6766 *Inorg. Chem.* **2010**, *49*, 6766–6774
DOI: 10.1021/ic101125m

Inorganic Chemistry
Article

Modular, Active, and Robust Lewis Acid Catalysts Supported on a Metal−Organic Framework

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Received June 3, 2010

Metal−organic frameworks (MOFs) have shown promise as heterogeneous catalysts because of their high crystallinity, uniform pores, and ability to be chemically and physically tuned for specific chemical transformations. One of the challenges with MOF-based catalysis is few systems achieve all of the desired features for a heterogeneous catalyst, including high activity, robustness (recyclability), and excellent selectivity. Herein, postsynthetic modification (PSM) of a MOF is used to synthesize a series of MOF catalysts that are highly robust and active for epoxide ring-opening reactions. In the following study, four metalated MOFs (UMCM-1-AMInpz, UMCM-1-AMInsal, UMCM-1-AMFesal, and UMCM-1-AMCupz) are examined as catalysts for β-azido and β-amino alcohol synthesis with epoxides of varying sizes and shapes using two different nucleophiles ($TMSN_3$ and aniline). The four MOFs are isostructural, exhibit good thermal and structural stability, and display different catalytic activities based on the combination of metal ion and chelating ligand immobilized within the framework. In particular, UMCM-1-AMInpz and UMCM-1-AMInsal act as robust, single-site catalysts with distinct selectivity for ring-opening reactions with specific nucleophiles. More importantly, one of these catalysts, UMCM-1-AMInpz, selectively promotes the ring-opening of *cis*-stilbene oxide in the presence of *trans*-stilbene oxide, which cannot be achieved with a comparable molecular Lewis acid catalyst. The results show that PSM is a promising, modular, and highly tunable approach for the discovery of robust, active, and selective MOF catalysts that combine the best aspects of homogeneous and heterogeneous systems.

As solid supports and matrixes for catalysis, metal−organic frameworks (MOFs) have garnered increasing attention because of their ability to capture advantages of both homogeneous and heterogeneous catalysts.[1−4] Homogeneous catalysts can be limited by thermal instability, cross reactivity (e.g., self-degradation), and the difficulty involved in isolating and reusing these catalysts.[5] Heterogeneous catalysts are generally more robust than homogeneous catalysts, but they are not easily functionalized and suffer from mass transport limitations.[6,7] MOF-supported catalysts may alleviate the limitations of homogeneous and heterogeneous systems while capturing the best features of each. The high porosity of MOFs allow for fast mass transport and interaction with substrates. MOFs also display high thermal stability, and the reactive active sites can be chemically tuned and modified like a homogeneous, single-site catalyst. Specifically, MOFs can be functionalized via their metal nodes or organic ligands through presynthetic[8] or postsynthetic[9] approaches. The metal ion and organic ligand(s) can be carefully chosen to produce a MOF with favorable attributes such as specific pore apertures, chiral topologies, and unsaturated metal centers. Likewise, the MOF can be further tuned after assembly by modifying the organic substituents on the ligand or by decorating the metal node.[10−21]

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The high crystallinity and uniform pores of MOFs suggest they can catalyze reactions with selectivity based on substrate size and shape.[7,22−24]

Despite these excellent features, the overall number of reported MOF catalysts still remains relatively low when compared to their use in areas such as gas sorption. Catalytic MOFs are still in their infancy with few systems showing high activity, selectivity, and recyclability.[1,2] Various MOFs have been explored as catalysts for transesterfications,[11] C−C bond formations,[16,22,24,25] epoxidations,[23] and many other reactions.[26−35] However, exerting precise control over the physical and chemical properties of the framework to improve catalytic activity and selectivity is not straightforward. Although early results have been promising, only a few studies provide evidence of MOF catalysts that are both selective and robust.[23,24]

In the following study, we show that postsynthetic modification (PSM)[9] can be used to carefully control the catalytic properties of a MOF. Presented herein are a series of MOFs that display unique activity and selectivity based on the features of the specific active site created within the framework. Four distinct MOFs were synthesized by modifying the same parent MOF (UMCM-1-NH_2)[36,37] with different combinations of chelating groups and metal ions (Scheme 1). All of the MOFs have similar structural and thermal stabilities, yet they display different catalytic behaviors under a given set of reaction conditions. The differences in catalytic activity provide strong evidence for the generation and tuning of well-defined, single-site catalysts within the MOF lattice. The findings presented demonstrate that (1) PSM can be utilized to produce a series of single-site MOF catalysts with different combinations of metal and organic components; (2) the MOFs are highly robust, active catalysts for epoxide ring-opening at extremely low catalyst (metal) loadings; (3) substrate selectivity can be achieved because of the size and shape of the MOF environment. More importantly, the substrate selectivity observed with the MOF catalysts are distinct from those found with purely homogeneous catalysts, illustrating that the pores of the MOF clearly create a specific environment for catalysis that can be used to generate novel patterns of selectivity. These results show that PSM can be used to prepare active, selective, and robust MOF catalysts.

Experimental Methods

General Procedures. Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). (*R,R*)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride was purchased from Sigma Aldrich. Samples were submitted to Robertson Microlit Laboratories for atomic absorption (AA) analysis. ^1H NMR spectra were recorded on a Varian FT-NMR spectrometer (400 MHz). UMCM-1-NH_2 was synthesized and activated as previously described.[36] UMCM-1-AMpz, UMCM-1-AMsal, UMCM-1-AMFesal, and UMCM-1-AM-Cupz were synthesized as previously described.[38] Formation of the corresponding TMS protected, β-azido alcohol, and β-amino alcohol products were confirmed by comparison with reported literature spectra.[39−46]

Metalation of UMCM-1-NH_2 and Derivatives. Unmodified UMCM-1-NH_2 (56 mg, 0.05 mmol) or modified UMCM-1-NH_2 (UMCM-1-AMpz and UMCM-1-AMsal, 56 mg, 0.05 mmol) in 2 mL of $CHCl_3$ was metalated with 1.0 equiv (0.05 mmol) of In(acac)$_3$. The mixture was left to stand at room temperature (RT) for 4 h. After decanting the solution, the crystals were washed with $CHCl_3$ (4 × 10 mL) and left soaking in $CHCl_3$ overnight. The rinse and wash cycle was repeated for an additional 2 days, and the crystals were left soaking in $CHCl_3$ until used.

Powder X-ray Diffraction (PXRD) Analysis. Approximately 15 mg of modified UMCM-1-NH_2 (typically soaked in $CHCl_3$) was air-dried before PXRD analysis. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 5 s/step, a step size of 0.02° in 2θ, and a 2θ range of 2−35°. The experimental backgrounds were corrected using the Jade 5.0 software package.

