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Bifunctional iridium-(2-aminoterephthalate)–Zr-MOF chemoselective catalyst for the synthesis of secondary amines by one-pot three-step cascade reaction ☆

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ABSTRACT

A simple and efficient method for the synthesis of N-alkyl amines via a cascade reaction (hydrogenation + reductive amination) using a new recyclable hybrid catalyst that combines the catalytic power of transition metal complexes with the architecture of metal organic frameworks (MOFs).

1. Introduction

Iridium-transition metal complexes are successful homogeneous catalysts, and their heterogenization over a solid matrix leads to the formation of solid recyclable molecular catalysts with well-defined active centers. In this sense, much effort has been done to design and develop adequate supports and heterogenization approaches that preserve the properties of the homogeneous catalyst and also improve their behavior by a cooperative effect between the metal complex and the support [1]. Another approach to transform a soluble catalyst (transition metal complex) into solid heterogeneous catalyst involves the synthesis of hybrid organic–inorganic structured porous materials [2] and coordination polymers [3]. Metal organic frameworks (MOFs) are one type of coordination polymers in which metal nodes are connected by organic linkers through strong bonds, forming crystalline hybrid microporous materials with a tridimensional network. In the last years, porous metal organic frameworks (MOFs) have aroused great interest for their potential application in gas separation [4] and storage [5,6], sensors, and catalysis [7]. The most remarkable features of these networks as catalysts are the easy recovery and reusability and structure-dependent catalysis [8]. However, recently networks have been shown present unique active site structures and adequate porosity for shape and size selectivity and for regio- and enantioselective reactions. Although several series of MOFs have shown unusual thermal and chemical stability, their use in catalysis and gas separations is still limited by the lack of functional and selective sites in the most stable MOF frameworks [9]. Among the possible routes to create functional networks, we can highlight the direct synthesis and post-synthetic functionalization (PSM) [10], grafting of active groups on the open metal sites [11], and encapsulation of active species [12].

In the present work, we have prepared by PSM, multisite MOF catalysts starting from amine-functionalized Zn-(IRMOF-3) [13] and stable Zr-based MOFs (UiO66-NH_2) [14]. These new materials can act as heterogeneous catalysts that combine the properties of soluble organometallic complexes with those of the MOF as support. The high stability of the Zr-MOF (UiO66-NH_2) compared with the IRMOF-3 is an incentive to use the former for heterogeneous catalysis.

One-pot type reactions, in which several steps are performed in the same reaction vessel, are of much interest to achieve more sustainable process [15] by avoiding intermediate separation and purification steps and minimizing energy consumption [16]. These transformations known as tandem, domino, or cascade reactions [17] have become an important area of research in organic

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☆ This work describes the one-pot direct reductive amination of carbonyl compounds with nitroarenes using new stable iridium-(2-aminoterephthalate)–Zr-MOF catalyst prepared by post-functionalization, employing molecular hydrogen as the reductant.

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chemistry [18,19]. Compounds containing a nitro group are of interest as building blocks for agrochemicals, dyes, pharmaceuticals, and ligands [20]. In particular, nitroarenes are one of the most readily available starting materials in organic synthesis since they can be produced from a range of aromatic starting materials [21]. One example is the hydrogenation of nitroarenes into anilines, and further transformation by alkylation, reductive alkylation, hydroamination, etc., to obtain their derivatives including heterocyclic compounds [22]. In the present work, we will show the preparation of stable Zr-MOF-Ir for the synthesis of mono N-alkyl amines through reductive amination of aldehydes with nitroarenes, in a three-step cascade reaction. The recycling of the catalytic materials has been studied and shows that Zr-MOF-Ir-catalysts are stable after multiple reuses.

2. Results and discussion

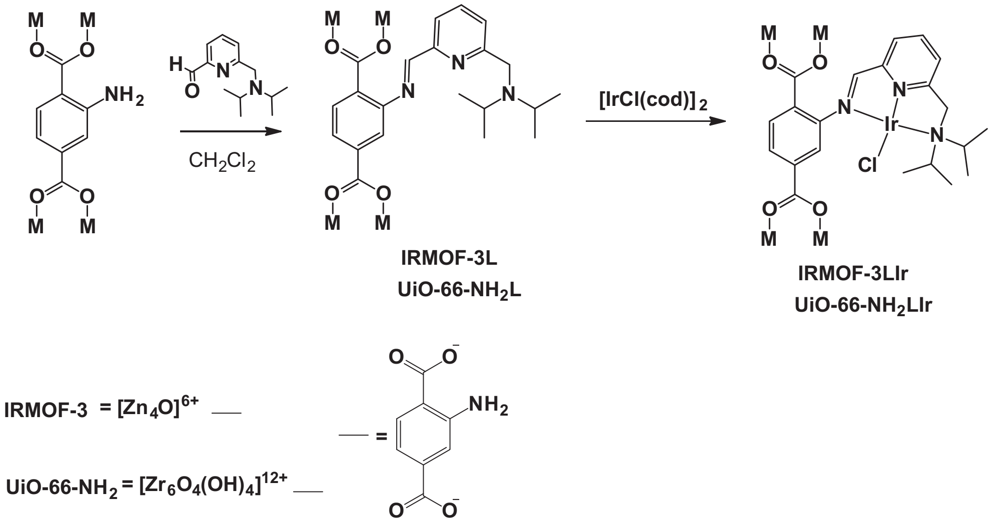
The starting materials for this study were IRMOF-3 [13] (used as reference catalyst) and UiO66-NH_2 [14], since the presence of NH_2 groups in the linker (2-aminoterephthalic acid) of the MOFs allows to functionalize the material by conventional reactions, and PSM-MOFs can be prepared according to the well-established procedures. IRMOF-3 consists of a Zn_4O tetrahedron connected with six carboxylates to give a three-dimensional cubic porous material ($Zn_4O(BDC\text{-}NH_2)_3$); it has been prepared, in the last years, by different groups [23,13a] with different textural properties. Rowsell et al., have synthesized IRMOF-3 solvothermally with BDC-NH_2 (BDC-NH_2 = 2-aminoterephthalic acid) and $Zn(NO_3)_2{\cdot}4H_2O$ in N,N-diethylformamide with a BET surface area of 2446 $m^2\,g^{-1}$. Gascon et al. obtain a high BET surface area of 3130 $m^2\,g^{-1}$ in the N_2 protection [23b]. When IRMOF-3 was synthesized by a "direct mixing" synthesis strategy at room temperature, samples with a BET surface area of 750 $m^2\,g^{-1}$ were obtained [13b,24]. This last strategy, using dimethylformamide (DMF) as solvent, was employed in this work, also obtaining IRMOF-3 with 750 $m^2\,g^{-1}$ BET surface area and pores of ~10 Å [13b]. Although the Zn(II)-based MOFs have many favorable aspects, their poor stability to moisture and protic solvents is likely to limit their applications. This prompted us to use here more stable, chemically resistant frameworks such as Zr(IV)-based MOFs [25]. UiO-66 (UiO for University of Oslo) consists of a Zr(IV)-carboxylate cluster $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(CO_2)_{12}$, which works as the secondary building unit (SBU) for the framework. The UiO-66 $[Zr_6O_4(OH)_4(BDC)_6]$ (BDC = 1,4-benzenedicarboxylate) shows high thermal stability due to the presence of an inner $Zr_6O_4(OH)_4$ core in which the triangular faces of the Zr_6-octahedron are alternatively capped with μ_3-O and μ_3-OH groups. Cohen and Lillerud independently discovered that the UiO-66 motif was very tolerant to functionalized ligands, allowing the synthesis of UiO-66 MOFs and the amino-functionalized UiO-66-NH_2 derivatives with the same topology [26]. IRMOF-3 materials were obtained starting from $Zn(NO_3)_2{\cdot}6H_2O$ and BDC-NH_2 in DMF at 105 °C (BET surface area = 750 $m^2\,g^{-1}$) [13b]. UiO-66-NH_2 was prepared by mixing $ZrCl_4$ and BDC-NH_2 in DMF, crystallization at 120 °C for 12–24 h, and activation by DMF exchange with ethanol followed by drying under vacuum (BET surface area = surface area of 800 $m^2\,g^{-1}$).

