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# One-Pot Multifunctional Catalysis with NNN-Pincer Zr-MOF: Zr Base Catalyzed Condensation with Rh-Catalyzed Hydrogenation

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We describe the postsynthetic modification of Zr-based metal organic frameworks (MOFs) containing chiral NNN-pincer ligands based on aminopyridineimines, as well as the subsequent formation of (NNN)-M-Zr-MOF complexes (M = Rh, Ir). With these new multifunctional materials, we performed a cascade of condensation reactions followed by hydrogenation of the resulting double bond. If the condensation reaction occurs between an aldehyde and ethyl nitroacetate, (NNN)-M-Zr-MOF complexes catalyze the one-pot synthesis of nitroalkenes, in

## Introduction

The heterogenization of transition-metal complexes over a solid matrix leads to the formation of solid recyclable molecular catalysts with well-defined active centers. Design and development of a suitable support to perform the immobilization of homogeneous catalysts, while improving their characteristics by a cooperative effect between the metal complex and the support, has been an important challenge in recent years.<sup>[1]</sup> The synthesis of hybrid organic-inorganic structured porous materials<sup>[2]</sup> and coordination polymers<sup>[3]</sup> is another way to prepare heterogeneous catalysts. Porous metal organic frameworks (MOFs) have recently attracted considerable interest for potential applications in gas adsorption,<sup>[4]</sup> separation,<sup>[5]</sup> catalysis,<sup>[6]</sup> gas storage,<sup>[7,8]</sup> and sensors and other technologies<sup>[9]</sup> because of their high porosity, thermal stability, and chemical suitability. Furthermore, an important property of MOFs with respect to other crystalline porous solids is the possibility to introduce chiral groups and two or more active

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which  $Zr^{V}$  Lewis sites play a role similar to that of the generally used Ti<sup>IV</sup> in homogeneous catalysis. These multifunctional hybrid catalysts retain their crystalline framework even after the reaction, and they were isolated easily from the reaction mixture through filtration and reused several times without a significant degradation in activity. Moreover, there was no contribution from leached active species and conversion was possible only in the presence of the solid catalyst.

sites<sup>[10]</sup> to generate multifunctional solid catalysts (e.g., acidbase, metal-acid, metal-base, or metal-metal catalysts)<sup>[11]</sup> to be used in domino reactions.<sup>[12]</sup> Nevertheless, the preparation recovery and reusability of multifunctional MOF catalysts has been an active research area in the past few years.<sup>[11,13-15]</sup> Herein, we describe the preparation of multifunctional Zrbased MOF (Zr-MOF) catalysts<sup>[16]</sup> containing metallic centers (Rh, Ir) along with Zr<sup>IV</sup> sites with Lewis acid properties and base groups incorporated as ligands; these catalysts can catalyze hydrogenation reactions.

The preparation of ligands, for instance, pincer-type ligands as in MOFs (linkers), for transition-metal complexes can provide appropriate stereochemical and electronic environments around active metal centers, which introduces additional active sites to the existing intrinsic active sites of MOFs.<sup>[17]</sup> Herein, we present the synthesis and coordination properties of a new family of pincer-type ligands with a pyridine backbone, one imine, and a chiral amine moiety (Scheme 2). These pincer-type ligands were incorporated into the Zr-MOF-UiO- $66-NH_2$  or UiO-67-NH<sub>2</sub> (UiO = Universitetet of Oslo)—through postsynthetic modification and as a result produced (NNN)-M-Zr-MOF heterogenized materials, which can be used as heterogeneous catalysts in a cascade condensation-hydrogenation reaction. We also report the tandem condensation and hydrogenation reactions that produce benzyl amino esters from commercially available aldehydes (benzaldehyde, 4-fluorobenzaldehyde, 4-nitrobenzaldehyde, and heptanal) and active methylene compounds (malononitrile, ethyl 2-nitroacetate, and ethyl 2-cyanoacetate) (Scheme 1). The resulting esters are attractive intermediates in medicinal chemistry, and their analogues have wide use in pharmaceutical chemistry<sup>[18]</sup> (as antidiabetic, analgesic, anti-inflammatory, and antithrombotic drugs) and organic synthesis. The recycling of the catalytic ma-



 $\begin{array}{l} R: C_{6}H_{5}, 4\text{-}FC_{6}H_{4}, 4\text{-}NO_{2}C_{6}H_{4}, C_{6}H_{13} \\ R^{1}, R^{2}: CN, CN; CN, COOEt; NO_{2}, COOEt; R^{3}: NH_{2} \\ \\ Zr\text{-}MOF: UiO66\text{-}NH_{2}, UiO67\text{-}NH_{2}; M: Rh, Ir \end{array}$ 

Scheme 1. Direct condensation-hydrogenation reactions in the one-pot reaction.



Scheme 2. Postmodification of UiO-66–NH<sub>2</sub> with pincer ligands. M = Rh, Ir.

terials has been studied, and they are found to be stable to multiple cycles.

