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A Zirconium Indazole Carboxylate Coordination Polymer as an Efficient Catalyst for Dehydrogenation-Cyclization and Oxidative Coupling Reactions

Xinxin Sang,^{†[a]} Xinyu Hu,^{†[a]} Rong Tao,^[a] Yilin Zhang,^[b] Haiyan Zhu,^[a] and Dawei Wang^{*[a]}

Dedication ((optional))

Abstract: Rational ligand design is crucial for achieving widespread applications of coordination polymers. The preparation, structural characterisation, and catalytic applications of zirconium (IV) coordination polymer (Zr-IDA), which was derived from 1-(carboxymethyl)-1Hindazole-5-carboxylic acid are reported. The Zr-IDA catalyst contains porous and highly crystalline particles with a quasi-spherical morphology around 100 nm in size, and Zr was coordinated with both O and N as shown by FT-IR and XPS measurements. Importantly, the Zr-IDA catalyst shows great activity, selectivity and stability in the oxidative coupling of benzyl cyanides with tert-butyl hydroperoxide to afford tert-butyl peresters, and the dehydrogenation cyclization of o-phenylenediamines with aromatic alcohols to afford 1,2-disubstituted benzimidazole derivatives. Mechanistic investigations were carried out to study these reactions and the developed catalytic system in more detail.

Introduction

Coordination polymers (CPs), mostly hybrid inorganic/ organic compounds, have received significant attention due to their structural diversity^[1] and potential applications in gas storage and separation,^[2] catalysis,^[3] pollutant degradation^[4] and drug delivery.^[5] The structures and properties of CPs are highly depending on the natures of metal centre and organic bridging ligands. Zirconium (Zr) is widely distributed in nature and biological systems. As a result, extensive efforts have been paid on the development of Zr-CPs. In the past several decades, a series of Zr-CPs employing simple organic ligands, such as *p*-phthalic

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acid, trimesic acid, *meso*-tetra(4carboxyphenyl)porphine have been developed. Owing to the high charge density of Zr^{IV} and its strong affinity to the carboxylate-based ligands, Zr-CPs were endowed with a promising capacity as heterogeneous catalysis. Several catalytic reactions over Zr-CPs have been developed, including Lewis acid catalysis,^[6] Brønsted acid catalysis,^[7] oxidation catalysis,^[8] biomimetic catalysis,^[9] electrocatalysis,^[10] and photocatalysis.^[11] However, further explorations of novel Zr-CPs for catalysis is still highly desirable.^[12]

The structure of the as-synthesized CPs is largely impacted by the ligand, specifically the size, configuration, substituent, rigidity/ flexibility and the category/number/position of the donor atom in the ligand. To date, many N/O/S-donored organic acids, organic bases, and other species have been designed to serve as ligands.^[13] Remarkably, nitrogen heterocyclic ligands have been seen numerous applications in CPs due to their well-known coordination chemistry and simple accessibility. Among them, pyrazine, imidazole and pyrazole-based heterocyclic systems have attracted increased interest in supra-molecular and metallicsupramolecular chemistry despite the fact that pyridinebased systems are still generally used, known as the 'bedrock' of nitrogen containing ligands. In addition, ligands incorporating more studies on exotic heterocyclic systems, such as fused-ring derivatives and mixed-heteroatom cyclic species, are rarely reported in literature. Such ligands afford additional merits including unique ligand field parameters, donor atom variability and new synthetically-available substitution patterns, which are not seen in simple heterocyclic systems. Fused five- and six-membered rings have been known as powerful scaffolds to produce a large variety of donor-atom geometries comparing to the traditional ligand cores. The overall network structures can be predicted based on geometries and functionalities of the basic ligands. As a class of aforementioned heterocycles, Indazole has demonstrated inherent advantages from a

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coordination chemistry point of view. Zr-CPs containing nitrogen-heterocyclic rings, especially the indazole derivatives, are better candidates for catalytic applications. Based on our previous work on ligands synthesis^[14] and borrowing hydrogen reactions,^[15] herein, we designed an efficient heterogeneous catalyst, Zr-CP (Zr-IDA) with 1-(carboxymethyl)-1H-indazole-5-carboxylic acid (H₂IDA) bearing an indazole moiety. The as-synthesized Zr-IDA revealed high catalytic efficiency in two types of reactions, including esterification of benzyl cyanides with *tert*-butyl peresters and dehydrogenation cyclization of *o*-phenylenediamines with aromatic alcohols to 1,2-disubstituted benzimidazoles.