MOFs can easily be modified by post-synthesis treatments with the aim of introducing functional groups that can act or be transformed into catalytic active sites [27]. Chelating groups, which can coordinate with a transition metal, can easily be introduced in MOFs [28]. For instance, IRMOF-3 reacts with salicylaldehyde to form the iminophenol ligand which reacts with Au(III) and V(V) complexes to give active catalysts in the hydrogenation of butadiene and in the oxidation of cyclohexene [13b,29]. UiO66-NH_2 has also been modified by reaction with salicylaldehyde (vapor-phase post-synthetic modification) [30] and with anhydrides [31], acting as an acid–base type catalyst for cross-aldol condensation reactions [14c]. Here, we present the importance of selecting properly the starting MOF material to be used as support for the preparation of heterogenized catalysts.

IRMOF-3 and UiO-66-NH_2 were reacted with 6-((diisopropylamino)methyl)picolinaldehyde as has been previously reported [13b]. The starting MOF was suspended in CH_2Cl_2 and treated with the aldehyde (Scheme 1) at room temperature for 30 min for IRMOF-3 (to prevent the loss of crystallinity) and for 24–48 h for the highly stable UiO66-NH_2. The reaction was then stopped by repeated washings of the solid material with CH_2Cl_2 and drying under vacuum. The contact time of this reaction is important for IRMOF-3, since it was observed that for contact times longer than 30 min the material obtained shows low crystallinity. According to the elemental analysis of the products obtained, a level of functionalization of 2% and 5% of the total —NH_2 groups for IRMOF-3 and UiO-66-NH_2, respectively, was achieved without losing the framework integrity. Meanwhile, iridium complexation by the iminopincer complex was almost quantitative. Increasing the degree of functionalization with imine for IRMOF-3 required longer contact times. Unfortunately, this caused a severe decrease in the crystallinity of the final material, as commented above. Since the consecutive iridium complexation is quantitative, a 3% functionalization of the imine allows introducing up to 1.4 wt% and 3 wt% of Ir in IRMOF-3 and UiO-66-NH_2, respectively. The values obtained here are typical values for metal loading in useful heterogenized catalysts. It appears then that the sterically demanding 6-((diisopropylamino)methyl)picolinaldehyde reacts preferentially at the surface and at the channel entrance, showing the characteristics of molecular sieves for MOFs.

Since the reaction is not complete, the FTIR spectra of the resulting samples (see Figs. S4 and S9 in Supplementary) are still dominated by the bands assigned to the parent groups and by the skeletal modes of the MOFs, mainly due to the presence of the organic aromatic ligands (i.e., bands at 1600–1585 cm^{-1}, 1500–1430 cm^{-1} and 700 cm^{-1}). The carboxylate anion has two strongly coupled C—O bonds with bond strengths between C=O and C—O. Bands between 1650 and 1550 cm^{-1} (s) correspond to asymmetrical stretching for the carboxylates, and the band near 1400 cm^{-1} (w) corresponds to symmetrical stretching. The presence of functional groups from post-synthetic modification of the starting IRMOF-3 or UiO-66-NH_2 can be observed in the full spectral range, being the intensity proportional to the level of conversion. The fraction of PSM was determined by normalizing FTIR spectra to the band at 760 cm^{-1}, assigned to the C—C vibrational mode in aromatic compounds (this band is relatively little affected by ring substituents) [14b], and which does not overlap with other vibrational modes. These samples will be hereafter referred to as IRMOF-3-L and UiO66-NH_2-L. The final step to prepare the Ir(I)-containing materials, IRMOF-3-LIr, UiO66-NH_2-LIr, consisted in reacting a suitable iridium precursor, $[IrCl(cod)]_2$, or $[Ir(cod)(THF)_2]BF_4$ with the imine-modified material. The preparative procedure is summarized in Scheme 1, while a detailed description of each step is given in the experimental section. The reaction with the aldehyde modifies UiO-66-NH_2 without degradation of the framework, even after extended reaction times and conversions, as indicated by the XRD results (see Fig. 1).