Thermal Analysis. Approximately 10−20 mg of MOF sample was used for thermogravimetric analysis (TGA) measurements. The MOF sample was either used directly after gas sorption analysis or dried at 90 °C under vacuum for 4−5 h. Samples were analyzed under a stream of dinitrogen using a TA Instrument Q600 SDT running from RT to 600 °C with a scan rate of 5 °C/min.

Brunauer−Emmett−Teller (BET) Surface Area Analysis. Approximately 40−60 mg of modified UMCM-1-NH_2 (stored in $CHCl_3$) was evacuated on a vacuum line for 2 h at RT.

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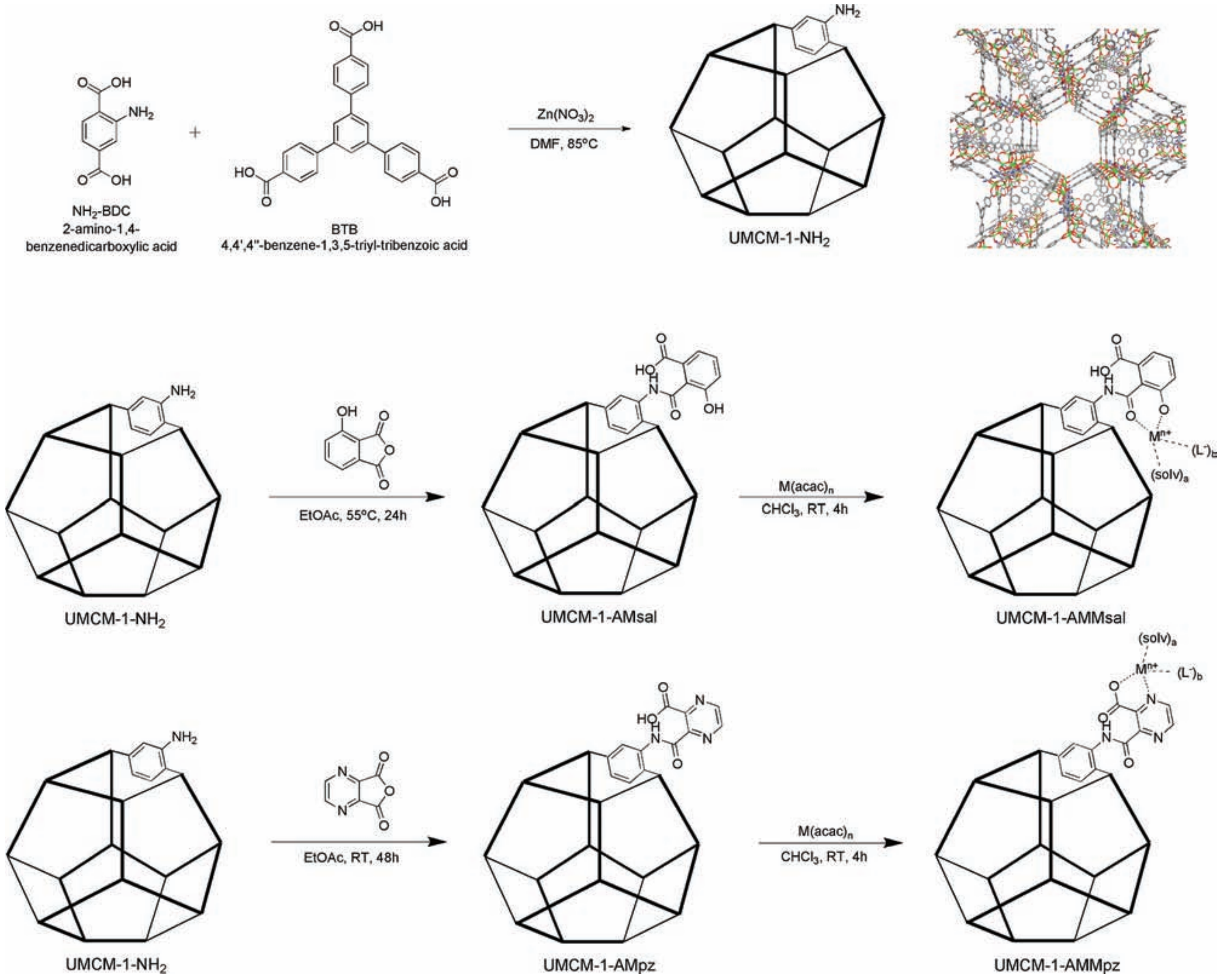
Scheme 1. Synthesis (Top) and Postsynthetic Modification (Bottom) of UMCM-1-NH_2[a]



[a] UMCM-1-NH_2 is modified with cyclic anhydrides and metalated with metal acacs (M = Fe^{3+}, Cu^{2+}, In^{3+}) to give UMCM-1-AMMsal (where M = Fe^{3+} or In^{3+}) and UMCM-1-AMMpz (where M = Cu^{2+} or In^{3+}).

The sample was then transferred to a preweighed sample tube and degassed at 25 °C on an Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was < 5 μmHg. The sample tube was re-weighed to obtain a consistent mass for the degassed MOF sample. BET surface area (m^2/g) measurements were collected at 77 K with dinitrogen on an Micromeritics ASAP 2020 Adsorption Analyzer using volumetric technique.

Epoxide Ring-Opening Catalysis with MOFs. UMCM-1-NH_2, UMCM-1-NH_2 treated with In(acac)$_3$, UMCM-1-AMCupz, UMCM-1-AMInpz, and UMCM-1-AMInsal were dried under vacuum at 90 °C for 4−5 h. UMCM-1-AMpz and UMCM-1-AMsal were dried at RT for 4−5 h. UMCM-1-AMFesal was activated as previously reported.[38] Dried MOF samples (15 mg, 0.014 mmol based on -NH_2) were placed into 4 mL dram vials. The MOF was immersed in 1 mL of $CDCl_3$, followed by epoxide (0.1 mmol), and $TMSN_3$ (0.1 mmol) or aniline (0.1 mmol). The reaction mixture was left standing at RT for 24 h and the supernatant was analyzed by ^{1}H NMR.

In(acac)$_3$ Control Reactions. In(acac)$_3$ (23 mg, 0.056 mmol) was dissolved in 4 mL of $CDCl_3$ followed by the addition of ligand (3-hydroxyphthalic anhydride, 2,3-pyrazinedicarboxylic anhydride, or salicylamide, 0.042 mmol). The mixture was sonicated for 15 min and was left to sit overnight. A portion (1 mL) of the $CDCl_3$ solution was transferred to a 4 mL dram vial followed by *cis*-2,3-epoxybutane (0.1 mmol) and nucleophile ($TMSN_3$ or aniline, 0.1 mmol). The reaction mixture was left standing at RT for 24 h, and the supernatant was analyzed by ^{1}H NMR.