Results and Discussion

This asymmetric N-heterocyclic carboxylic ligand was synthesized and characterized following the procedures in supporting information. Next, the coordination polymer Zr-IDA was prepared by a solvothermal method with acetic acid as modulator. The synthesized Zr-IDA was first characterized by Fourier transform (FT-IR), scanning infrared spectroscopy electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and N₂ adsorptiondesorption examination. As shown in Fig. 1a, the FT-IR spectra of H₂IDA and Zr-IDA both displayed the characteristic asymmetric vibrations $v_{as}(CO_2)$ (H₂IDA, 1728 and 1675 cm⁻¹; Zr-IDA, 1664 cm⁻¹) and symmetric vibrations $v_s(CO_2)$ (H₂IDA, 1382 cm⁻¹; Zr-IDA, 1250 cm⁻¹) of the carboxylate groups. On the other hand, the asymmetric and symmetric vibrations of the carboxylate anions were spaced at a different wavenumber, 282 cm⁻¹ in Zr-IDA in contrast to 478 and 425 cm⁻¹ seen in H₂IDA, indicating the successful coordination of the carboxylate groups to Zr^{4+} ions. The large spacing between $v_{as}(CO_2)$ and $v_s(CO_2)$ reflects a unidentate coordination mode of the carboxylate group in Zr-IDA. A new peak at 795 cm⁻¹, which can be attributed to the Zr-N bond (Fig.S1), suggests the coordination between Zr and N in Zr-IDA.^[16] To determine the morphology of MOF particles, SEM was performed. The results revealed that the powder contained quasi-spherical particles at a size of around 100 nm (Fig.1b), which was not appropriate for single-crystal analysis. Energydispersive X-ray (EDX) further confirmed the formation of Zr-IDA (the insert of Fig.1b). To evaluate the crystallinity, the materials were investigated by

XRD and the results shown in Figure 1c suggested that the obtained Zr-IDA was highly crystallized. It is isomorphous with the reported Zr-BTB shown in Fig. S2. The Zr₆ cluster shown in Fig.1b was linked by the carboxylate linker to give rise to a framework. As shown in N₂ adsorption-desorption isotherm (Figure 1d), the surface area and pore volume of Zr-IDA were 225 m² g⁻¹ and 0.549 cm³ g⁻¹, respectively. TGA analysis showed that the prepared catalyst had a low weight loss of 3.5% at 200 °C as a result of desorption of water and ethanol previously adsorbed on the catalyst^[17] and had good stability at reaction temperatures (below 200 °C) (Fig. S3[†]). About 50% wt can be retained even at 800 °C, manifesting a high zirconium content in Zr-IDA. The final residues are zirconia and porous carbon. The nano-sized morphology and porous structure suggested that Zr-IDA had great potential to be a good catalyst.



Figure 1. Characterization of Zr-IDA. FT-IR spectra (a), SEM image (b), powder XRD pattern spectrum (c), and N_2 adsorption-desorption isotherm (d).

Furthermore, X-ray photoelectron spectroscopy (XPS) was performed to analyze the chemical state of different elements in Zr-IDA. The XPS survey spectrum of Zr-IDA (Fig. 2a) showed the presence of the principal C 1s, O 1s, N 1s and Zr 3d core levels. The molar ratio of N and Zr is about 1:1, indicating the metal center and the linker has a ratio of 2:1 as deduced via FT-IR. The possible component was $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_6(H_2O)_6(IDA)_3$. The O1s spectra of Zr-IDA and H₂IDA are compared in Fig. 2b. These spectra were deconvoluted to two or three components. O1s peak at 533.2 eV was assigned to C-OH