The functionalization process was also studied, by ESI-MS analysis (see Supporting material) on digested samples of UiO-66-NH_2 and PSM-derivatives. Due to the stability of UiO-66 MOFs in acidic media, hydrofluoric acid (HF) was chosen to digest the materials, taking into account the high affinity of Zr for fluoride. The starting UiO-66-NH_2 was also digested and used as reference. The negative mode mass spectra obtained showed a base peak at m/z 180 that corresponds to $H_2BDC\text{-}NH_2$ (Fig. S15a, $[H_2BDC\text{-}NH_2 + H]^-$). The negative mode mass spectra obtained for $H_2BDC\text{-}NH_2L$ clearly show a base peak at m/z 383 (Fig. S15b, $[H_2BDC\text{-}L + H]^-$), which



Scheme 1. Post-modification of IRMOF-3 and $UiO\text{-}66\text{-}NH_2$.

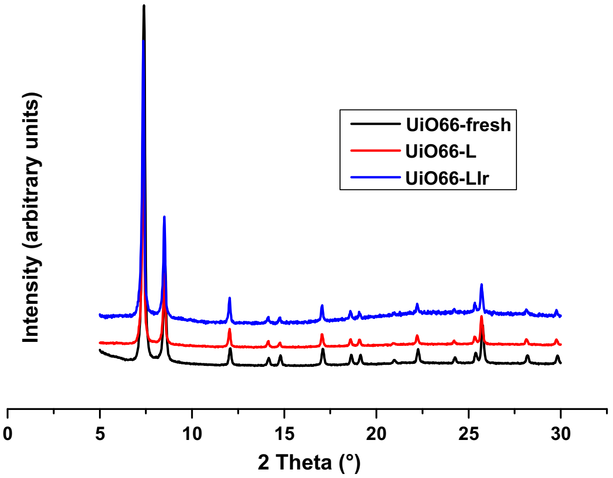


Fig. 1. X-ray diffraction patterns of $UiO\text{-}66\text{-}NH_2$, UiO-66-L, UiO-66-[LIr]$BF_4$.

corresponds to the modified ligand. The spectra of H_2BDC-[LIr] show a peak at m/z 677 (Fig. S15c, {[H_2BDC-[LIr(MeOH)]BF_3 + H}$^-$). Last, HF cleaves also the Zr cluster itself, and the fluoro complex $[ZrF_5]^-$ is readily discerned (Fig. S15). ^1H NMR spectra after digestion of the MOFs under acidic conditions indicate that the ligands remained in UiO-66-L and UiO-66-[LIr]BF_4 materials (Fig. S14).

The stability of the modified UiO66-NH_2-MOFs was examined by means of TGA. The modified samples show thermal stabilities comparable to that of UiO66-NH_2 with decomposition temperatures near 350 °C in air (Fig. S16).

The N_2 adsorption–desorption isotherms obtained at 77 K on the functionalized UiO66-NH_2-MOF are type-I isotherms (Fig. S17). And it indicates that most of the porosity of the original material is retained after functionalization of the linker. Indeed, BET surface area of 637 m^2/g, total pore volume of 0.28 $cm^3\,g^{-1}$, and pore diameter of 2.7 nm are obtained for UiO-66-L, while for UiO-66-[LIr]BF_4 they are 568 m^2/g, 0.25 $cm^3\,g^{-1}$, and 2.71 nm, respectively; decrease in surface area can be related to the presence of a large ligand and the corresponding iridium complex.

All UiO-66-NH_2-modified samples remain crystalline after functionalization (Fig. 1). All XRD peaks observed for the as-synthesized UiO-66-NH_2 are also observed with the post-synthetically modified materials. XRPD pattern of UiO-66-NH_2-modified materials remains unaltered when heated up to 300 °C in air, demonstrating that the materials are thermally stable.

Finally, scanning electron microscopy (SEM) experiments confirmed that the particle size remains unchanged during ligand formation, as no significant particle size increase or decrease was observed via this technique (Fig. 2)

2.1. Iridium MOF catalyst for reductive amination of aldehydes: comparison with homogeneous catalysts

Development of catalysts that allow performing one-pot multistep reactions is of interest since it avoids intermediate separation and purification steps with the corresponding benefits in energy

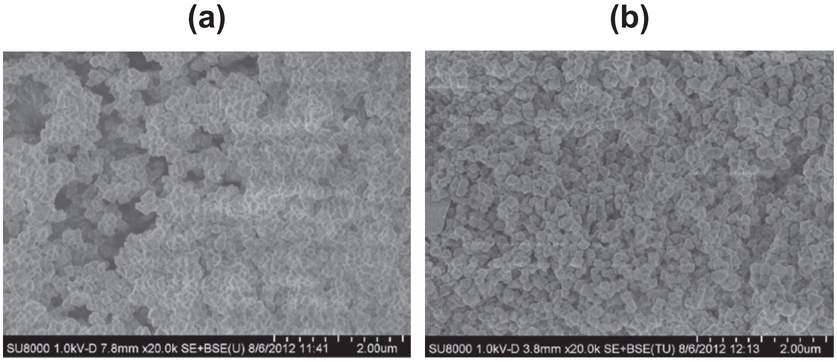
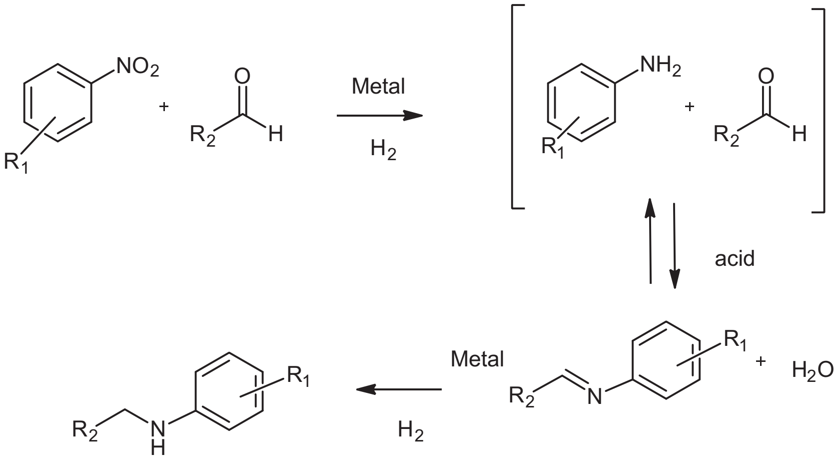


Fig. 2. SEM images for UiO-66-L (a) and UiO66-NH_2-[LIr]BF_4 (b).