### **Results and Discussion**

Herein, Zr<sup>IV</sup>-based MOFs (UiO-66 and UiO-67)<sup>[19]</sup> were selected as supports. UiO-66 is a rigid, chemically robust MOF with the empirical formula [Zr<sub>6</sub>(µ<sub>3</sub>-O)<sub>4</sub>(µ<sub>3</sub>-OH)<sub>4</sub>(BDC)<sub>6</sub>] (BDC = 1,4-benzenedicarboxylate) that serves as the secondary building unit (SBU) for the framework. The SBU is assembled from six Zr<sup>IV</sup> ions, each with a square antiprismatic coordination geometry composed of eight oxygen atoms. Each SBU is bound by 12 carboxylate groups from 12 BDC ligands. The structure of UiO-66 demonstrates that it is composed of octahedral (diameter =  $\approx 11$  Å) and tetrahedral (diameter =  $\approx 8$  Å) cages in a 1:2 ratio and the cages are connected by triangular windows (diameter =  $\approx 6$  Å).<sup>[20]</sup> Surface area values for UiO-66 were found between 1100 and 1200 m<sup>2</sup>g<sup>-1</sup>. Lillerud and co-workers report the preparation of one isoreticular structure: UiO-67 microcrystalline powder from the 4,4'-biphenyldicarboxylate (BPDC) ligand. The isoreticular structure of UiO-67 was confirmed by using powder XRD. The Langmuir surface area of UiO-67 was reported to be 3000 m<sup>2</sup>g<sup>-1</sup>, and the estimated size of window pores was 8 Å.<sup>[19]</sup> UiO-66 demonstrates high chemical and thermal stability and is stable in polar protic solvents, such as water and several alcohols. However, the extended isoreticular UiO-67 has lower chemical stability with respect to water, which was confirmed by powder XRD during dynamic light scattering measurements.<sup>[19c]</sup> Thus, UiO-66 and its BDC analogues have been studied extensively whereas reports on UiO-67 derivatives have been limited. As for thermal stability, thermogravimetric analysis (TGA) indicates that UiO-66 and UiO-67 demonstrate weight losses only at temperatures as high as 540 °C. The amino-functionalized UiO-66–NH<sub>2</sub> and UiO-67–NH<sub>2</sub> derivatives were found to have the same topology<sup>[16d,21]</sup> and were prepared by mixing ZrCl<sub>4</sub> and BDC-NH<sub>2</sub> or BPDC-NH<sub>2</sub> in DMF, with acetic acid as a modulator, crystallization at 120 °C for 12-24 h, and DMF exchange with ethanol followed by drying under vacuum (BET surface area = 800 and 1800  $m^2g^{-1}$ , respectively). The postsynthetic transformation of amines into imines has previously been reported<sup>[22]</sup> and used to anchor catalytically active exo-framework metal centers into MOFs.<sup>[23]</sup> Herein, UiO-66-NH<sub>2</sub> and UiO-67-NH<sub>2</sub> were functionalized easily through conventional chemical reactions performed in two steps: the NH<sub>2</sub> groups in the linker (2-aminoterephthalic acid or 3-amino-[1,1'-biphenyl]-4,4'-dicarboxylic acid) react with an aminopyridinealdehyde to form the corresponding imine NNNpincer Zr-MOF, which reacts with the appropriate starting metal complex to give the corresponding heterogenized (NNN)-M-Zr-MOF complex (M = Rh, Ir).

Thus, a starting cream powder of UiO-66-NH<sub>2</sub> was suspended in CH<sub>2</sub>Cl<sub>2</sub> and treated with (S)-N-(tert-butyl)-1-((6-formylpyridin-2-yl)methyl)pyrrolidine-2-carboxamide ((S)-L2) or (S)-6-((hexahydropyrrolo[1,2-a]pyrazin-2(1H)-yl)methyl)picolinaldehyde ((S)-L3)<sup>[11a,24]</sup> (Scheme 2) at room temperature for 24-48 h; this caused a color change from cream to yellow. The reaction was then stopped by repeated washing of the solid material with CH<sub>2</sub>Cl<sub>2</sub> and drying under vacuum. The elemental analysis indicates that a functionalization of approximately 17% (for L2) and 5% (for L3) of the total NH<sub>2</sub> groups was produced without losing the integrity of the framework. The final step to prepare the UiO-66-NH2-LM and UiO-67-NH2-LM catalysts (M = Rh, Ir) involved reacting a suitable precursor, [M(cod)- $(THF)_2]BF_4$  (M = Rh, Ir; cod = cyclooctadiene), with the iminemodified material. The preparative method is summarized in Scheme 2, and a detailed description is given in the Experimental Section.

