JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Cite This: J. Am. Chem. Soc. 2018, 140, 17394−17398

pubs.acs.org/JACS

Reversible Metalation and Catalysis with a Scorpionate-like Metallo-ligand in a Metal−Organic Framework

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Supporting Information

ABSTRACT: The installation of metallo-ligands in metal−organic frameworks (MOFs) is an effective means to create site-isolated metal centers toward single-site heterogeneous catalysis. Although trispyrazolyborate (Tp) and tripyrazolylmethane (Tpm) form one of the most iconic classes of homogeneous catalysts, neither has been used as a metallo-ligand for the generation of MOFs thus far. Here, we show that upon in situ metalation with Cu^I, a tricarboxylated Tpm ligand reacts with $ZrOCl_2$ to generate a new MOF exhibiting neutral scorpionate-like chelating sites. These sites undergo for facile demetalation and remetalation with retention of crystallinity and porosity. When remetalated with Cu^I, the MOF exhibits spectroscopic features and catalytic activity for olefin cyclopropanation reactions that are similar to the molecular $[Cu(CH_3CN)Tpm^*]PF_6$ complex (Tpm* = tris(3,5-dimethylpyrazolyl)methane). These results demonstrate the inclusion of Tp or Tpm metallo-ligands in a MOF for the first time and provide a blueprint for immobilizing Tpm* catalysts in a spatially isolated and well-defined environment.

Seminal work by Trofimenko in the 1960s spurred the synthesis and study of a massive number of scorpionate metal complexes.[1,2] The prototypical ligands, trispyrazolylborate (Tp) and trispyrazolylmethane (Tpm), are straightforward to synthesize and offer vast latitude of electronic and steric control through functionalization of the pyrazole rings.[3] Scorpionate-type ligands often bind metals in a facial, κ^3 manner, thus leaving multiple sites open for substrate binding. This has led to numerous applications in organometallic and bioinorganic chemistry.[3−10] Despite their potential utility, the simplest, unfunctionalized, and thus sterically most unencumbered scorpionates are often ineffective for catalysis because they preferentially form the homoleptic ML_2 complexes with first-row transition metals. Indeed, the installation of bulky substituents at the pyrazole-3 position, which prevents the formation of the homoleptic complexes, is pivotal for functional molecular chemistry with scorpionates.[11] Although bulky substituents are an effective entry point for reactivity with scorpionate-bound metals, the very need for bulky substituents would be obviated if the scorpionate ligand were immobilized in a solid matrix. Isolation of such complexes on silica,[12,13] polystyrene,[14,15] and carbon materials[16] illustrate this principle well. However, the structural heterogeneity of these supports makes any attempts to understand and control the active site difficult.[12−16]

One class of hybrid solids that provide exceptional structural uniformity are metal−organic frameworks (MOFs).[17] These materials' ability to preserve a molecule-like coordination environment in a rigid and well-defined solid is highlighted by their utility as single-site heterogeneous catalysts[18,19] and as catalyst promoters.[20] The anionic Tp itself is mimicked by the coordination environment of secondary building units (SBUs) of a series of azolate-based MOFs.[21,22] Metal substitution at these SBUs[23,24] provided heterogeneous catalysts for a range of processes including ethylene oligomerization, polymerization, and C−H amination.[25−27] It is harder, however, to devise or modify existing MOFs to mimic the neutral Tpm ligand,[28] whose metal complex chemistry often critically diverges from that of Tp.[29−32]

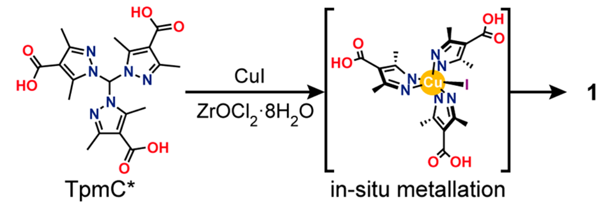
An alternative approach to site-isolation in MOFs is the use of metallo-ligands, which can have the added benefit of decoupling function, limited to the metallo-ligand, from structure, supported by the SBU. A number of canonical chelating ligands and homogeneous catalysts have been modified and introduced as linkers in MOFs.[33−44] Inspired by this methodology, we sought to isolate MOFs with Tpm metallo-ligands. Here, we show that 1,1′,1′′-methanetriyltris-(3,5-dimethyl-1*H*-pyrazole-4-carboxylic acid) (TpmC*), a Tpm-tricarboxylate, forms a porous MOF with Zr SBUs, whose scorpionate moieties can be postsynthetically demetalated and remetalated readily, with retention of structural integrity. We further demonstrate the utility of this new solid scorpionate catalyst with the use of Cu^I-metalated MOF in cyclopropanation catalysis.