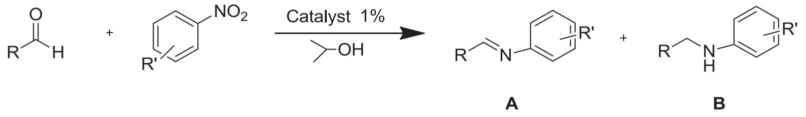
saving and minimization of waste. In this sense, the reductive amination reaction is one important transformation that allows the direct conversion of carbonyl compounds into amines using simple operations [32]. The reaction offers compelling advantages over other amine syntheses, including shortness, wide commercial availability of substrates, mild reaction conditions, and no need to isolate the imine intermediate. The resulting secondary amines and their derivatives are highly versatile building blocks for various organic substrates and are extremely important pharmacophores in numerous biologically active compounds owing to their interesting physiological activities [33]. Several reagents for reductive amination have recently been reported [34]. Although the reductive alkylation of amines with aldehydes is a common process, only few papers describe the reaction under hydrogenation conditions, and for example, a Pd/C [35,36] catalyst has been reported to be active though the reported substrate scope is limited to aliphatic aldehydes. Imine formation from aldehydes and nitroarenes has been reported with Au/TiO_2 catalysts [37] or Au/Fe_2O_3 [38]. More recently, it has been reported that gum acacia-supported palladium nanoparticles [39] and a polymer-supported palladium catalyst [40] promote reductive N-alkylation of nitroarenes using molecular hydrogen as reductant and methanol as solvent. In the present work, we report on the application of Ir-MOF catalyst for the atom economic synthesis of mono N-alkyl amines through reductive amination of aldehydes with nitroarenes in the presence of hydrogen. The process involves firstly a chemoselective reduction of the nitro compound to the corresponding amine with hydrogen in the presence of the carbonyl substrate on the iridium site. Then, while in a consecutive step, the condensation between the aromatic amine and the carbonyl group would occur on the acid sites of the catalyst (MOF) (Scheme 2). Finally, the hydrogenation of the resulting imine with the Ir-complexes will give the secondary amine.

Catalytic evaluation of both Ir-MOF-based catalysts was performed by mixing them with the nitroarenes and carbonyl compounds in isopropanol in a batch reactor. A series of initial experiments using benzaldehyde and nitrobenzene as model reactants has allowed us to establish the adequate reaction conditions for obtaining secondary amines in high yields within a reasonable reaction time. After that, the reaction has been extended to different aldehydes and nitroarenes. Under optimized reaction conditions, the scope of the reaction was explored with structurally and electronically diverse aldehydes and different nitroarenes. As shown in Table 1, various aldehydes were reductively aminated with nitrobenzene under 6 bar pressure of molecular hydrogen. The aldehydes used for this study included aromatic and aliphatic aldehydes. Irrespective of the electronic nature of the substituent, aromatic aldehydes react well to give the corresponding products in good yields (Table 1, entries 1–6). On the other hand, aliphatic aldehydes underwent the reductive amination rapidly and gave



Scheme 2. One-pot synthesis of secondary amines by using [Ir]-catalysts.

Table 1
MOF-[LIr]-catalyzed one-pot reductive amination of aldehydes with nitrobenzene under H_2 atmosphere in isopropanol.[a]



Entry	Catalyst	R	R′	Conv. (%)[b]	Sel. (%) amine (B)
1	LIr	Ph	H	100	66
2	IRMOF-3-LIr	Ph	H	98	99
3	UiO-66-LIr	Ph	H	99	99
4	UiO-66-LIr	Ph	4-I	90	70 (98, 48 h)
5	UiO-66-LIr	Ph	4-Br	80 (95, 48 h)	65 (97, 48 h)
6	UiO-66-LIr	OMePh	H	99	99
7	UiO-66-LIr	C_6H_{13}	H	99	99
8	UiO-66-LIr	C_6H_{13}	4-I	98	100
9	UiO-66-LIr	C_6H_{13}	*o*-OCH_3	100	99

[a] Reaction conditions: nitrobenzene (1.0 mmol), aldehyde (1.5 mmol), [Ir] (1 mol%), isopropanol (1 ml), PH_2: 6 bar, T: 100 °C, time: 24 h.
[b] Referred to nitrobenzene.

Table 2
Recycling experiments with MOF-based-[LIr]$^+$ catalysts.

Cycle	Catalyst	t (h)	Conv. (%)	Sel. (%) amine (B)
1	UiO-66-LIr	24	99	99
2		24	99	99
3		24	99	99
4		24	99	99
1	IRMOF-3-LIr	24	98	99
2		24	–	–

Cat. 1 mol% based on Ir, T: 100 °C, PH_2: 6 bar.

the products in excellent yield without the formation of byproducts (Table 1, entries 7–9).

2.2. Recycling experiments and heterogeneity

To study whether the reaction using solid [Ir]-MOF catalysts occurred on the solid or was catalyzed by Ir species potentially leached in the liquid phase, two separate experiments were conducted with benzaldehyde and nitrobenzene. In the first experiment, the reaction catalyzed by UiO-66-LIr was terminated after 7 h, and the conversion of nitrobenzene was found to be 20%. At this point, the catalyst was separated from the reaction mixture and the reaction was continued with the filtrate for an additional 24-h. period. In the second experiment, the reaction was terminated after 7 h at 20% conversion and the catalyst removed. The reaction was then continued with the filtrate for additional 17 h. In both cases, the conversion within the filtrates remained almost unchanged. Ir was not detected in the filtrate in either experiment by ICP-AES. These studies demonstrate that the Ir bound to the support during the reaction is active and the reaction proceeds on the solid.