The resulting UiO-66 microcrystalline powders were shown to possess the same structure as the parent UiO-66–NH<sub>2</sub> material, which was confirmed by power XRD (Figure 1). The chemical stability of the UiO-66–NH<sub>2</sub>–L derivatives was found to be similar to that of UiO-66, with good tolerance to polar solvents, such as water, methanol, ethanol, dichloromethane, and DMF. The materials also demonstrated thermal stability with decomposition temperatures near 350 °C in air, which are comparable

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Figure 1. XRD patterns of a) UiO-66–NH<sub>2</sub> (A), UiO-66–NH<sub>2</sub>–L3 (B), and UiO-66–[L3Rh]BF<sub>4</sub> (C), and b) UiO-66–NH<sub>2</sub>–[L2Ir]BF<sub>4</sub> (A), UiO-66–NH<sub>2</sub>–L2 (B).

to those of other UiO-66 derivatives, as confirmed by TGA (Figure S21a).

The FTIR spectra demonstrate bands assigned to C-C aromatic vibrational modes at 1600-1585, 1500-1430, and 700 cm<sup>-1</sup>. The carboxylate anion has two strongly coupled C-O bonds, with bond strengths between C=O and C-O. Bands at 1650–1550 cm<sup>-1</sup> (s) correspond to the asymmetrical stretching for the carboxylates, and the band at approximately 1400 cm<sup>-1</sup> (w) corresponds to symmetrical stretching. The presence of functional groups during the postsynthetic modification of the starting UiO-66-NH<sub>2</sub> can be observed in the full spectral range, with intensity depending on the conversion percentage. The full spectra are given in the Supplementary Information (Figures S5 a-c and S12). The percentage of functionalization can be determined by normalizing the FTIR spectra to the band at 760 cm<sup>-1</sup> assigned to the C–C vibrational mode in aromatic compounds (this band is relatively little affected by ring substituents),<sup>[16b]</sup> and no overlap from other vibrational modes is observed. Hereafter, these samples are referred to as UiO-66-NH<sub>2</sub>-L.

The analysis of the <sup>1</sup>H NMR spectra and electrospray ionization mass spectrometry (ESI-MS) spectra after the digestion of MOFs under acid conditions indicate that the ligands and Ir complexes remained in all Plastarch materials (Figures S13-S15). Hydrofluoric acid was used to digest the materials because of the high affinity of Zr for fluoride. The initial UiO-66-NH<sub>2</sub> was digested and the negative-mode mass spectra obtained showed a base peak at m/z 180 corresponding to  $H_2BDC-NH_2$  ([ $H_2BDC-NH_2+H$ ]<sup>-</sup>). The negative-mode mass spectra obtained for  $H_2BDC-NH_2-L2$  showed peaks at m/z 346  $(H_2BDC-NH_2-L2-COOH)$  and 563  $(ZrBDC-NH_2-L2+Na)$ , which corresponded to the modified ligand. The spectra for H<sub>2</sub>BDC-[L2Ir] showed a peak at m/z 512 ([L2Ir] + MeOH), 675 ([H<sub>2</sub>BDC-[L2Ir(MeOH)] + H], and 841 (ZrBDC-NH<sub>2</sub>-[L2Ir]BF<sub>4</sub>+Na+H). The ESI-MS spectra for  $H_2BDC-NH_2-L3$  showed peaks at m/z362 (H<sub>2</sub>BDC-NH<sub>2</sub>L3-COOH); a peak for H<sub>2</sub>BDC-[L3Ir] was observed at m/z 601 ({[H<sub>2</sub>BDC–[L3Ir] + H}), and peaks for H<sub>2</sub>BDC– [L3Rh] were observed at m/z 727 ({[H<sub>2</sub>BDC–[L3Rh(cod)BF<sub>4</sub>] + Na}), 639 ([H<sub>2</sub>BDC-[L3Rh(cod)]), and 541 ([L3Rh(cod)BF<sub>4</sub>]). Finally, hydrofluoric acid cleaved the Zr cluster, and the fluoro complex [ZrF<sub>5</sub>]<sup>-</sup> was discerned readily in the mass spectra, with a peak at m/z 185. The <sup>1</sup>H NMR spectra after the digestion of MOFs under acid conditions indicated that the ligands remained in UiO-66-NH2-L, UiO-66-NH2-[LIr]BF4, and UiO-66-NH<sub>2</sub>-[LRh]BF<sub>4</sub> materials.

The N<sub>2</sub> adsorption–desorption isotherms (obtained at 77 K) of functionalized UiO-66–NH<sub>2</sub> MOF samples indicated that the materials demonstrate type I isotherms (Figure S22). All isotherms were found to retain porosity despite the functionalization of the linker. The BET surface areas were found to be  $650 \text{ m}^2\text{g}^{-1}$ , total pore volume  $0.25 \text{ cm}^3\text{g}^{-1}$ , and pore diameter 2.69 nm for UiO-66–L2;  $500 \text{ m}^2\text{g}^{-1}$ ,  $0.20 \text{ cm}^3\text{g}^{-1}$ , and 2.51 nm for UiO-66–[L3Ir]BF<sub>4</sub>; and 266 m<sup>2</sup>g<sup>-1</sup>,  $0.25 \text{ cm}^3\text{g}^{-1}$ , and 3.34 nm for UiO-66–[L3Rh]BF<sub>4</sub>. The decrease in the BET surface area is mostly due to the increase in the mass of the material (attributed to the presence of a large ligand and the corresponding Rh or Ir complex) rather than due to loss of porosity.