Epoxide Ring-Opening Catalysis with Cr(salen)Cl. The experiments described were adapted from a literature procedure.[47] *cis* or *trans* epoxide (2,3-epoxybutane or stilbene oxide, 0.1 mmol) and 5 mol % (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride (Cr(salen)Cl) were dissolved in 50 μL of $CDCl_3$ in a 4 mL dram vial. $TMSN_3$ or aniline (0.1 mmol) was added, and the vials were placed on a shaker for 24 h at RT. The reaction mixture was directly analyzed by ^{1}H NMR without further purification.

Results

We[38] and others[18] have demonstrated that UMCM-1-NH_2, a highly porous MOF composed of Zn_4O clusters coordinated by 4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid (BTB) and 2-amino-1,4-benzenecarboxylic acid (NH_2−BDC) could be postsynthetically modified with a chelating group and

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Table 1. Atomic Absorption (AA) Analysis of UMCM-1-NH_2 Treated with In(acac)$_3$, UMCM-1-AMInpz, and UMCM-1-AMInsal

MOF (UMCM-1)	metal	theoretical	experimental
-NH_2 + In(acac)$_3$[a]	Zn^{2+}	25.26	24.30 ± 0.55
	In^{3+}	N/A	0.50 ± 0.28
-AMInpz[b,c]	Zn^{2+}	22.40	21.48 ± 0.77
	In^{3+}	4.92	3.76 ± 0.56
-AMInsal[b,d]	Zn^{2+}	23.09	22.41 ± 0.46
	In^{3+}	3.55	2.96 ± 0.25

[a] Based on three independent samples. [b] Based on six independent samples. [c] Assuming 50% modification. [d] Assuming 35% modification.

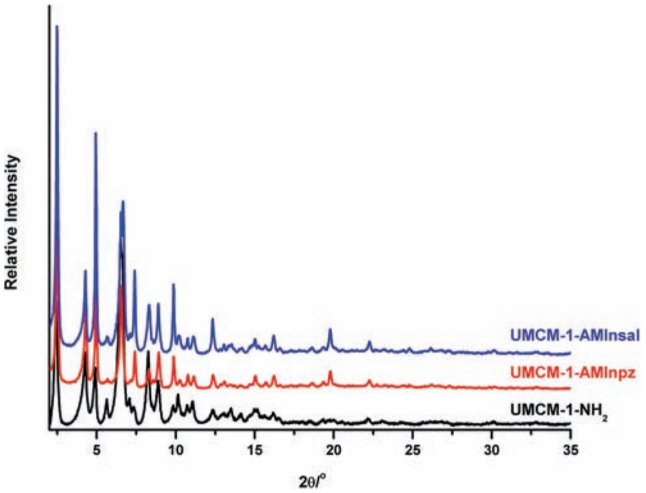

Figure 1. PXRD comparison of UMCM-1-NH_2 (black), UMCM-1-AMInpz (red), and UMCM-1-AMInsal (blue).

subsequently metalated. The successful preparation of two modified derivatives, UMCM-1-AMpz and UMCM-1-AMsal, which are appended with pyrazinedicarboxylate and salicylate substituents (Scheme 1) was previously described.[38] The reaction conditions used convert 50% and 35% of the amine sites into the desired chelating groups for UMCM-1-AMpz and UMCM-1-AMsal, respectively. UMCM-1-AMsal and UMCM-1-AMpz were metalated with Fe(acac)$_3$ and Cu(acac)$_2$ to give the metalated MOFs UMCM-1-AMFesal and UMCM-1-AMCupz. To further exploit this system, metalation of UMCM-1-AMpz and UMCM-1-AMsal with different metals was investigated, and the resulting MOFs were examined as Lewis acid catalysts. After several attempts with different metal sources, it was determined that UMCM-1-AMpz and UMCM-1-AMsal could be cleanly metalated with In(acac)$_3$. Similar to previous studies with Cu(acac)$_2$ and Fe(acac)$_3$, In^{3+} binding was confirmed by atomic absorption (AA) analysis (Table 1). UMCM-1-AMpz, UMCM-1-AMsal, and UMCM-1-NH_2 exposed to 1 equiv of In(acac)$_3$ were found to contain 3.76, 2.96, and 0.5 wt % of In^{3+}. These values, when compared with theoretical loadings (e.g., one metal ion per chelator site), indicate that more than 70% of the metal binding sites are occupied for both UMCM-1-AMpz and UMCM-1-AMsal, while only residual binding is observed for the unmodified UMCM-1-NH_2.

UMCM-1-AMInpz and UMCM-1-AMInsal were further examined by PXRD, TGA, and dinitrogen gas sorption. The PXRD patterns of UMCM-1-AMInpz and UMCM-1-AMInsal were found to be identical to the parent MOF (Figure 1), thus confirming that the metalation had no effect on the structural stability of the framework. Single crystal X-ray diffraction data of UMCM-1-AMInpz revealed the framework consists of octahedral Zn_4O SBUs coordinated by four BTB and two NH_2−BDC ligands. The MOF has large hexagonal pores framed by the BTB ligands and smaller pores defined by both BTB and NH_2−BDC ligands (Supporting Information, Figures S1 and S2). The framework topology, along with the cell parameters (space group = $P6_3/m$; a = b = 41.3685 Å, c = 17.5097 Å; $\alpha = \beta = 90°$, $\gamma = 120°$; V = 25950 Å^3) are similar to the parent MOF.[38] A nitrogen atom was located and assigned on the benzenedicarboxylate ligand; however, the modified substituents could not be located in the electron density map because of incomplete modification of the sites and positional disorder of the modified NH_2−BDC ligand. Both metalated MOFs were stable up to 400 °C (Supporting Information, Figure S3), and BET surface area measurements confirmed the modified MOFs remained highly porous with surface areas of ~3200 m^2/g.

UMCM-1-AMFesal was previously determined to be an active, robust catalyst for the Mukaiyama aldol reaction, which involves C−C bond formation between an aromatic aldehyde and silyl enol.[24,48] Notably, UMCM-1-AMFesal exhibited exceptional catalytic activity with low Fe^{3+} loadings. In an attempt to identify new catalysts, UMCM-1-AMCupz, UMCM-1-AMInpz, and UMCM-1-AMInsal were tested for activity in the Mukaiyama aldol reaction under the previously reported conditions. We anticipated that these MOF catalysts might show comparable or better activity based solely on increased metal loading relative to UMCM-1-AMFesal; however, little or no reactivity was seen with these other metalated MOFs despite attempts to increase the catalyst loading and reaction time (data not shown).