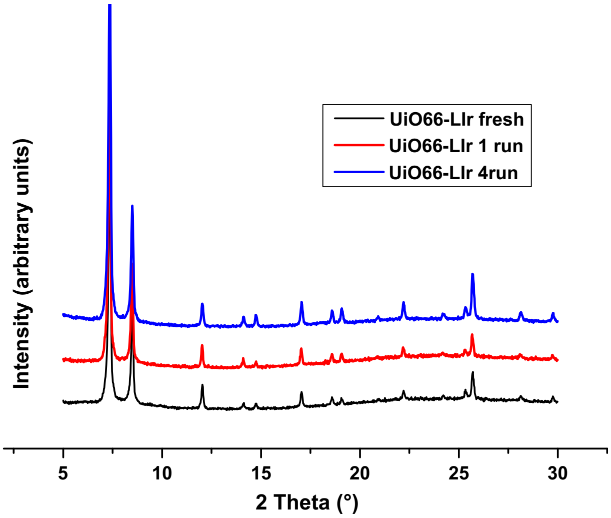


Fig. 3. XRPD of UiO66-[LIr]BF_4 after four runs.

As can be seen from the results in Table 2, UiO-66-LIr can be recovered by simple filtration in air and reused without significant loss of catalytic activity, at least after four cycles, whereas IRMOF-3-LIr and soluble complexes could be used only once, since they were completely deteriorated at the end of the first catalytic run (Fig. S14).

Hot filtration tests for UiO-66-LIr proved that the catalytic activity was associated with the solid exclusively, and no reaction occurred when the catalyst was removed from the reaction media. The overall structure of the material remained intact after the catalytic experiments (Fig. 3), and we can consider that the catalyst is stable under reaction conditions. SEM images for fresh and recovered materials show, also, that structure was maintained after the reaction (Fig. 4). Fig. 5 shows the representative TEM images conducted to analyze whether particles are formed during catalysis, and we see no evidence for the formation of nanoparticles. Nevertheless, it should be considered that the content of Ir in the sample is very low.

3. Conclusions

We have developed a simple and efficient method for the synthesis of N-alkyl amines via reductive amination in the presence of hydrogen using a new readily recoverable hybrid catalyst that combines the catalytic activity of transition metal complexes with the architecture of metal organic frameworks (MOFs). This protocol can be used to generate a diverse range of N-alkyl amines in good to excellent yields. The simple procedure for catalyst preparation, easy recovery, and reusability of the catalyst is expected to contribute to its utilization for the development of benign chemical processes and products.

4. Experimental section

Starting materials were purchased and used without further purification from commercial suppliers (Sigma–Aldrich and Alfa Aesar). Dried, distilled, and deoxygenated solvents were used.

4.1. Materials preparation

The Zn and Zr-MOFs were prepared according to the corresponding procedures reported in the original references: IRMOF-3 [12], UiO-66-NH_2 [13a] X-ray diffraction (Phillips X'Pert, Cu Kα radiation) was used to confirm the expected crystalline structure

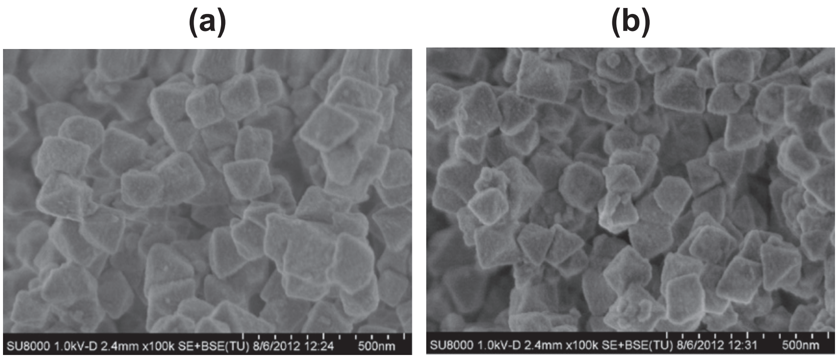


Fig. 4. SEM images for UiO66-NH_2-[LIr]BF_4 fresh (a) and UiO66-NH_2-[LIr]BF_4 recycled (b).

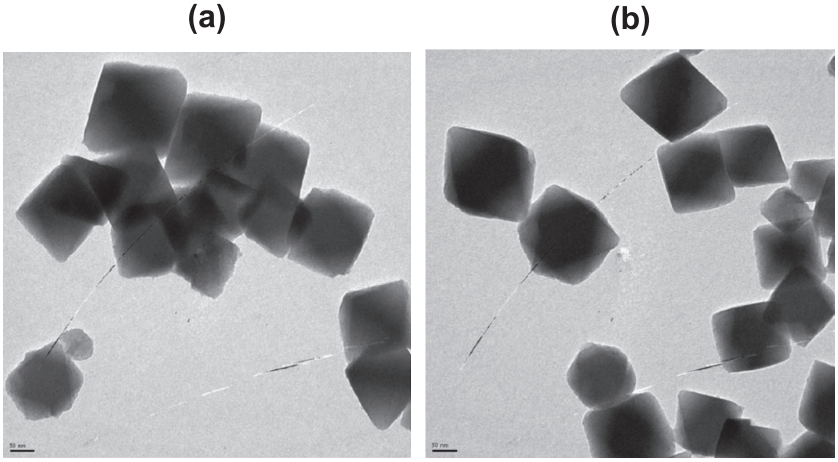


Fig. 5. TEM images of UiO66-NH_2-[LIr]BF_4: (a) fresh and (b) recovered after reaction.

of the materials. All substances and reagents used were commercially available and used as received. The reaction and analytic methodology are given in Supplementary material.