Finally, SEM experiments confirmed that the particle size remains unchanged during the ligand formation, because no significant increase or decrease in particle size was observed by using this technique (Figures 2a–c and S23).

The postsynthetic modification of UiO-67-NH<sub>2</sub> was performed similar to that for UiO-66-NH<sub>2</sub>; the diffraction peaks for the fresh UiO-67-NH<sub>2</sub> materials were in agreement with those published in the literature.<sup>[19a,25]</sup> UiO-67 derivatives lost their crystallinity after modification in both moist and dry conditions, although the collapse is most pronounced when water is present in the system; this is in agreement with the decreased porosity (Figure 3). The materials demonstrated thermal stability with decomposition temperatures near 450 °C in air, which was confirmed by TGA (Figure S21). UiO-67-NH<sub>2</sub>-L derivatives were characterized by using FTIR spectroscopy, <sup>13</sup>C NMR spectroscopy, SEM, and so on (spectra are given in the Supplementary Information), and the results are similar to those discussed previously for UiO-66-NH<sub>2</sub> materials. The ESI-MS spectra for digested samples show peaks at m/z 507 for {H<sub>2</sub>BPDC-NH<sub>2</sub>-L3 + Na}, 639 for  $\{H_2BPDC-NH_2-[L3Rh]+Na+MeOH\}$ , and 750 for  $\{H_2BPDC-NH_2-[L3Rh(cod)]+Na+MeOH\}$ . The apparent modification of the morphology of the materials is observed in SEM

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Figure 2. SEM images of a) UiO-66–NH $_2$ –L2, b) UiO-66–NH $_2$ –[L2Ir]BF $_4\prime$  and c) UiO-66–NH $_2$ –[L3Rh]BF $_4.$ 

images presented in Figures 3 b and S26. The octahedral shape of the crystals is observed. The material demonstrates some surface roughness; however, the overall shape of the crystals is preserved.

#### **Catalytic applications**

To examine the catalytic ability of (NNN)–M–Zr-MOF materials, several reactions have been performed: 1) Knoevenagel-type condensation for base properties, 2) cascade condensation–olefin-nitro hydrogenation reactions for the ability to operate as a multifunctional system, and 3) one-pot cascade reaction.

#### Base catalytic properties

Several studies on the use of MOFs as solid catalysts (with acid<sup>[27]</sup> and basic<sup>[28]</sup> properties) for condensation reactions<sup>[26]</sup> have been reported. In the perfectly crystalline UiO-66-type MOF with the  $[Zr_6O_4(OH_4)]^{12+}$  cluster and 12 bidentate linkers, Zr has a maximum coordination number of 8,<sup>[19a]</sup> which, after





Figure 3. a) Powder XRD patterns of UiO-67–NH<sub>2</sub>–MOF: UiO-67–NH<sub>2</sub> (A); UiO-67–NH<sub>2</sub>–LRh (B). b) The SEM image of UiO-67–NH<sub>2</sub>–MOF.

dehydroxylation, has a coordination number of 7 that makes Zr act as a Lewis acid in different reactions.<sup>[29]</sup> Of these reactions, cross-aldol condensations have been catalyzed by UiO-66-type MOFs.<sup>[30]</sup>

Ethyl nitroacetate was an ideal methylene compound used to obtain  $\alpha$ -nitrocinnamates and acrylates, which are versatile building blocks in organic synthesis owing to their reactivity as good Michael acceptors and owing to the possibility of converting either the nitro or the ester group into other functional groups.^{[31,32]} The synthesis of functionalized  $\alpha\text{-nitroalkenes}$ often required multistep synthesis, even in the presence of toxic and expensive reagents (TiCl<sub>4</sub>).<sup>[31,33]</sup> The preparation of nitroalkenes with ZrCl<sub>4</sub> (which is a stronger Lewis acid, cheaper, and environmentally friendly than the previously used TiCl<sub>4</sub>) as a catalyst and Et<sub>3</sub>N as a base has been reported.<sup>[34]</sup> Taking this work into consideration, and given that the UiO-66-NH<sub>2</sub> MOF has Zr<sup>IV</sup> Lewis acid in the structure and the ligand (BDC-NH<sub>2</sub>) has amino groups or their derivatives, we believed that these bifunctional systems could act as catalysts for the synthesis of  $\alpha$ -nitrocinnamates. Thus, we report the use of the efficient UiO-66-NH<sub>2</sub> MOF derivatives as catalysts for the condensation reaction between aldehydes and malononitrile and ethyl cyanoacetate catalyzed by basic sites and obtain 100% conversion of the adduct after 6 h (Table 1, entries 8, 9, and 16-18). We have also performed the one-pot synthesis of  $\alpha$ -nitrocinnamates with UiO-66-NH2 derivatives (catalysts with basic and Lewis acid sites). The results are reported in Table 1.