With this observation in hand, other Lewis acid catalyzed reactions were explored, in particular reactions that had not been widely studied with other MOF catalysts.[1,2] Epoxide ring-openings, which are important processes for generating stereocontrolled organic intermediates, are an attractive target.[49] MOF catalysts are appealing platforms for epoxide ring-opening reactions because these reactions generally occur in the presence of a Lewis acid catalyst and a nucleophile (e.g., thiols, alcohols, aromatic amines) under fairly mild conditions.[44,50] Many homogeneous catalysts have been utilized for epoxide ring-openings, including metal salen complexes (e.g., Cr^{3+}, Co^{2+}, Mn^{2+})[49,51] and metal salts with or without additives.[45] One of the biggest challenges in these ring-opening reactions is regioselective control as the nucleophile can attack either position of the epoxide ring.[52]

According to recent MOF reviews,[1,2] only three MOFs have been explored as epoxide ring-opening catalysts. In one report, Cu(asp)(bpe)$_{0.5}$(H_2O)$_{0.5}$(MeOH)$_{0.5}$ (asp = aspartic acid, bpe = 1,2-bis(4-pyridyl)ethylene) was protonated in a postsynthetic manner to produce Cu(D/L-asp)bpe$_{0.5}$(HCl)(H_2O) as an active Brønsted acid catalyst for methanolysis of *cis*-2,3-epoxybutane.[29] The MOF was found to be heterogeneous and gave the expected alcoholysis product with yields as high as 70%, but the MOF was unable to catalyze the reaction with larger epoxides and alcohols because of a

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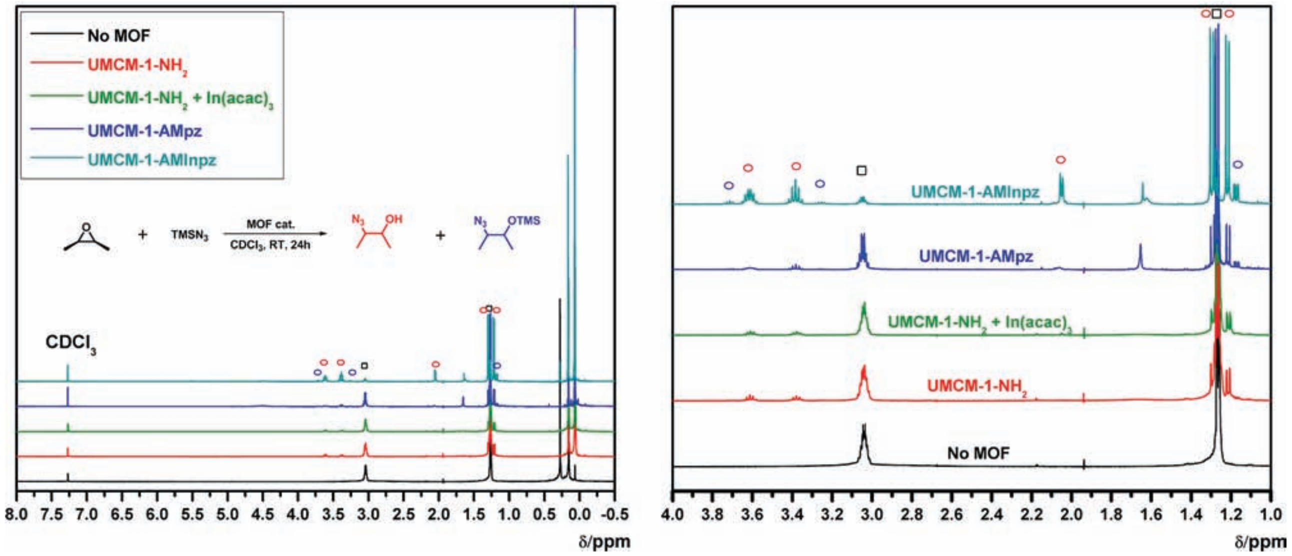
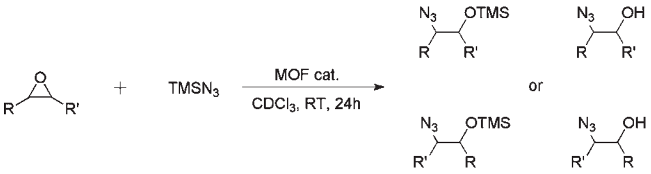


Figure 2. ^1H NMR supernatant comparison between different MOF materials with epoxide and $TMSN_3$. Epoxide starting material is indicated by black squares, alcohol product is indicated by red circles, and TMS protected product is indicated by blue circles.

Scheme 2. MOF Catalyzed Epoxide Ring-Opening Reactions with $TMSN_3$ as the Nucleophile[a]



[a] The MOF catalysts produce either a mixture of the TMS protected and β-azido alcohol products or only the β-azido alcohol.

restricted pore size. Two other MOFs, $[Cu_2(5,5'BDA)_2(H_2O)_2]MeOH\cdot 2H_2O$ (BDA = 2,2′-dihydroxy-1,10-binaphthalene-5,5′-dicarboxylate) and $Cu(Bpy(H_2O)_2(BF4)_2(bpy)$ (denoted as Cu-MOF), were examined as catalysts for amino alcohol synthesis.[30,31] Both MOFs were found to be size selective, but they displayed modest conversions ($<50\%$) and no evidence was provided about robustness of these catalysts.

Given the encouraging results from these previously reported systems, the metalated UMCM MOFs were analyzed for their performance as epoxide ring-opening catalysts. We chose to focus on amino alcohols, which are important intermediates for the development of pharmaceuticals, chiral auxiliary reagents, and are common backbones in natural and synthetic products.[52] As a starting point, *cis*-2,3-epoxybutane and trimethylsilylazide ($TMSN_3$) were selected as the epoxide and nucleophile. The reaction between epoxides and $TMSN_3$ generally leads to the formation of TMS protected alcohols, which are subsequently deprotected and reduced to give the corresponding amino alcohol (Scheme 2).[39] Although *cis*-2,3-epoxybutane and $TMSN_3$ have been reported with other catalysts,[44] this particular combination has not been demonstrated using a MOF system.