Direct reaction of TpmC* with $ZrOCl_2$ led to exclusive formation of amorphous materials, likely due to the flexibility of the ligand, whose idealized C_{3v} symmetry is not favored in the absence of a metal ion. To lock the ligand into the C_{3v} symmetry, we reasoned that metalation may be necessary prior to or concomitant with MOF formation. Indeed, reaction of TpmC* with $ZrOCl_2$ in the presence of excess CuI and benzoic acid in *N*,*N*-dimethylformamide (DMF) at 120 °C for 48 h yields $\{[Zr_6O_4(OH)_4(C_6H_5COO)_4]_3(CuITpmC^*)_8\}$ (**1**) as a white microcrystalline powder (Scheme 1). Because cubic microcrystals of **1** (Figure 1c, S1) are too small for single-crystal X-ray diffraction analysis, the structure of **1** was determined by Rietveld analysis of high-quality powder X-ray

Received: October 15, 2018
Published: November 30, 2018

DOI: 10.1021/jacs.8b11085
J. Am. Chem. Soc. 2018, 140, 17394−17398

Scheme 1. Synthesis of 1



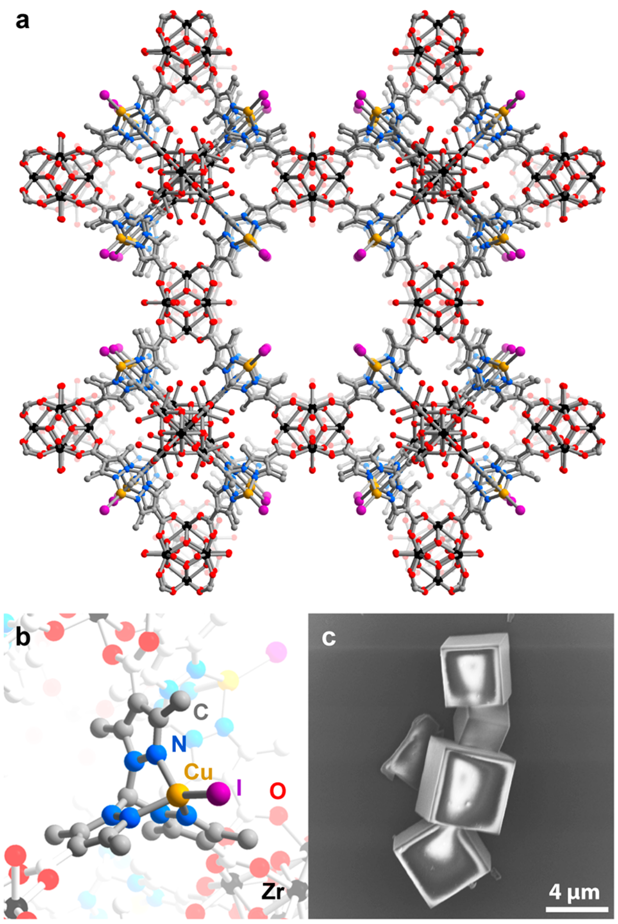
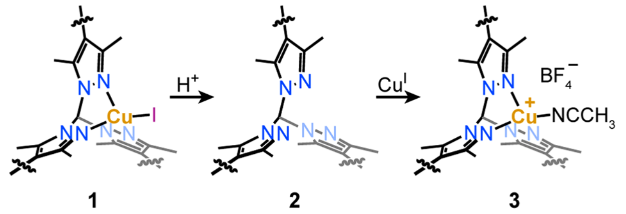


Figure 1. (a) Partial X-ray diffraction structure of **1**. Hydrogen atoms, guest molecules, and benzoates are omitted for clarity. (b) Close-up view of the Tpm*-like coordination environment. (c) Scanning electron microscopy (SEM) image of **1**.

diffraction (PXRD) data (Figure S2). The MOF crystallizes in the cubic $Pm\bar{3}m$ space group with three-dimensionally interconnected channels lined by iodide anions pointing toward the center of the pores (Figure 1a). The idealized[45] accessible pore diameter is 8.3 Å. Because each $Zr_6O_4(OH)_4(CO_2)_{12}$ SBU is 8-connected, and each metallo-ligand bridges three SBUs, the MOF is a 3,8-connected network with the ***the*** topology, similar to BUT-12,[46] another zirconium-based MOF with 3-fold symmetric ligands, and first observed in a tetrazolate MOF.[47] This topology also gives rise to vertex-sharing octahedral cages with accessible cavities of 8.1 Å diameter and windows of 2.5 Å, in which the SBUs constitute vertices and linkers act as triangular faces. Benzoates, H_2O, or HO^- complete the four vacancies in the equatorial σ_h plane of each SBU. Within the metallo-ligand, Cu^I adopts a distorted pseudotetrahedral geometry (Figure 1b) with bond distances and angles nearly identical to those found in molecular Tpm*CuI.[48]