Table 1. UiO-66(67)-catalyzed      Knoevenagel-type      condensation. <sup>[a]</sup>										
	0	Zr-MOF,	15% R	2						
	$R^{H} + R^{1}$	R <sup>2</sup> toluene 1		/						
		toldono, i	100 0 R.000							
Entry	Catalyst	R	$R^1$ , $R^2$	Yield	E/Z ratio <sup>[b]</sup>					
				[%]						
1	IRMOF-3 <sup>[c]</sup>	Ph	NO <sub>2</sub> , COOEt	25	50:50					
2	UiO-66–NH <sub>2</sub>	Ph	NO <sub>2</sub> , COOEt	90	50:50					
3	UiO-67–NH <sub>2</sub>	Ph	NO <sub>2</sub> , COOEt	100	40:60					
4	UiO-67–NH <sub>2</sub>	4-FPh	NO <sub>2</sub> , COOEt	100	50:50					
5	UiO-67–NH <sub>2</sub>	4-NO₂Ph	NO <sub>2</sub> , COOEt	50	50:50					
6	UiO-67–NH <sub>2</sub>	4-OMePh	NO <sub>2</sub> , COOEt	60	40:60					
7	UiO-67–NH <sub>2</sub>	C <sub>6</sub> H <sub>13</sub>	NO <sub>2</sub> , COOEt	65	50:50					
8	UiO-67–NH <sub>2</sub>	Ph	CN, CN	100	-					
9	UiO-67-NH <sub>2</sub>	Ph	CN, COOEt	100	20:80					
10	UiO-66-NH2-L2	Ph	NO <sub>2</sub> , COOEt	100	40:60					
11	UiO-66-NH <sub>2</sub> -L3	Ph	NO <sub>2</sub> , COOEt	100	40:60					
12	UiO-66-NH <sub>2</sub> -L3	4-FPh	NO <sub>2</sub> , COOEt	100	30:70					
13	UiO-66-NH <sub>2</sub> -L3	4-OMePh	NO <sub>2</sub> , COOEt	20	40:60					
14	UiO-66-NH <sub>2</sub> -L3	2,4,6-OMePh	NO <sub>2</sub> , COOEt	10	40:60					
15	UiO-66-NH <sub>2</sub> -L3	C <sub>6</sub> H <sub>13</sub>	NO <sub>2</sub> , COOEt	100	50:50					
16	UiO-66-NH <sub>2</sub> -L2	Ph	CN, CN	100 <sup>[d]</sup>	-					
17	UiO-66-NH <sub>2</sub> -L2	Ph	CN, COOEt	100 <sup>[d]</sup>	100					
18	UiO-66-NH <sub>2</sub> -L3	Ph	CN, COOEt	85 <sup>[e]</sup>	100					
19	UiO-66–NH <sub>2</sub> –L3Ir	Ph	NO <sub>2</sub> , COOEt	30	50:50					
20	UiO-66-NH <sub>2</sub> -[L3Rh]	Ph	NO <sub>2</sub> , COOEt	100	50:50					
[a] All	[a] All reactions were performed with substrates impregnated in toluene									
using 15 wt% of Zr-MOFs (5 mol%, based on Zr) at 100 °C for 24 h;										
[b] Determined from <sup>1</sup> H NMR analysis; [c] IRMOF-3 = $Zn_{*}O(BDC-NH_{*})$ ;										

The activity of the UiO-66–NH $_2$  catalyst for the condensation reactions was then compared with that of UiO-67–NH $_2$  (the

[d] 6 h; [e] 4 h.

linker is [1,1'-biphenyl]-3-amine) and postfunctionalized UiO-66(67)–NH<sub>2</sub>–L2 or UiO-66(67)–NH<sub>2</sub>–L3. Notably, a higher reaction rate was achieved for the pincer-functionalized Zr-MOFs. As shown in Table 1, the expected  $\alpha$ -nitrocinnamates and acrylates were obtained as *E/Z* mixtures in good to excellent yields and the Z isomer was always the major isomer. It is known that for the reaction catalyzed by ZrCl<sub>4</sub>/Et<sub>3</sub>N,<sup>[34]</sup> 4 mmol of ZrCl<sub>4</sub> per 2 mmol of benzaldehyde is necessary, whereas in this work a much lower amount of Zr was used because the reaction was performed with 5–15 wt% of Zr-MOFs (2–5 mmol% based on Zr).