4.2. Synthesis of IRMOF-3, [$Zn_4O(BDC\text{-}NH_2)_3$]. (BDC-NH_2 = 2-aminoterephthalate)

Triethylamine (1.6 g, 15.81 mmol) was dropwise added to a mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (1.21 g, 4.07 mmol) and BDC-NH_2 (0.371 g, 2.05 mmol) in DMF (40 ml) and stirred for 2 h at room temperature. The resulting pale yellow solid was collected by centrifugation and washed twice with DMF. The solid was thrice immersed in $CHCl_3$ during 3 days, and the solid was finally dried in air at 60 °C. This washing procedure removes most of the DMF solvent molecules, although the presence of an IR absorption band at 1660 cm^{-1} in the spectrum of the washed sample indicates that some adsorbed DMF still remains inside the pores. The structure of the material was confirmed by X-ray diffraction, prior and after washing with $CHCl_3$.

Elemental analysis was performed on samples outgassed under vacuum (100 °C, 12 h). $Zn_4O(BDC\text{-}NH_2)_3$: Calculated: C, 35.35; H, 1.84; N, 5.16%. Found: C, 34.61; H, 1.87; N, 5.14%. ^{13}C NMR (CP MAS): 116, 126, 132, 137, 149, 175 (COO) ppm (see Fig. S1).

4.3. Post-synthetic modification of IRMOF-3 IRMOF-3-L, [$Zn_4O(BDC\text{-}NH_2)_{3-x}(BDC\text{-}L)_x$] (L = 6-((diisopropylamino)methyl)picolinaldehyde)

In a typical procedure, freshly prepared IRMOF-3 (1 g, 1.2 mmol) was dispersed in 15 ml CH_2Cl_2. To this slurry, a solution of aldehyde (500 mg, 4.1 mmol) in CH_2Cl_2 (15 ml) was dropwise added at room temperature, and the mixture was stirred for additional 30 min. The sample was collected by centrifugation, washed twice with CH_2Cl_2, and dried in air at 60 °C. Elemental analysis was performed on samples outgassed under vacuum (100 °C, 12 h). Zn_4O $(BDC\text{-}NH_2)_{2.94}(L)_{0.06}$ (corresponding to 2% amine functionalization): Calculated: C, 35.84; H, 1.97; N, 5.15%. Found: C, 32.40; H, 2.27; N, 5.04%. ^{13}C NMR (CP MAS): 18.2 (CH_{3iPr}), 30.9, 51.6 (CH_{iPr}), 117.3, 123.8, 132.9, 137.7, 150.0, 164.0 (imine C=N), 174.6 (COO) ppm (see Figs. S2 and S4).

4.4. Synthesis of IRMOF-3-LIr, [$Zn_4O(BDC\text{-}NH_2)_{3-x}([LIrCl]_x)$]

Sample IRMOF-3-L (1 g) was dispersed in 15 ml CH_2Cl_2. To this slurry, a solution of $[IrCl(cod)]_2$·(200 mg, 0.3 mmol) in 15 ml CH_2Cl_2 was dropwise added at room temperature, and the mixture was stirred for an additional hour. The sample was collected by centrifugation, washed twice with CH_2Cl_2, and dried in air at 60 °C. Elemental analysis was performed on samples outgassed under vacuum (100 °C, 12 h). $Zn_4O(BDC\text{-}NH_2)_{2.94}(BDC\text{-}LIrCl)_{0.06}$: Calculated: C, 35.25; H, 1.94; N, 5.06%. Found: C, 33.62; H, 2.49; N, 4.99%. The amount of iridium in the final solid was determined by ICP-AES. Calculated: Ir, 1.39%. Found: Ir, 1.38%. ^{13}C NMR (CP MAS): 19.0 (CH_{3iPr}), 30.8, 51.4 (CH_{iPr}), 118.2, 125.8, 132.8, 138.4, 150.3, 162.4 (imine C=N), 175.6 (COO) (see Figs. S3 and S5).

4.5. Synthesis of Zr(BDC-NH_2) (UiO-66-NH_2)

Synthesis of Zr-based metal organic framework was performed in a 250-ml round-bottomed flask using a procedure similar to that previously described [13a]. $ZrCl_4$ (0.4 g, 1.7 mmol) in DMF (75 ml) was dispersed by ultrasound at 50–60 °C, and acetic acid (2.85 ml, 850 mmol) was added. A DMF solution (25 ml) of the linker, 2-aminoterephthalic acid (0.311 g, 1.7 mmol), was added to the clear solution; finally, water (0.125 ml, 0.007 mmol) was added to the solution. The tightly capped flask is sonicated at 60 °C and kept in a bath at 120 °C under static conditions for 24 h. After 24 h, the solutions were cooled to room temperature and the precipitate was isolated by centrifugation and washed with DMF (10 ml).

The suspension was centrifuged and the solvent was decanted off. The obtained particles were washed with ethanol several times in the same way as described for washing with DMF. Finally, the solid was dried under reduced pressure (80 °C, 3 h). This standard washing procedure yielded the materials denoted with “as-synthesized”. (Yield: 577 mg). $Zr_6O_4(OH)_4(BDC\text{-}NH_2)_6$: Calculated: C, 32.87; H, 1.95; N, 4.79. Found: C, 32.09; H, 2.34; N, 4.83%.

4.6. Synthesis of UiO-66-NH_2-L, [$Zr_6O_4(BDC\text{-}NH_2)_{6-x}L_x$] (L = 6-((diisopropylamino)methyl) picolinaldehyde)

UiO-66-NH_2 (1.5 g, 1.6 mmol) was dispersed in 15 ml CH_2Cl_2. To this slurry, a solution of aldehyde (375.0 mg, 1.7 mmol) in CH_2Cl_2 (5 ml) was dropwise added at room temperature, and the mixture was stirred for additional 6 h. The sample was collected by centrifugation, washed twice with CH_2Cl_2, and dried in air at 70 °C. Elemental analysis was performed on samples outgassed under vacuum (100 °C, 12 h). $Zr_6O_4(OH)_4(BDC\text{-}NH_2)_{5.7}(BDC\text{-}L)_{0.3}$: (corresponding to ~5% amine functionalization): C, 34.35; H, 2.19; N, 5.09; Calculated: C, 34.35; H, 2.19; N, 5.09%. Found: C, 34.45; H, 2.64; N, 5.07%. ^{13}C NMR (CP MAS): 17.8 (CH_{3iPr}), 45.8 (CH_{iPr}), 50.6 (CH_2), 116.1, 123.0, 132.1, 138.5, 151.4, 162.8 (imine C=N), 171.2 (COO) (see Fig. S7).