and 531.9 eV to C(O)OH. The component located at 530.7 eV is attributed to O-Zr bonds, which can also be assigned to lattice oxygen. Obviously, oxygen in C-OH participated in the coordination and crystallization during the Zr-IDA formation. As seen in Fig 2c, Zr 3d exhibited two main peaks at 182.9 and 185.3 eV in Zr-terephthalic acid (Zr-BDC), corresponding to Zr-O linkage in the frameworks.^[18] In addition, a new Zr-N peak at 183.6 eV emerged in Zr-IDA, indicating the coordination participation of N. This can be further confirmed from N1s XPS spectra in Fig. 2d where a N1s peak was found at 399.5 eV, corresponding to pyrazole nitrogen.^[16] Pyrazole nitrogen of H₂IDA was originally deconvoluted to two peaks at 399.1 eV and 399.7 eV. However, a core-level chemical shift of pyrazole nitrogen was produced after coordination, and compromised to 399.5 eV in Zr-IDA. Overall, the compromise of pyrazole nitrogen and emergence of Zr-N peak in Zr-IDA were taken as evidence that N was successfully coordinated to Zr sites in Zr-IDA frameworks.^[19] Introducing electron-donating groups (i.e. pyrrolic N) into the metal sites enhanced the electron density of the metal clusters^[20] and strengthened electrostatic field distributions in the pores, which may eventually impact the catalytic performance of Zr-IDA frameworks.[21]



Figure 2. (a) XPS survey spectrum, (b) O 1s XPS spectrum, (c) Zr 3d XPS, spectrum and (d) N 1s XPS spectrum of Zr-IDA.

The borrowing hydrogen concept^[22] is an elegant means for the sustainable and green formation of C-N or C-C bonds.^[23-26] The first step in this process involves the use of a metal catalyst for the oxidation of an alcohol via dehydrogenation, a widely used transformation in natural product synthesis.^[27] For example, the biologically active 1,2-disubstituted benzimidazole derivatives have attracted much attention due to their broad spectrum of biological and pharmacological properties.^[28] Recently, we disclosed a copper catalyzed dehydrogenation cyclization for the preparation of 1,2-disubstituted benzimidazole. However, the results were not satisfactory to us and the developed heterogeneous BINAP-Cu catalyst could only be obtained in low yield.^[29] With our continued efforts in developing efficient catalyst, we next explored the catalytic activity of Zr-IDA in the synthesis of benzimidazole derivatives.

Firstly, optimum conditions were established based on the model reaction between 1,2-phenylenediamine and alcohol (2a) (Table 1). Various bases and solvents were screened to optimize the reaction. When using K₂CO₃, Cs₂CO₃ and K₃PO₄, the reaction yield was quite low and it was even negligible when Et₃N was employed (Table 1, entries 1-4). Surprisingly, the yield of product 3a could be improved as high as 91% with KOH as the base and toluene as the solvent (Table 1, entry 5). It should be noted that the yield of product (3a) was only 40% without a base. Correspondingly, no product was detected without the catalyst Zr-IDA (Table 1, entries 6 and 7). Solvent screening indicated that toluene was the best solvent in this transformation while dioxane and acetonitrile produced lower yields (Table 1, entries 8 and 13). Dimethyl formamide, dichloromethane, dichloroethane and ethyl acetate hardly led to any desired product (<5% yield, Table 1, entries 9-12). Next, the catalytic performance of various Zr-based catalysts was studied under the optimized conditions. No desired product was obtained by using ZrCl₄ and ZrO₂ as the catalyst. For Zr-BDC and Zr-BTC (Zrterephthalic acid and Zr-trimesic acid), moderate yield could be observed. This affirmed the important role of IDA ligand in the catalytic activation of Zr-IDA in the present condensation reaction. Overall, the highest yield of 1,2disubstituted benzimidazole was obtained when using Zr-IDA as the catalyst in toluene with KOH as the base.





| 2 | Zr-IDA | NEt ₃ | Toluene | <5 |
|----|-------------------|--------------------------------|---------|----|
| 3 | Zr-IDA | Cs_2CO_3 | Toluene | 38 |
| 4 | Zr-IDA | K ₃ PO ₄ | Toluene | 20 |
| 5 | Zr-IDA | КОН | Toluene | 91 |
| 6 | Zr-IDA | none | Toluene | 40 |
| 7 | none | КОН | Toluene | <5 |
| 8 | Zr-IDA | КОН | Dioxane | 33 |
| 9 | Zr-IDA | КОН | DMF | <5 |
| 10 | Zr-IDA | КОН | DCM | <5 |
| 11 | Zr-IDA | КОН | DCE | <5 |
| 12 | Zr-IDA | КОН | EtOAc | <5 |
| 13 | Zr-IDA | КОН | MeCN | 25 |
| 14 | Zr-BTC | КОН | Toluene | 64 |
| 15 | Zr-BDC | КОН | Toluene | 52 |
| 16 | ZrO_2 | КОН | Toluene | <5 |
| 17 | ZrCl ₄ | КОН | Toluene | <5 |
| | | | | |

[a] Reagents and conditions: 1a (1.0 mmol), 2a (2.5 mmol), [M] (2 mol%, 0.02 mmol), base (2.0 mmol), solvent (3 mL), reflux, 8 h.
[b] Isolated yield.