We then decided to investigate the scope and limitations of the reaction of a range of aldehydes and active methylene compounds with our new catalysts in toluene (Table 1). As shown in the table, ethyl cyanoacetate or malononitrile and benzaldehyde furnished the product in high yields and lower reaction time compared with ethyl nitroacetate. Aromatic aldehydes provided the expected products in good yields, but were not affected by electronic factors. In addition, the reaction with aliphatic aldehydes such as *n*-heptanal gave the expected product in good yields.

The heterogeneity and recyclability of UiO-66–NH<sub>2</sub>–L2 in the condensation of benzaldehyde and ethyl nitroacetate were examined. After stirring the reaction mixture for 3 h in the presence of the catalyst, UiO-66–NH<sub>2</sub>–L2 was removed through filtration. After the removal of UiO-66–NH<sub>2</sub>–L2, the reaction did

not proceed, which revealed the catalytic activity of (NNN)–Zr– MOF derivatives. The catalyst demonstrates good recyclability, is easily isolated from the reaction suspension through filtration, and can be reused without loss of activity for at least three cycles and gave yields of approximately 90% (see data in Table S1).

Analysis of the powder XRD results for the reused catalyst revealed that UiO-66–NH<sub>2</sub>–L2 and UiO-66–NH<sub>2</sub>–L3 could maintain their crystallinity during the reaction, which indicates the high stability of (NNN)-UiO-66 derivatives (Figure 4a). The UiO-67 catalysts were also recycled and activity was maintained (see data in Table S1), even though crystallinity was lost significantly. Thus, UiO-66–NH<sub>2</sub>–L3 seems to be a suitable catalyst compared to UiO-67–NH<sub>2</sub>–L3 on the basis of the stability issue (Figure 4b).

# UiO-66–NH $_2$ derivatives as catalysts for the cascade olefination–hydrogenation reactions of aldehydes

Organic chemical synthesis performed through one-pot, tandem, domino, or cascade reactions<sup>[35]</sup> has become a significant area of research in organic chemistry<sup>[36]</sup> because such processes improve atom and process economies. The success of multistep sequential or multicomponent one-pot transforma-



Figure 4. a) Powder XRD patterns of UiO-66–NH<sub>2</sub>–L3 after recycling. UiO-66–NH<sub>2</sub>: 1 cycle (–); 2 cycles (–); 3 cycles (–). b) Powder XRD patterns of UiO-67–NH<sub>2</sub>–L3 after recycling. UiO-67–NH<sub>2</sub>: 1 cycle (–); 2 cycles (–); 4 cycles (–).

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tions requires a balance of equilibrium and a suitable sequence of reversible and irreversible steps.<sup>[37]</sup>

The development of catalysts for one-pot multistep reactions is important, as chemists aim at minimizing the use of reagents and solvents as well as at reducing intermediate separation and purification steps.[12, 38] An example of a multistep sequential process using differentiated bifunctional acid-metal catalysts was the cyclization of citronellal followed by hydrogenation to yield menthol in a one-pot synthesis<sup>[39]</sup> or the acetal hydrolysis followed by condensation and subsequent hydrogenation.[40] As **Table 2.** MOF–[LM]-catalyzed cascade reaction of aldehydes and ethyl nitroacetate: olefination<sup>[a]</sup>–alkene hydrogenation–nitro hydrogenation reactions.<sup>[b]</sup>

Entry	Catalyst	Reaction	R	Conv. <sup>[c]</sup>	t	Selectivity [%]	
	·	mode		[%]	[h]	Product B	Product C
1	$UiO-67-NH_2+UiO-67-NH_2-[L3Rh]$	two step <sup>[d]</sup>	Ph	100	48	5	95
2	UiO-67–NH <sub>2</sub> –[L3Rh]	one pot <sup>[e]</sup>	Ph	100	30	100	-
3	UiO-67–NH <sub>2</sub> –[L3Rh]	one pot <sup>[e]</sup>	Ph	100	48	40	60
4	UiO-67–NH <sub>2</sub> –[L3Rh]	one pot <sup>[e]</sup>	Ph	100	72	10	90
5	UiO-67–NH <sub>2</sub> –[L3Rh]	one pot <sup>[f]</sup>	Ph	100	44	97	3
6	UiO-67–NH <sub>2</sub> –[L3Rh]	one pot <sup>[f]</sup>	Ph	100	72	20	80
7	$UiO-67-NH_2-[L3Rh]+DIOP$	one pot <sup>[e]</sup>	Ph	100	48	60	40
8	$UiO-66-NH_2-L3+UiO-66-NH_2-[L3Rh]$	two step <sup>[d]</sup>	Ph	100	48	95	5
9	UiO-66–NH <sub>2</sub> –[L3Rh]	one pot <sup>[e]</sup>	Ph	100	34	100	-
10	UiO-66–NH <sub>2</sub> –[L3Rh]	one pot <sup>[e]</sup>	4Me-Ph	100	48	100	-
11	UiO-66–NH <sub>2</sub> –[L3Rh]	one pot <sup>[e]</sup>	4F-Ph	100	44	98	-
12	UiO-66–NH <sub>2</sub> –[L2Ir]	one pot <sup>[f]</sup>	Ph	30	24	50	50
			<i>c</i>			1 10/ 0	