4.7. Synthesis of UiO-66-NH$_2$-LIr, [$Zr_6O_4(BDC\text{-}NH_2)_{6-x}(BDC\text{-}LIrCl)_x$]

UiO-66-NH$_2$-L (1 g) was dispersed in 15 ml CH_2Cl_2. To this slurry, a solution of $[IrCl(cod)]_2$·(200 mg, 0.3 mmol) in 15 ml CH_2Cl_2 was added at room temperature, and the mixture was stirred at reflux for 12 h. The sample was collected by centrifugation, washed twice with CH_2Cl_2, and dried in air at 70–80 °C. Elemental analysis was performed on samples outgassed under vacuum (100 °C, 4 h). $Zr_6O_4(OH)_4(BDC\text{-}NH_2)_{5.7}([BDC\text{-}LIrCl])_{0.3}$: Calculated: C, 32.48; H, 2.15; N, 4.82%. Found: C, 34.12; H, 2.39; N, 4.82%. The amount of iridium in the final solid was determined by ICP-AES. Calculated: Ir, 3.15%; Found: Ir, 3.11%. ^{13}C NMR (CP MAS): 17.9, 21.2 (CH_{3iPr}), 45.7 (CH_{iPr}), 116.9, 123.2, 131.7, 138.5, 151.4, 165.6 (imine C=N), 171.4 (COO) (see Figs. S8 and S9).

4.8. Synthesis of UiO-66-NH$_2$-[LIr]$^+$, [$Zr_6O_4(OH)_4(BDC\text{-}NH_2)_{6-x}([LIr]BF_4)_x$]

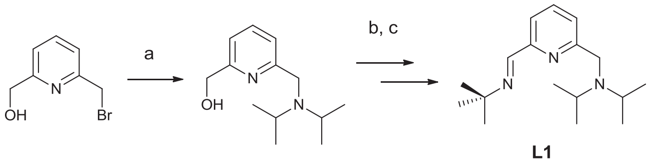
$AgBF_4$ (8.7 mg, 0.044 mmol) was added to a solution of $[IrCl(cod)]_2$·(15 mg, 0.022 mmol) in 10 ml THF at room temperature, and the mixture was stirred for 1 h; then, AgCl was filtered and the solution containing $[Ir(COD)]BF_4$ added to a suspension of UiO-66-NH$_2$-L (100 mg) in 10 ml THF. The mixture was stirred for 10 h; the solid was collected by centrifugation, washed twice with THF, and dried in air at 70 °C. Elemental analysis was performed on samples outgassed under vacuum (100 °C, 4 h). $Zr_6O_4(OH)_4(BDC\text{-}NH_2)_{5.7}L_{0.1}([LIr]BF_4)_{0.2}$. Calculated: C, 32.70; H, 2.17; N, 4.85%. Found: C, 32.92; H, 2.56; N, 4.54%. The amount of iridium in the final solid was determined by ICP-AES. Calculated: Ir, 2.11%; Found: Ir, 1.85%.

4.9. Catalyst characterization

General considerations and characterization methods are presented in supporting information.

4.10. Preparation of homogeneous [IrL] complex

4.10.1. Synthesis of the ligand



a: K_2CO_3/NR_1R_2; b: $(COCl)_2$, DMSO, −50 °C; c: t-$BuNH_2$/AcN.

4.10.2. (E)-2-(tert-Butyliminomethyl)-6-diisopropylaminomethylpyridine, (L)

To a stirred solution of 2-formyl-6-diisopropylaminomethylpyridine (440 mg, 2 mmol) in ethanol (25 ml) was added *tert*-butylamine (230 μl, 2.2 mmol) and freshly activated molecular sieves 4 Å (2 g), after stirring for 14–16 h at room temperature, the reaction mixture was filtered through celite, concentrated under reduced pressure to yield pure (*E*)-2-(*tert*-butyliminomethyl)-6-diisopropylaminomethylpyridine (545 mg, 99%). Anal. Calc. for $C_{17}H_{29}N_3$ (275.4): C, 74.1; H, 10.6; N, 15.3. Found: C, 74.3; H, 10.8; N, 15.6%. MS (*m*/*z*): 275 [M$^+$], 218 [M$^+$-*t*-Bu], 176 [M$^+$-Et$_2$N], 162, 120. IR (KBr, cm^{-1}): ν_{CHalip} 2967 (vs), 1645 (m), 1589 (m) $\nu_{C=C}$, $\nu_{C=N}$; 1454 (m), 1382 (m), 1363 (s) δ_{CH}, 1205 (m) ν_{C-C}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 8.32$ (s, 1H, N=CH); 7.84 (t, 1H$_{Py}$, $J_{HH} = 4.4$ Hz); 7.64 (d, 2H$_{Py}$, $J_{HH} = 4.7$ Hz); 3.80 (m, 2H, —CH$_2$—); 3.03 (sept, 2H, 2 —CH$_{iPr}$, $J_{HH} = 6.6$ Hz); 1.28 (s, 9H, 3 —CH$_{3tBu}$); 1.00 (d, 12H, 4 —CH$_{3iPr}$, $J_{HH} = 6.6$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 163.7$ (C$_{Py}$); 156.8 (N=CH); 154.3 (C$_{Py}$); 136.7 (CH$_{Py}$); 122.6 (CH$_{Py}$); 118.2 (CH$_{Py}$); 57.7 (C$_{tBu}$); 51.4 (—CH$_2$—); 48.9 (2C, 2 —CH$_{iPr}$); 29.6 (3 —CH$_{3tBu}$); 20.7 (4 —CH$_{3iPr}$).