The heterogeneity and stability of the catalyst was evaluated by removing the catalyst from the reaction mixture after reaction for 2 h, and then the reaction mixture was stirred in the absence of solid for another 6 h. The conversion of substrate was detected (Fig.S4), verifying that the Zr-IDA-catalyzed reaction was heterogeneous and indicating that the leaching of zirconium species into the liquid phase was negligible during the reaction.

With the optimal condition established, the reaction scope was investigated using Zr-IDA as the catalyst. It was found in Scheme 1 that the electronic nature of the substituent group(s) on the ring of the benzylic alcohol have negligible effect on the condensation product within this scope of investigation, but the position of the substituents made a difference. Substitution at the *para* position gave a better yield of the desired product relative to the *ortho* or *meta* positions (Scheme 1). Notably, the Zr-IDA catalyst was also efficient when thiophene derivative (Scheme 1, **3q**) was involved, giving the product in 83% yield.



[a] Conditions: 1 (1.0 mmol), 2 (2.5 mmol), Zr-IDA (2.0 mol%), KOH (2.0 mmol), toluene (3 mL), 8 h, 110 °C. ^[a]
 ^[b] Isolated yields based on 1.

Scheme 1. Zr-catalyzed the synthesis of benzimidazoles.^[a,b]



^[a] Conditions: 4 (1.0 mmol), 5 (1.2 mmol), Zr-IDA (2.0 mol%), KOH (2.0 mmol), MeCN (3 mL), 10 h, 80 °C.
 ^[b] Isolated yields based on 4.

Scheme 2. The oxidative coupling of benzyl cyanides with *tert*-butyl hydroperoxide.^[a,b]

Encouraged by such promising results, we further employed the above method to the synthesis of *tert*-butyl peresters, a value building block encountered in a large number of organic transformations.^[30] Herein, we investigated the preparation of tert-butyl peresters via Zrcatalyzed oxidative coupling of benzyl cyanides with tertbutyl hydroperoxide (TBHP). Gratifyingly, substituted 2phenylacetonitrile could be esterified by TBHP to produce the corresponding tert-butyl peresters in high yields as Scheme 2. shown in Notably, subjecting the phenylacetonitrile containing hydroxy (-OH) substituent delivered the desired product 6d in excellent yield of 95%. Again, the electron effect of substituent has less impact on this transformation, while the reaction seems to be not sensitive to the position of substituent. The reaction proceeded well in most cases by using phenylacetonitrile with para-orienting groups. In contrast, substrates with cyclic-substituents (6m-60) led to diminished product yield because of the steric hinderance issue. Besides TBHP, cumene hydroperoxide and 2-hydroperoxy-2-methylbutane were also effective oxidants as evidenced with the isolation of **6q-6x** in 80%-96% yield (Scheme 2).

Mechanism exploration

Catalyst investigation

Zr catalyst has emerged as a useful tool in organic synthesis due to its low cost and widespread existence. Additionally, zirconium could be tuned through changing ligands, which donates a good stability and activity to zirconium compounds.^[31] However, compared to other noble metal catalysts, zirconium catalysts generally revealed low catalytic activity in borrowing hydrogen reactions and relative transformations, which highlights the challenges in its development. When Zr-CIA catalyst^[32] was initially used to synthesize the biologically active benzimidazole derivatives in this work, results observed were not ideal (Scheme 3), which might be caused by the low activity of zirconium when binding with indole-skeleton ligand.



Scheme 3. Catalysts investigation.

Several nitrogen containing ligands were subsequently evaluated in order to produce the best zirconium catalysts in terms of stability and catalytic activity. To our delight, indazole skeleton ligand has shown high efficiency in stabilizing the zirconium catalysts. However, studies regarding the catalytic activity of zirconium complexes in dehydrogenative cyclization are extremely rare. Inspired by Zr-catalyzed borrowing hydrogen reactions previously developed in our group,^[32] we used this newly developed Zr-IDA to catalyze the synthesis of 1,2-disubstituted benzimidazole. Interestingly, this economically-synthesized Zr catalyst exhibited high efficiency in borrowing dehydrogenative cyclizations, affording 1,2-disubstituted benzimidazole derivatives in high yields.