[a] T = 110 °C; solvent toluene (1 mL); [b] All reactions were performed in toluene with 1 mol% of the catalyst (containing Rh); [c] Determined from GC and <sup>1</sup>H NMR analysis by using ethyl nitroacetate; [d] Two-step reaction: glass reactor + Autoclave Engineers; [e] One-pot reaction: glass reactor with manometer; [f] Autoclave Engineers device. Decomposition of catalyst was observed.

mentioned above,  $\alpha$ -nitrocinnamates and acrylates are versatile building blocks in organic synthesis owing to the possibility of converting either the nitro or the ester group into other functional groups. To examine the catalytic ability of UiO-67– NH<sub>2</sub> derivatives as multifunctional catalysts, we chose as a model the reaction between an aldehyde and ethyl nitroacetate that yields product A (ethyl 2-nitro-3-phenylacrylate), which, in the presence of hydrogen, gives product B (ethyl 2nitro-3-phenylpropanoate) and/or product C (ethyl 2-amino-3phenylpropanoate)—the metal-catalyzed reaction (Scheme 3). We have obtained the final products B and C by using either a two-step reaction or a one-pot reaction.

To obtain these products, in the first case, the UiO-67–NH<sub>2</sub>–L catalyst was suspended in toluene and then benzaldehyde and ethyl nitroacetate were added. The condensation product of these reactants, product A, formed, and the aldehyde was completely consumed within 24 h (Table 2). The product was isolated through filtration and added to a suspension of UiO-67–NH<sub>2</sub>–[LRh] in toluene; the reaction mixture was then transferred to an autoclave (heated to 80 °C under 6 bar hydrogen for 10 h; 1 bar=0.1 MPa), which yielded the corresponding benzyl amine (product C in Scheme 3; Table 2, entry 1) as the sole product. If the reaction was performed in the presence of UiO-66–NH<sub>2</sub>–L3 + UiO-66–NH<sub>2</sub>–[L3Rh], then only product B was formed (without the isolation of the corresponding acrylate) in high yield (Table 2, entries 8 and 9).



Scheme 3. M-Zr-MOF-catalyzed cascade condensation–olefin-nitro hydrogenation reaction. R = Ar; M = Rh, Ir.

We found that the one-pot reaction of benzaldehyde and ethyl nitroacetate in the presence of a catalytic amount of UiO-67-NH<sub>2</sub>-[LRh] derivative in toluene at 100 °C yielded product A, with 100% conversion after 24 h. Then, hydrogen (5 bar) was incorporated into the reaction media and the hydrogenation of the resulting double bond was completed after 6 h. If desired, the process can proceed, and finally, the reduction of NO<sub>2</sub> occurs, which yields the corresponding benzyl amino derivative (Scheme 3 and Table 2, entries 4 and 6). Next, the UiO-66-NH<sub>2</sub>-[LRh]-catalyzed reaction can selectively lead to the reduction of the double bond, which yields the corresponding ethyl 2-nitro-3-phenylpropanoate or 2-nitro-3-(p-tolyl)propanoate if the substrate is 4-methylbenzaldehyde (Table 2, entries 9-11). The same reaction catalyzed by UiO-66-NH<sub>2</sub>-[LIr] gave only 30% yield (product selectivity = 50%) and the Ir catalyst decomposes under reaction conditions (Table 2, entry 12).

Notably, the reaction of benzaldehyde and ethyl nitroacetate in the presence of UiO-66– $NH_2$ –[L3Rh] with 0.11 mol% of the catalyst (containing Rh) gives selectively the corresponding hydrogenated product in 97% yield after 44 h (total condensation–alkene hydrogenation reactions). If the reaction continues, the hydrogenation of the nitro group can be achieved after an additional 24 h.

To study the effect of the chiral amino group on asymmetric induction in cascade reactions, we measured the optical rotation of product C obtained through the cascade reaction but

we have not observed enantioselectivity in this reaction, even in the presence of a chiral diphosphine, such as DIOP [DIOP = 2,3-(isopropylidenedioxy)-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane)] (Table 2, entry 7).