4.10.3. Synthesis of [IrLCl] (LIr)

In a 100-ml round-bottomed Schlenk flask, 50 mg (0.18 mmol) of the ligand (L) was dissolved in 5 ml of CH_2Cl_2 under N_2. This solution was then treated with a red solution of 60.6 mg (0.091 mmol) $[Ir(C_8H_{12})Cl]_2$ in 20 ml CH_2Cl_2. The solution was stirred for an additional hour. The solvent was removed in vacuum until 5 ml, pentane was added to the mixture and an orange solid was obtained. After drying the residue for several hours in vacuum, the analytically pure product was obtained in 70% yield (63.9 mg; 0.13 mmol). Anal. Calc. for $C_{25}H_{41}ClIrN_3$ (611.3): C, 49.1; H, 6.8; N, 6.9; Ir, 31.4; Found: C, 48.5; H, 6.4; N, 6.4 Ir, 30.5%. MS (ES$^+$, *m*/*z*): 612.3 (M$^+$, 10), 576.3 ([Ir(cod)(L)]$^+$, 40), 276 (L$^+$, 100). IR (KBr, cm^{-1}): ν_{CHarom} 3092 (w); ν_{CHalip} 2974 (s), 2937 (m) 2882 (m); $\nu_{C=C}$, $\nu_{C=N}$ 1700 (m), 1635 (s) 1594 (s), 1465 (s); δ_{CH} 1397 (s), 1379 (s), 1367 (s); ν_{C-C}, 1209 (s), 1153 (s), 1095 (m); $\delta_{CHout\ plane}$ 806 (m), 776 (m); ρ_{CH} 556 (m), 503 (m). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.89$ (s, 1H, N=CH); 8.13 (d, 1H$_{Py}$, $J = 7.9$ Hz,); 7.79 (t, 1H$_{Py}$, $J = 7.7$ Hz); 7.48 (d, 1H$_{Py}$, $J = 7.5$ Hz,); 5.28 (d, 1H, —CH$_2$—, $J_{HH} = 18.4$ Hz); 4.41 (d, 1H, —CH$_2$—, $J_{HH} = 18.4$); 3.40 (br); 3.15 (q, 2H, —CH$_{iPr}$, $J_{HH} = 6.6$ Hz); 2.32 (br); 1.75 (s, 9H, 3 —CH$_{3tBu}$); 1.12 (d, 6H, —CH$_{3iPr}$, $J_{HH} = 2.2$ Hz); 1.09 (d, 6H, —CH$_{3iPr}$, $J_{HH} = 2.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 166.7$ (N=CH); 160.2 (C$_{Py}$); 154.4 (C$_{Py}$); 136.3 (CH$_{Py}$); 125.3 (CH$_{Py}$); 123.8 (CH$_{Py}$); 61.7 (C$_{tBu}$); 53.6 (—CH$_2$—); 48.9 (2C, 2 —CH$_{iPr}$); 31.4 (3 —CH$_{3tBu}$); 21.05, 20.08 (4 —CH$_{3iPr}$).

4.10.4. Synthesis of [IrL]X (X = BF$_4$)

A solution of 70 mg (0.11 mmol) of the complex $[Ir(C_8H_{12})Cl]_2$ in 15 ml THF was placed in Schlenk tube, $AgBF_4$ (22.3 mg, 0.11 mmol) was added and immediately AgCl appears in the reaction media. The mixture was stirred for 1 h, AgCl was removed, and ligand L (30.3 mg, 0.11 mmol) was added to the filtrate upon which the color of the solution changed to orange. After 3 h at 40 °C, the solvent was removed in vacuum and the residue was washed in portions with 15 ml of pentane. After 5-h drying in vacuum, the orange product was obtained in 90% yield (68 mg, 0.10 mmol). MS (ES$^+$, *m*/*z*): 659.3 [M$^+$, [Ir(cod)(L)]BF$_4$, 20), 592.3 ([Ir(cod)(L)(H$_2$O)], 10), 276 (L$^+$, 80).

4.11. Catalytic measurements

Selective domino hydrogenation of nitroaromatics in the presence of aldehydes was performed in a closed glass microreactor (2.0 ml, SUPELCO) equipped with a magnetic bar, and sensors for both temperature and pressure control. The reactor had also connections to allow gas supply, and also an outlet for samples to be taken at different time intervals. The reactants nitroarene (2.2 μl for nitrobenzene, 0.02 mmol)) and aldehyde (3.5 μl for benzaldehyde, 0.03 mmol) were added to the suspension of catalyst (2.4 mg, 2×10^{-4} mmol iridium) in isopropanol (1 ml). The reactor was hermetically sealed, pressurized with hydrogen at six bars, and heated at 100 °C under continuous stirring. Small liquid aliquots (≈100 μl) were taken. The progress of the reaction was monitored by GC–MS. The reaction mixture was filtered, and the solvent was removed under reduced pressure to give the crude product. It was purified by column chromatography on silica gel using hexane-ethyl acetate mixture as eluent.

4.12. The stability of IRMOF-3-LIr, ZrMOF-LIr catalysts

The stability of MOF-Ir was investigated in the selective formation of secondary amines. IRMOF-3-LIr decomposes after one run (see Fig. S14), whereas UiO66-LIr was recovered unaltered after at least four run (Fig. S15).

4.13. The recycling of IRMOF-3-LIr, ZrMOF-LIr in the domino reaction

After completion of the reaction, the catalyst was recovered by the separation of solid MOF-Ir from liquid after an extensive centrifugation. Washing the recovered catalyst with CH_2Cl_2 for three times and then ether, the catalyst was dried at 60 °C for 12 h and reused. The ZrMOF-LIr catalyst showed consistent activity for four cycles.

4.14. The hot filtration test of ZrMOF-LIr catalyst

A mixture of ZrMOF-LIr (2.4 mg, 2×10^{-4} mmol Ir), nitrobenzene (2.2 µl, 0.02 mmol), benzaldehyde (3.5 µl, 0.03 mmol), and isopropanol (1.0 ml) was put into a closed glass reactor (2.0 ml, SUPELCO) and was extensively stirred (ca. 1000 rpm) at 100 °C for 2 h. The conversion is 20%. Then, the solid catalyst was quickly separated after filtration of the reactant mixtures. And the liquid was kept at 100 °C with extensively stirring for 24 h. The conversion was 22%. It is found that the blank thermal reaction without any catalyst for this reaction at 100 °C is ca. 2% (see Fig. S16).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.12.004.

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