Reactions with metalated MOFs (UMCM-1-AMInpz, UMCM-1-AMInsal, UMCM-1-AMCupz, UMCM-1-AMFesal) were conducted in $CDCl_3$ for 24 h at RT. After 24 h, the crude supernatants were directly analyzed by ^1H NMR to determine percent substrate conversion. The ^1H NMR of neat *cis*-2,3-epoxybutane shows a multiplet at 3.05 ppm, which is indicative of the *meso* protons, and a doublet at 1.25 ppm, which corresponds to the methyl protons (Figure 2). Analysis of the reaction supernatants by ^1H NMR showed the presence of two new multiplets at 3.6 and 3.8 ppm as well as two new doublets in the upfield region, thus confirming generation of the ring opened product (Figure 2). Surprisingly, the product did not match the reported spectra of 2-azido-3-(trimethylsilyloxy)butane, although trace amounts of the TMS product were detected. A new peak was also present at 2.05 ppm that had equivalent integration with the protons at 3.6 and 3.8 ppm. Examination of similar reactions in the literature between epoxides with $TMSN_3$ (vide infra) indicated that the product obtained was the corresponding β-azido alcohol.[44] Synthesis of the β-azido alcohol generally requires an additional deprotection step; however, in situ deprotection takes place with the MOF catalyst.

Monitoring of these reaction mixtures by ^1H NMR (RT, 24 h) showed that all the metalated MOFs could catalyze the reaction, but with varying degrees of activity (Figure 3). On average, UMCM-1-AMInpz had the highest conversion under the reported conditions at 78%. UMCM-1-AMInsal was less active with 56% conversion, while UMCM-1-AMFesal and UMCM-1-AMCupz both had significantly lower conversions of 30% and 11%, respectively. On the basis of these results alone, the In^{3+} metalated MOFs appear to be more active when compared with Fe^{3+} and Cu^{2+}. To confirm that the catalysis was occurring because of the presence of the Lewis acid centers and not just the unmodified MOF itself, several control reactions were performed. UMCM-1-NH_2, UMCM-1-NH_2 treated with $In(acac)_3$, UMCM-1-AMpz, and UMCM-1-AMsal were prepared and examined under similar reaction conditions. UMCM-1-NH_2, UMCM-1-NH_2 treated with $In(acac)_3$, and UMCM-1-AMsal all showed $<10\%$ conversion, and UMCM-1-AMpz was slightly more active with ~16% conversion. None of the control reactions displayed the high activity observed with UMCM-1-AMInpz.

Reactions with a different nucleophile were examined as well. Aniline was chosen because it had been previously used in other MOF systems,[30,31] which provided a point of comparison (Scheme 2). Similar to the $TMSN_3$ experiments,

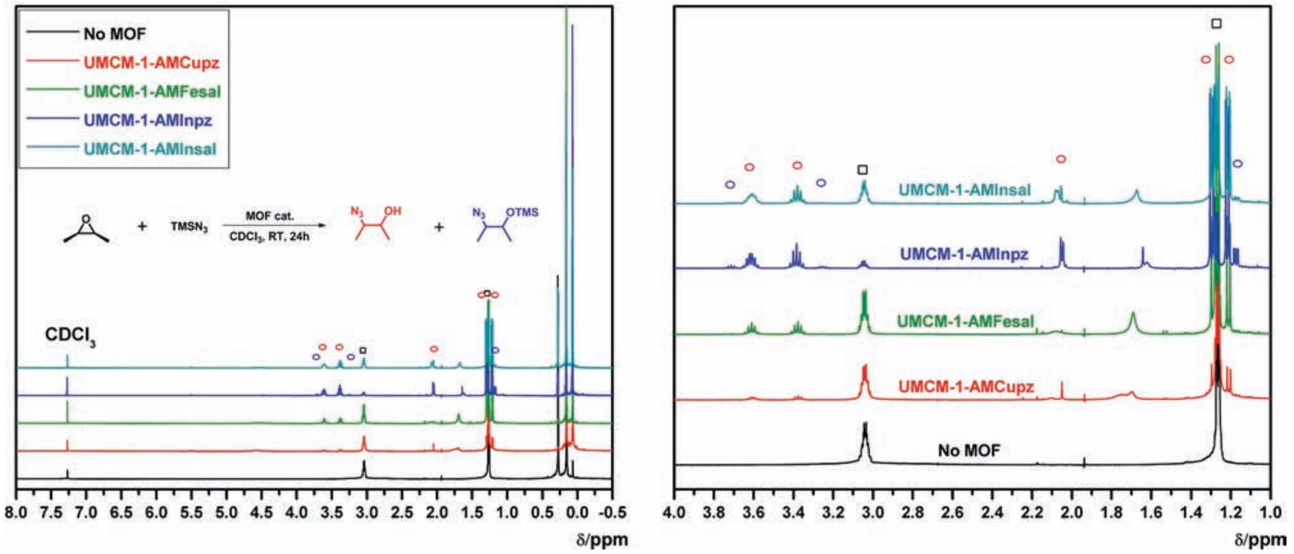


Figure 3. ^{1}H NMR supernatant comparison between metalated MOF catalysts with epoxide and TMSN$_3$. Epoxide starting material is indicated by black squares, alcohol product is indicated by red circles, and TMS protected product is indicated by blue circles.

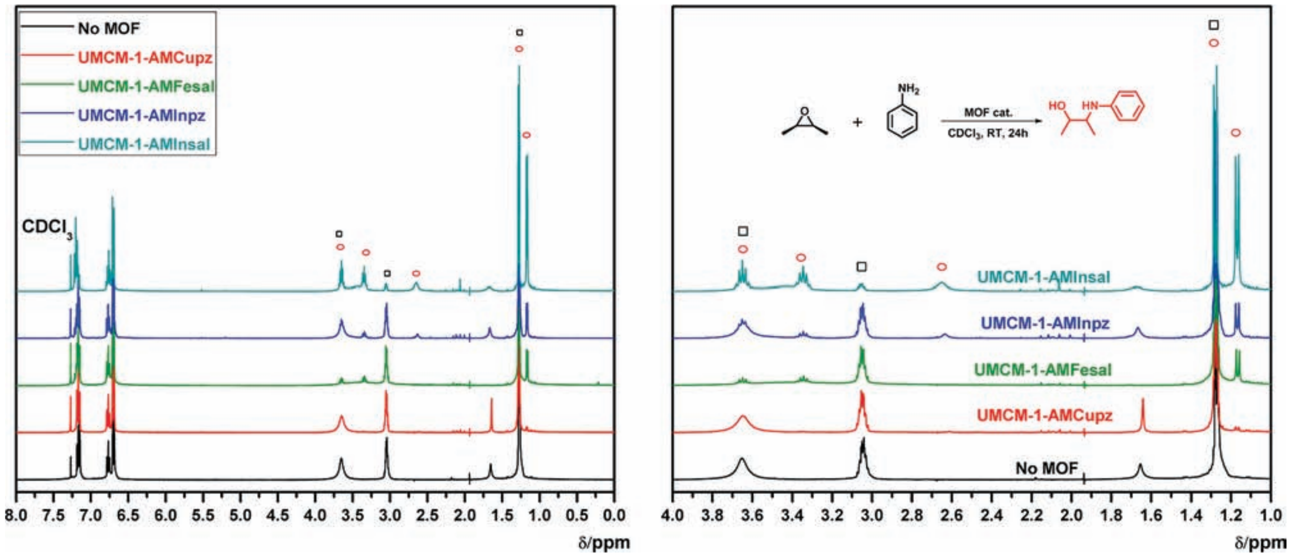
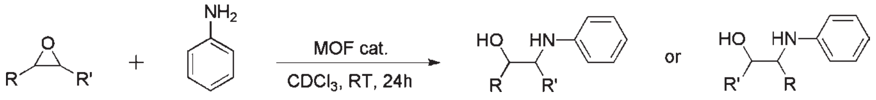


Figure 4. ^{1}H NMR supernatant comparison between metalated MOF catalysts with epoxide and aniline. Epoxide starting material is indicated by black squares, and the product is indicated by red circles.