The capture of intermediates

To better understand this Zr-catalyzed transformation, the capture of intermediates was conducted to clarify the reaction mechanism. We were pleased to find that intermediate aldehyde **A** could be isolated in 36% yield (see supporting information for details). Meanwhile, intermediate bisimine **C** was separated in 19% yield when benzyl alcohol was treated with Zr-IDA (Scheme 4). These observations provided convincing evidence for the production of bisimine intermediate during the reaction, which was also seen in the studies of Cu and Ru metal calatysts in literature.^[28,32] Moreover, trace amount (6%) of imine **B** (2-(benzylideneamino)aniline) was found during this process in this experiment, which was somewhat different from the process with Cu or Ru as the catalysts.^[29,33]



Scheme 4. The capture of intermediates.

Proposed reaction mechanism

According to the preliminary experimental results, a possible reaction mechanism for Zr-catalyzed 1.2disubstituted benzimidazole synthesis was proposed including two possible reaction pathways (Scheme 5). Pathway I might undergo bisimine process after followed condensation, by the cyclization and rearrangement, whereas the other pathway might undergo the monoimine process twice, followed by a condensation, cyclization, condensation and rearrangement sequence.





Scheme 5. The possible reaction mechanism.

Although the Zr-IDA catalyst could accelerate the synthesis of *tert*-butyl peresters apparently, the exact mechanism for this reaction was not clear at this moment. Subsequently, given previous results,^[30b] a plausible mechanism was proposed in Scheme 4 and a radical progress might be possible (Scheme 6).



Scheme 6. The possible mechanism for the synthesis of *tert*-butyl perester.

To further elucidate the reaction mechanism, we next attempted to identify or isolate intermediate under mild conditions. When the catalyst loading was reduced to 0.5 mol% at lower temperature, the intermediate **7** was obtained in 8% yield (Scheme 7). Although a mixture of compounds was obtained, this result indicated that pathway II was also possible.



Scheme 7. The synthesis of intermediate 7.

To evaluate the stability and reusability of the Zr-IDA catalyst during recycling process, the coupling reaction of benzyl cyanide with TBHP was investigated. In each cycle, the catalyst was recovered by centrifugation, washed with fresh CH₃CN (10 mL, 3 times), and then reused for the next run.

The results showed that no considerable decrease in conversion, yield and selectivity of the catalyst was found after five cycles, suggesting a relatively high stability of the catalyst. (Fig. 3). After five cycles, Zr-IDA catalyst was further characterized by SEM and powder XRD, and compared with the freshly prepared catalysts (Fig. S5 and Fig. S6). It could be seen that the morphology of the catalyst has no obvious change after multiple uses. Although the XRD pattern did not fully match with that of the original catalyst, the strongest diffraction peak was maintained, implying that the structural integrity of the Zr-IRA was well preserved after five cycles. The inconsistency seen in XRD patterns is likely an outcome of an active species formed during catalyzing and reusing, the identification of which remained unclear at this moment.^[34]



Fig 3. Recycled experiments.

Meanwhile, the summary for the synthesis of 1,2disubstituted benzimidazole derivatives from benzyl alcohols and 1,2-phenylenediamines through dehydrogenation strategy was listed in Table 2.^[35] It was observed that Zr-IDA catalytic system has certain advantages in the recyclability and yield.

Table 2. Comparison with previously reported systems."

| $ \begin{array}{c} $ | OH Catalyst Conditior | is S | | 3a |
|--|--|-------|---------------|-----------|
| Catalyst | Conditions | Yield | Recyclability | Reference |
| [(Cp*)lr(LSe-S)*Cl][PF6] | KO <i>t</i> Bu, 80 °C, 6 h | 92% | No | 35b |
| NNS-Mn | KOH, 140 °C, 20 h | 79% | No | 35d |
| Pd-HAP | 90 °C, 24 h | 40% | - | 35a |
| Pd(OAc) ₂ /TPPMS | 120 °C, 20 h | 15% | | 35c |
| [Cu(binap)I] ₂ @HT | K ₂ CO ₃ , 90 °C, 12 h | 78% | Yes | 29b |
| TAP-Cu | KO <i>t</i> Bu, 120 °C, 24 h | 70% | No | 29a |
| Zr-IDA | KOH, 110 °C, 8 h | 90% | Yes | This work |

Conclusions

In conclusion, we have developed a novel porous coordination polymer Zr-IDA from 1-(carboxymethyl)-1H-indazole-5-carboxylic acid. This heterogeneous catalyst Zr-CPs containing an indazole moiety revealed good catalytic activity in the synthesis of 1,2-disubstituted benzimidazole derivatives and *tert*-butyl peresters. In addition, this Zr-IDA catalyst was able to show good reusability.

