/L. After five repeated cycles, the Ir leaching was found to be 5.1 ug/L, which was almost negligible. Thus, these experiments demonstrated that POP-Ir had excellent stability and regenerating capability.



Scheme 7. Recycling experiments.

After recycling experiments, the catalyst POP-Ir was collected and characterized by X-ray photoelectron spectroscopy (XPS) again after washed three times with methanol. The content of iridium was reduced from 4.4% to 4.3% through elemental analysis (Table S2). After eliminating instrumental errors and unavoidable loss, this result was satisfactory. By comparing the data and the peak fitting of C, Cl, P and Ir before and after the recycling experiment, we could find that the two experimental results were almost identical (Figure S4). The XPS spectra indicated that [Cp*IrCl₂]₂ was loaded on the POP and POP-Ir had strong stability in this condition.

Finally, the gram scale synthesis of N, N-dimethyl-6phenyl-1,3,5-triazine-2,4-diamine (**6a**) was attempted to illustrate the practicality of this POP-Ir catalytic system. It was disclosed that more than 10 grams of 1,3,5-triazine derivative (**6a**) could be obtained in 83% yield, which further revealed that POP-Ir catalyst has good catalytic performance in the synthesis of 1,3,5-triazine derivatives (Scheme 8).



Scheme 8. The synthesis of 1,3,5-triazine derivative in a large scale.

In conclusion, we developed a novel heterogeneous iridium catalyst, which was synthesized from phosphorus-doped porous organic polymer through coordination bonds. This supported catalyst POP-Ir was fully characterized and proved to be effective for borrowing hydrogen reaction of diphenyl phosphinamides with benzyl alcohols, leading to high yields and selectivity. This POP-Ir catalyst could be used to catalyze the synthesis of triazine derivatives through acceptorless dehydrogenation of biguanides with benzyl alcohols. This type of porous and stable catalysts expands the application potential of heterogeneous catalysts and wider fields including the products and important synthesis of natural intermediates synthesis. To further investigate and enrich the diversity of this type of heterogeneous

catalyst, the development of POPs using other molecular skeletons or metals is currently ongoing in our group.

Experimental Section

General procedure for synthesis of POP-Ir (1a)

Under N₂ atmosphere, POP-PPh₃ (1.0 g, 2.94 mmol), [Cp*IrCl₂]₂ (80 mg, 0.10 mmol) and dry methanol (10 mL) was added to an oven-dried 50 mL Schlenk tube equipped with a stir bar. Then, the tube was closed and the resulting mixture was stirred at room temperature for 12 h. After the reaction, the solid changed from white to yellow and the volume became clear. Solids were obtained bv centrifugation washed with methanol and and dichloromethane three times each before dried.

General procedure for the reaction of diphenylphosphonic amides and benzyl alcohols

To 25 mL reaction tube was added diphenylphosphonic amide (0.5 mmol), benzyl alcohol (0.55 mmol), catalyst **1a** (10 mg, 4% loading, w/w), KOH (0.2 equiv.). Then, toluene (1.0 mL) was added and the mixture was stirred at 110 °C for 4 h. The solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 1:1) afforded the desired compound **4**.

General procedure for the reaction of biguanides and benzyl alcohols

To 25 mL reaction tube was added biguanide (0.5 mmol), benzyl alcohol (0.55 mmol), catalyst **1a** (10 mg, 4% loading, w/w), *t*-BuOK (1.5 equiv). Then, 1,4-dioxane (1.0 mL) was added and the mixture was stirred at 100 °C for 10 h. The solvent was removed under reduced pressure carefully and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the desired compound **6**.

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