Scheme 3. MOF Catalyzed Epoxide Ring-Opening Reactions with Aniline As the Nucleophile



the crude reaction supernatant was analyzed by ^{1}H NMR after reaction for 24 h at RT. Product formation was easily confirmed by the presence of two new multiplets at 3.8 and 4.7 ppm along with a new broad peak at around 2.6 ppm, which corresponds to the hydroxyl group of the product (Figure 4). These peak shifts were identical to reported β-amino alcohol spectra.[45] After testing all the metalated MOFs, the activity of the catalyst was found to be different with aniline as the nucleophile (Scheme 3). In this case, UMCM-1-AMInsal had the highest conversion at 86%, followed by UMCM-1-AMFesal with 34% and UMCM-1-AMInpz with 30% (Table 2). UMCM-1-AMCupz did not show any activity despite previous evidence that Cu^{2+} MOFs are capable of promoting epoxide aminolysis.[30,31] Analogous control experiments, as described with TMSN$_3$ above, were also performed with aniline as the nucleophile. All of the control reactions showed less than ~13% conversion.

Additional controls were performed to confirm that the metalated MOFs were indeed the catalytic source for epoxide ring-opening. Initial control reactions with no MOF showed that epoxide ring-opening did not occur at all. Likewise, removal of the metalated MOFs (e.g., UMCM-1-AMInpz and UMCM-1-AMInsal) from the reaction supernatant completely halted the progress of the reaction (Supporting Information, Table S3, Figures S6 and S7). Control reactions with In(acac)$_3$ and various

Table 2. Percent Conversions of MOF Catalyzed Reactions between Different Epoxides and $TMSN_3$[a]

epoxide										
R	R′	no MOF	UMCM-1-NH_2	UMCM-1-$NH_2 + In^{3+}$	UMCM-1-AMpz	UMCM-1-AMsal	UMCM-1-AMInpz	UMCM-1-AMInsal	UMCM-1-AMCupz	UMCM-1-AMFesal
Me	Me	no rxn	8 ± 6	10 ± 4	16 ± 7	7 ± 4	78 ± 9[b]	56 ± 2[b]	11 ± 5	35 ± 14[b]
$\text{-(CH}_2\text{)}_3\text{-}$		no rxn	2 ± 1	4 ± 3	4 ± 2	5 ± 4	53 ± 3[b]	43 ± 5[b]	3 ± 4	26 ± 3
H	Ph	no rxn	19 ± 8	27 ± 7	41 ± 9	19 ± 11	70 ± 2	54 ± 6	32 ± 7	53 ± 1
Ph	Ph[c]	no rxn	2 ± 2	1 ± 1	1 ± 1	3 ± 1	48 ± 8	17 ± 10	4 ± 2	9 ± 2
Ph	Ph[d]	no rxn	no rxn	no rxn	no rxn	no rxn	no rxn	no rxn	no rxn	no rxn

[a] All values are the result of three independent experiments. [b] Based on four independent trials. [c] Cis. [d] Trans.

Table 3. Percent Conversions of MOF Catalyzed Reactions between Different Epoxides and Aniline[a]

epoxide										
R	R′	no MOF	UMCM-1-NH_2	UMCM-1-$NH_2 + In^{3+}$	UMCM-1-AMpz	UMCM-1-AMsal	UMCM-1-AMInpz	UMCM-1-AMInsal	UMCM-1-AMCupz	UMCM-1-AMFesal
Me	Me	no rxn	no rxn	9 ± 7	8 ± 6	13 ± 2	30 ± 7	86 ± 11	1 ± 2	34 ± 6
$\text{-(CH2)}_3\text{-}$		no rxn	no rxn	1 ± 1	2 ± 2	1 ± 1	20 ± 7	58 ± 12	no rxn	22 ± 8
H	Ph	no rxn	5 ± 4	14 ± 3	20 ± 1	12	49 ± 1	~99	16 ± 1	43 ± 1
Ph	Ph[c]	no rxn	no rxn	no rxn	no rxn	no rxn	no rxn	6 ± 2	no rxn	no rxn
Ph	Ph[d]	no rxn	no rxn	no rxn[b]	no rxn[b]	no rxn	no rxn[b]	no rxn	no rxn[b]	no rxn

[a] All values are the result of three independent experiments. [b] Based on two independent experiments. [c] Cis. [d] Trans.

ligands (salicylamide, 3-hydroxyphthalic anhydride, and 2,3-pyrazinedicarboxylic anhydride) were also set up to determine if trace amounts of the metal source and ligands could act as homogeneous catalysts. Despite using 10 mol % loadings, no significant reactivity was seen from any of the controls, indicating that $In(acac)_3$ metal source alone is a poor catalyst for epoxide ring-opening.

Stability of MOF Catalysts. Overall, UMCM-1-AMInpz and UMCM-1-AMInsal were found to be the most active catalysts, but for different ring-opening reactions. UMCM-1-AMInpz was highly active for the reaction with $TMSN_3$ while UMCM-1-AMInsal showed a preference with aniline as the nucleophile. Several tests were performed with the two MOFs to understand their chemical stability postcatalysis. Overall, both MOFs remained stable after three catalytic cycles with complete retention of reactivity. On average, UMCM-1-AMInpz maintained 76% conversion over three cycles, while UMCM-1-AMInsal gave 82% conversion (Supporting Information, Table S1). It should be noted that UMCM-1-AMInpz and UMCM-1-AMInsal represent extremely low loadings of In^{3+} under the reaction conditions used. As mentioned earlier, UMCM-1-AMInpz and UMCM-1-AMInsal have metal loadings of 3.76 and 2.96 wt %, which corresponds to 0.5 mol % (0.00053 mmol) and 0.4 mol % (0.00041 mmol) of In^{3+}. PXRD indicated that the MOFs maintained their structural integrity after catalysis (Supporting Information, Figures S4 and S5). Samples were prepared for AA analysis pre- and postcatalysis to determine if metal was leaching from the MOF. On the basis of three independent samples, it was determined that < 10% leaching of either Zn^{2+} or In^{3+} occurs for UMCM-1-AMInpz and UMCM-1-AMInsal after three catalytic cycles (Supporting Information, Table S2).