Control experiments confirmed that the intact UiO- $66-NH_2-[LRh]$  catalyst was responsible for the observed catalytic activity, because once the solid catalyst was removed through filtration at low conversion the reaction stopped (hot filtration experiment; Figure S29). Moreover, no evidence was found for the

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dissolution of the catalyst. To test the recyclability of the UiO-66–NH<sub>2</sub>–[LRh] catalyst, this catalyst was subject to four cycles in the one-pot reaction (Table S2). The reaction was driven to completion in each cycle. The decreased activity of the catalyst was evident from an increase in the required time for the reaction completion, which was correlated with a slight loss of long-range crystallinity (Figure 5 a). The recyclability of the UiO-67 catalysts was also studied, and it has been found that the stability of these catalysts is much lower than that of the UiO-66–NH<sub>2</sub>–[LRh] catalysts. The crystallinity of UiO-67–NH<sub>2</sub>–[LRh] decreased significantly after five recycles (Figure 5 b).

### Conclusions

Multifunctional catalysts based on Zr-based metal organic frameworks containing guest-accessible NNN-pincer groups have been prepared. They can act as a bifunctional acid and base catalyst with the Zr (Lewis) and amine and amide groups located in the linkers for condensation reactions, and by incorporating a transition metal through coordination with the guest-accessible NNN-pincer groups, the combination of acid, basic, and hydrogenation active sites leads to a hybrid material that behaves as a multifunctional Zr-base-transition metal cat-



**Figure 5.** a) Powder XRD patterns of UiO-66–NH<sub>2</sub>–[L3Rh]BF<sub>4</sub> before and after recycling: before (–); recovered (–). b) Powder XRD patterns of UiO-67–NH<sub>2</sub>–[L3Rh]BF<sub>4</sub> before and after recycling: before (–); 1 cycles (–); 3 cycles (–).

alyst for one-pot cascade condensation-hydrogenation reactions. The simple method for catalyst preparation, its easy recovery, and its reusability is expected to contribute to the use of the catalyst for the development of benign chemical processes and products.

#### **Experimental Section**

#### Material preparation

The Zr-MOF (UiO-66–NH<sub>2</sub>) was prepared according to the methods reported in the original references.<sup>[16a]</sup> XRD (Philips X'Pert X-ray diffractometer using CuK<sub>α</sub> radiation) was used to confirm the expected crystalline structure of the materials. Starting materials were purchased from commercial suppliers (Sigma–Aldrich and Alfa Aesar) and used without further purification. Dried, distilled, and deoxygenated solvents were used. The detailed preparation and characterization of the MOF catalysts as well as the process of the catalytic reactions are given in the Supporting Information.

#### **Catalytic study**

Knoevenagel-type condensation reactions: The condensation reaction between benzaldehyde and ethyl nitroacetate with UiO-66-NH<sub>2</sub> derivatives as catalysts was performed in a magnetically stirred round bottom flask. A mixture of the catalyst (0.015 g, 5 mol%) and benzaldehyde (0.2 mL, 1.9 mmol) was kept in a 15 mL flask. The reactants in the flask were stirred for 5 min to disperse the Zr-MOF. Ethyl nitroacetate (0.023 g, 1.8 mmol) was then added, and the resulting mixture was stirred at 100 °C. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, filtering through a short silica gel pad, and analyzing by using GC-MS. Finally, the reaction mixture was filtered and the solvent was removed under reduced pressure to give the crude product. The crude product was purified by using column chromatography on silica gel, with hexane-ethyl acetate mixture as an eluent. The Zr-MOF catalyst was separated from the reaction mixture through centrifugation, washed with toluene, dried under vacuum, and reused. For the leaching test, the catalytic reaction was stopped after 4 h, analyzed by using GC, and centrifuged to remove the solid catalyst. The reaction solution was then stirred for 24 h.

#### Cascade reactions:

1) Two-step reaction: Glass reactor + Autoclave Engineers device: The condensation reaction was performed as described above in the presence of the UiO-66–NH<sub>2</sub>–L2Rh catalyst (1 mol%, containing Rh). Upon the completion of the reaction, the content was transferred to an autoclave reactor. Then, we added toluene (40 mL), purged with nitrogen, and pressurized with hydrogen (80 °C, 6 bar).

2) One-pot reaction: The condensation reaction was performed as described above in the presence of the UiO-66–NH<sub>2</sub>–L2Rh catalyst (1 mol%, containing Rh). Upon the completion of the reaction, hydrogen (6 bar) was introduced and the progress of the reaction was followed by using GC–MS. The one-pot reaction was also performed in an Autoclave Engineers device.

**Recycling experiments**: At the end of the process, the reaction mixture was centrifuged and the catalyst residue washed to completely remove any remaining products and/or reactants. The solid was reused, and any change in the catalytic activity was observed.

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# **FULL PAPERS**

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One-Pot Multifunctional Catalysis with NNN-Pincer Zr-MOF: Zr Base Catalyzed Condensation with Rh-Catalyzed Hydrogenation



**Preparation wons half the battle:** Multifunctional catalysts based on Zr-based metal organic frameworks containing guest-accessible NNN-pincer groups have been prepared. The combination of acid, basic, and hydrogenation active sites leads to a hybrid material that behaves as a multifunctional Zr-base-transition metal catalyst for one-pot cascade condensation-hydrogenation reactions.