Experimental Section

Preparation of Zr-containing coordination polymer Zr-IDA

To 500 mL round-bottom bottle was successively added methyl 1H-indazole-5-carboxylate (3.524 g, 20 mmol), methyl 2-bromoacetate (7.649 g, 50 mmol), anhydrous potassium carbonate (11.057 g, 80 mmol) and MeCN (100 mL). The reaction mixture was refluxed for twenty hours and monitored by TLC until complete disappearance of 1Hindazole-5-carboxylat (a) was confirmed. Then the mixture was added water and extracted with ethyl acetate. The combined organic phases were washed with dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the title compound methyl 1-(2-methoxy-2oxoethyl)-1H-indazole-5-carboxylate in 90% yield as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s, 1H), 8.16 (s, 1H), 8.09 (dd, J = 8.8, 1.4 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 5.20 (s, 2H), 3.95 (s, 3H), 3.76 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.03, 167.10, 141.99, 135.92, 127.76, 124.70, 124.10, 123.52, 108.58, 52.69, 52.12, 50.27.

To a mixed solution of THF-H₂O (v/v = 1:1) (200 mL) and LiOH·H₂O (1 g) was successively added the solution of the upper yellow solid (20 mmol) in THF/H₂O (1:1) (200 mL) at room temperature. After eight hours, the reaction was acidified to pH 2 by adding an aqueous solution of 1N HCl, the acid product 1-(carboxymethyl)-1H-indazole-5carboxylic acid (H₂ICA) was washed with H₂O, then evaporated to dryness to afford H₂ICA in 94 % yield. Yellow solid. ¹H NMR (400 MHz, DMSO) δ 13.03 (s, 2H), 8.38 (d, *J* = 78.0 Hz, 2H), 7.85 (d, *J* = 94.9 Hz, 2H), 5.34 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 170.04, 168.04, 142.27, 135.72, 127.29, 124.45, 123.89, 123.86, 110.29, 50.53.

A mixture of ZrCl₄ (0.046 g, 0.200 mmol), 1-(carboxymethyl)-1H-indazole-5-carboxylic acid (H₂ICA) (0.044 g, 0.200 mmol) was dissolved in a 10:1 (ν/ν) DMF/HOAc mixture of (11 mL) in a 15-mL Teflon reactor. The mixture was heated in an oven at 120 °C for 48 h and then cooled to room temperature. The obtained mixture was filtered, successively washed by DMF and ethanol twice, and finally heated at 80 °C for 5 h to give yellow powder.

Representative procedure for the preparation of benzimidazoles

To 20 mL Schlenk tube was added Zr-IDA (2.0% mmol), toluene (3 mL), alcohols (2.5 mmol), amines (1.0 mmol) and

KOH (2.0 mmol). The mixture was heated and stirred under 110 °C for 8 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (v/v=5:1) as eluent to give the desired product.

Representative procedure for the oxidative coupling of benzyl cyanides with *tert*-butyl hydroperoxide.

To 20 mL Schlenk tube was added Zr-IDA (2.0% mmol), MeCN (3 mL), benzyl cyanides (1.0 mmol), *tert*-butyl hydroperoxides (1.2 mmol) and KOH (2.0 mmol). The mixture was heated and stirred under 80 °C for 10 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (v/v=20:1) as eluent to give the desired product.

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Coordination Polymer Catalysis



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A Zirconium Indazole Carboxylate Coordination Polymer as an Efficient Catalyst for Dehydrogenation-Cyclization and Oxidative Coupling Reactions

Rational ligand design is crucial for achieving widespread applications of coordination polymers. The preparation, structural characterisation, and catalytic applications of zirconium (IV) coordination polymer (Zr-IDA), which was derived from <u>1</u>-(carboxymethyl)-1H-indazole-5-carboxylic acid are reported. The Zr-IDA catalyst contains porous and highly crystalline particles with a quasi-spherical morphology around 100 nm in size. The Zr-IDA catalyst shows great activity, selectivity and stability in the oxidative coupling and the dehydrogenation cyclization.

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