Size Selectivity. The metalated MOFs were examined with other epoxides of varying sizes and shapes to determine if the MOF catalysts demonstrated any substrate selectivity (Tables 2 and 3). Other epoxides that have been commonly studied in literature, such as cycloalkane epoxides and terminal epoxides were employed, specifically cyclopentene oxide and styrene oxide. Cyclopentene oxide was examined under the same reaction conditions as used for *cis*-2,3-epoxybutane. For the $TMSN_3$ reactions, UMCM-1-AMInpz had the highest conversion of 53%, followed by UMCM-1-AMInsal with 43%, UMCM-1-AMFesal with 26%, and UMCM-1-AMCupz with < 5%. Switching the nucleophile to aniline resulted in UMCM-1-AMInsal having the highest conversion at 58%, while UMCM-1-AMInpz and UMCM-1-AMFesal both had similar conversions of ~20% and UMCM-1-AMCupz gave no conversion.

The metalated MOFs were more active with styrene oxide in comparison with cyclopentene oxide. UMCM-1-AMInpz gave the highest conversion of 70% for the reaction with $TMSN_3$ while UMCM-1-AMInsal and UMCM-1-AMFesal both gave conversions of ~53%. Furthermore, UMCM-1-AMCupz showed 32% conversion while the other MOF controls had conversions as high as 40%. Despite the unexpectedly high conversions obtained with the control MOFs, the results still indicate that the metalated systems, such as UMCM-1-AMInpz, show the highest activity.

Similar trends were also seen when cyclopentene oxide and styrene oxide were coupled with aniline. UMCM-1-AMCupz and the control MOFs were still active, but showed lower conversions of ~20%, which may be due to the larger size of aniline in comparison with $TMSN_3$. UMCM-1-AMInpz and UMCM-1-AMFesal had similar conversions between 40 and 50%. UMCM-1-AMInsal essentially catalyzed the reaction to completion (~99%); however, two products were discovered in the reaction mixture. The high activity of UMCM-1-AMInsal unexpectedly resulted in two products: the major product (68%) was determined to be 2-phenylamino-2-phenylethanol by ^1H and ^{13}C NMR.[43,46,53] The minor product (32%) was identified as the bis-alkylated product, 2,2′-(phenylazanediyl)bis(2-phenylethanol), as confirmed by high resolution mass spectrometry and ^{13}C NMR. Bis-alkylation between epoxides and aniline has been

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(53) Bedore, M. W.; Zaborenko, N.; Jensen, K. F.; Jamison, T. F. *Org. Process Res. Dev.* **2010**, *14*, 432–440.

previously reported; however, the specific product formed here, 2,2′-(phenylazanediyl)bis(2-phenylethanol), has not been previously reported, to the best of our knowledge (Supporting Information, Figure S31).[53] As expected, running the same reaction with increased amounts of styrene oxide (2 equiv) results in the production of more 2,2′-(phenylazanediyl)bis(2-phenylethanol), while using increased amounts of aniline (4 equiv) results in ~90% conversion to 2-phenylamino-2-phenylethanol (Supporting Information, Figure S32).

To complete the size selectivity study, *cis*- and *trans*-stilbene oxide were examined. *cis*-Stilbene oxide underwent ring-opening in the presence of $TMSN_3$ with some of the metalated MOF catalysts (Table 2). UMCM-1-AMInpz gave 48% conversion while UMCM-1-AMInsal, UMCM-1-AMFesal, and UMCM-1-AMCupz had conversions of 17%, 9%, and 4%, respectively. The overall activity dropped drastically for all MOFs upon switching the nucleophile to aniline (Table 3). UMCM-1-AMInsal was the only MOF that showed some catalytic activity, but the yield was very low (6%). In contrast to *cis*-stilbene oxide, *trans*-stilbene oxide did not undergo ring-opening with either nucleophile in the presence of any of the MOF catalysts. To ensure that *trans*-stilbene oxide was not poisoning the catalyst, the MOF catalysts (e.g., UMCM-1-AMInpz and UMCM-1-AMInsal) were recycled and shown to still be competent for the reaction between *cis*-2,3-epoxybutane and both nucleophiles ($TMSN_3$ with UMCM-1-AMInpz and aniline with UMCM-1-AMInsal). All control reactions showed negligible activity with *cis*- or *trans*-stilbene oxide and either $TMSN_3$ or aniline.

Size selectivity studies were also performed with different aniline derivatives using UMCM-1-AMInsal as the catalyst. As mentioned previously, UMCM-1-AMInsal was found to be the most active material for the ring-opening reaction between *cis*-2,3-epoxybutane and aniline. Therefore, the reaction of *cis*-2,3-epoxybutane with aniline, 2-methylaniline, and 2,6-dimethylaniline in the presence of UMCM-1-AMInsal was examined under identical reaction conditions. All three aniline derivatives were found to readily react with the epoxide, with 86%, 93%, and 56% conversion for aniline, 2-methylaniline, and 2,6-dimethylaniline, respectively (Supporting Information, Figure S33). The sterically encumbered 2,6-dimethylaniline is not as good of a substrate, but it does not completely shut down the reaction, and hence, the MOF catalyst appears reasonably tolerant of substituents on the nucleophile for this reaction.

Discussion

PSM is an advantageous approach for modifying materials that would otherwise be difficult or impossible to synthesize through conventional solvothermal MOF synthesis. Multiple functionalities can be incorporated into the MOF with better control over substituent type and degree of modification.[20] For example, $UMCM-1-NH_2$ was transformed into UMCM-1-AMpz and UMCM-1-AMsal, which were furthered metalated with Fe^{3+}, Cu^{2+}, or In^{3+}. As a result, four MOFs catalysts with different metals and supporting ligands were readily produced by simply modifying a well-characterized MOF. It is important to note that all these MOFs are isostructural and have similar thermal stabilities; however, the MOFs display different catalytic activity based on their metal ion and supporting ligand combinations.

The difference in catalytic activity is most clearly demonstrated with UMCM-1-AMInpz and UMCM-1-AMInsal. Both MOFs have similar In^{3+} loadings and microporosities, yet their organic substituent, a pyrazinedicarboxylate versus a salicylate, dictates their catalytic activity and specificity for different reactions. UMCM-1-AMInpz was found to be best when using $TMSN_3$ as the nucleophile for epoxide ring-opening, while UMCM-1-AMInsal proved to be better when the nucleophile was aniline. As shown in Tables 2 and 3, the most active MOF catalyst for a given reaction (i.e., nucleophile) is the same for every epoxide substrate, highlighting the importance of having a specific metal−ligand combination active site. In general, both In^{3+} loaded MOFs were better catalysts for these epoxide ring-opening reactions than either UMCM-1-AMFesal or UMCM-1-AMCupz.

Catalytic activity can also be affected by the orientation and accessibility of the catalytic sites (e.g., metal−ligand combinations) within the framework. Previous studies with $UMCM-1-NH_2$ indicated that the efficiency of PSM is influenced by a combination of both pore and reagent size/shape.[36] The results obtained here show that catalysis can be similarly affected. The orientation and accessibility of the catalytic site is dependent on how the metal−ligand unit fits within the pore based on the size and shape of the chelating ligand, the metal ion coordination geometry, and the size and shape of the pore. Depending on the outcome, the position of the catalytic site can affect how the substrates (e.g., epoxide and nucleophiles) interact with the catalytic site and with each other. For this particular MOF catalytic system, the exact composition of the catalytic site has not been fully characterized (i.e., the ancillary ligands on the metal center have not been determined) and the metal sites have not been located by single crystal X-ray diffraction (to determine their precise orientation within the MOF). However, the reactions with different substrates suggests certain properties about the catalytic site. For example, the metalated MOFs are catalytically competent for the ring-opening of *cis*-stilbene oxide, but not *trans*-stilbene oxide. As mentioned previously, the UMCM MOFs have two types of pores: a large hexagonal pore and a smaller pore. On the basis of the framework topology and the crystal structure obtained of UMCM-1-AMInpz, the catalytic site can be directed into either pore. On the basis of the catalysis results with *cis*/*trans* epoxides, we infer that the catalytic site is more localized within the smaller pore, where access and nucleophilic attack of the *trans*-epoxides would be more constrained. This is consistent with the structure of the UMCM MOFs (Supporting Information, Figure S2), where the BDC ligands are tightly arranged around the smaller pores, while the BTB ligands frame the larger pores. Although their sizes are similar, the shape of *cis*- and *trans*-stilbene oxide are quite different, and this likely affects the ability of the latter to effectively interact with and be activated by the catalytic sites. While *trans*-stilbene may be able to access the interior of the MOF, it may be (a) sterically unable to interact with the metal site, or it (b) can interact with the metal site, but is in an orientation that makes nucleophilic attack unfavorable.

Literature reports for the catalytic ring-opening of stilbene oxide are scarce. Unfortunately, reactions involving the ring-opening with $TMSN_3$ were not found;[54] however, several reports with aniline are available.[45,47] According to one literature report, *cis*- and *trans*-stilbene oxide successfully undergo ring-opening with aniline in the presence of Cr(salen)Cl with yields of ~90%.[47] Under similar reaction conditions as described for the MOF catalysts, this Cr(salen)Cl catalyst can couple both *cis*- and *trans*-stilbene oxides with either nucleophile. The Cr(salen)Cl catalyst gave yields of 94% and 68% with *cis*- and *trans*-stilbene oxide, respectively, in the presence of $TMSN_3$. Similarly, with aniline, conversions of 43% and 60% were obtained with *cis*- and *trans*-stilbene oxide. To highlight the differences in substrate selectivity of the soluble versus MOF-based catalyst, Cr(salen)Cl and UMCM-1-AMInpz were tested as catalysts with a 1:1 mixture of *cis*- and *trans*-stilbene oxide using $TMSN_3$ as the nucleophile. Fortunately, the epoxide starting materials have sufficiently distinct ^{1}H NMR spectra (particularly the resonances at 4.38 ppm and 3.89 ppm for *cis*- and *trans*- epoxides, respectively) to monitor the conversion of each substrate within the mixture. As expected, Cr(salen)Cl catalyzed the conversion of both *cis*- and *trans*-stilbene oxide, while UMCM-1-AMInpz only catalyzed the ring-opening of *cis*-stilbene oxide (Supporting Information, Figures S34 and S35). To further confirm the selectivity, the same experiment was performed with *cis*-2,3-epoxybutane and *trans*-2,3-epoxybutane. By itself, *trans*-2,3-epoxybutane is essentially ~99% converted with Cr(salen)Cl, while only ~20% conversion is observed with UMCM-1-AMInpz as the catalyst (Supporting Information, Figure S36). A 1:1 mixture of *cis*- and *trans*-2,3-epoxybutane with $TMSN_3$ was examined with both Cr(salen)Cl and UMCM-1-AMInpz. In the mixed system, both epoxides were ~99% converted using Cr(salen)Cl; however, *cis*-2,3-epoxybutane was the dominant epoxide turned over with UMCM-1-AMInpz (Supporting Information, Figure S37) with ^{1}H NMR analysis suggesting a conversion of ~90% for *cis* and ~10% for *trans*. This shows that the MOF-based UMCM-1-AMInpz catalyst elicits unique, stereochemistry-based substrate selectivity, not achieved by a soluble catalytic system, while maintaining comparable activity at a lower catalyst loading.

Conclusions

The MOF UMCM-1-NH_2 was functionalized with chelating groups and metal ions to produce active Lewis acid catalysts. The systematic investigation of several UMCM-1-NH_2 derivatives have revealed two MOFs (UMCM-1-AMInpz and UMCM-1-AMInsal) to be excellent catalysts for epoxide ring-opening reactions to generate β-azido alcohols and β-amino alcohols. This is the first description of a MOF catalyst capable of preparing β-azido alcohols. These MOF catalysts show excellent thermal and structural stability, retain good activity over several cycles, and display selectivity with respect to the epoxide substrate not seen with other Lewis acid catalysts. By using PSM, a single MOF platform has been modified with different combinations of metal ions and chelating ligands to produce MOFs with distinctive catalytic activities. Future work will continue to employ PSM as a method toward fine-tuning and enhancing the catalytically properties of MOFs. For example, functionalization with multiple substituents that can impart additional interactions (e.g., chirality, hydrogen bonding, etc.) may be used to improve catalytic activity as well as substrate specificity and regioselective reactivity. It may be possible, with the optimum combination of substituents, to discover MOF catalysts with the best qualities of both homogeneous and heterogeneous systems and with biomimetic activity and selectivity.

Acknowledgment. We thank Sergio J. Garibay for helpful discussions and Dr. Y. Su for performing the mass spectrometry experiments. This work was supported by UCSD, the National Science Foundation (CHE-0546531, new MOF synthesis; CHE-9709183, CHE-0116662 and CHE-0741968 instrumentation grants), and the Department of Energy (DE-FG02-08ER46519, MOF modification for gas sorption).

Supporting Information Available: Further details are given in Figures S1−S33 and Tables S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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