The ligands in **1** are quantitatively demetalated and made available for ulterior metal sequestration by a simple acid treatment. Thus, reacting as-synthesized **1** with a mixture of DMF and HCl reduces the Cu content of the MOF from 7.54 Cu per formula unit to essentially zero, as determined by inductively coupled plasma mass spectrometry (ICP-MS). This treatment thus provides the Cu-free MOF $\{[Zr_6O_4(OH)_4X_4(H_2O)_4]_3(TpmC^*)_8\}$ (**2**, X = $HCOO^-$ or HO^-). X-ray photoelectron spectroscopy (XPS) further confirmed the absence of Cu in **2** (Figure S3). Importantly, acid treatment also removes all bound benzoates, as determined by ^{1}H NMR spectroscopy of a digested sample of **2** (Figure S4), while the morphology and crystallinity remain unaltered, as confirmed by SEM and PXRD, respectively (Figures S1, S5). Furthermore, ^{1}H NMR spectroscopy of digested **2** shows no noticeable decomposition of the TpmC* ligand (Figure S4), allowing us to confidently describe **2** as the free-base MOF, with a connectivity and topology identical to **1** (Scheme 2).

Scheme 2. Postsynthetic Demetallation and Remetallation of 1



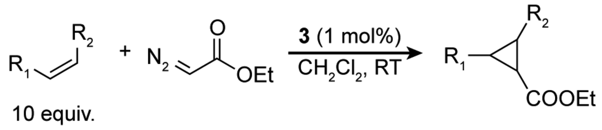
Thermogravimetric analyses (TGA) showed that whereas **1** has no significant mass loss up to 250 °C, **2** exhibits rapid weight loss above 180 °C (Figure S6). Even heating **2** at 120 °C under dynamic vacuum for approximately 15 h already leads to loss of crystallinity, as may be expected for a MOF made with the more flexible free-base ligand. Therefore, **2** was activated under dynamic vacuum at only 110 °C. An N_2 adsorption experiment for activated **2** at 77 K revealed a permanently porous material displaying a Type I isotherm whose BET fit gave an apparent surface area of 1795 ± 15 m^2/g (Figure S7).

With free-base **2** in hand, we sought to demonstrate the utility of this material toward catalysis by remetalating the TpmC* ligands. As proof of principle, we chose to emulate the reactivity of the molecular complex $[(CH_3CN)Cu^ITpm^*]PF_6$, a known homogeneous olefin cyclopropanation catalyst[49] easily prepared by reaction of Tpm* with $[Cu(CH_3CN)_4]PF_6$.[50] Similar to the synthesis of the molecular complex, soaking activated **2** in an acetonitrile solution of $[Cu(CH_3CN)_4]BF_4$ gives rise to crystalline $\{[Zr_6O_4(OH)_4(X)_4(H_2O)_4]_3[Cu(CH_3CN)BF_4]_x(TpmC^*)_8\}$ (**3**, $x \approx 0-4$, X = HO^- or $HCOO^-$) (Scheme 2, Figure S5). Surprisingly, the final metalation level plateaus at approximately 4 Cu equivalents per formula unit, or 50% of the available TpmC* ligands (Figure S8). Although metal ions can attach to Zr clusters,[51−54] a control experiment where NU-1000, a material with similar 8-connected SBUs but no metal-chelating ligands,[55] was treated with the same Cu^I precursor showed minimal incorporation of Cu^I (SI). Thus, in **3**, the majority of copper ions are ligated within the TpmC* scorpionate pocket. Upon activation at 95 °C, **3** exhibits a BET surface area of

1554 ± 5 m^2/g, slightly lower than that of **2**, as expected with the introduction of $[Cu(CH_3CN)]^+$ moieties and BF_4^- within the pores (Figure S7). Additional evidence for the scorpionate coordination environment of Cu within **3** comes from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis upon dosing with carbon monoxide. The strong band at 2110 cm^{-1} (Figure S9) is very close to the reported value of 2113 cm^{-1} for the analogous molecular complex $[Cu(CO)\text{-}Tpm^*]PF_6$.[50] Finally, the major components of the Cu_{2p} peaks in the XPS spectrum of **3** are similar to those found in the XPS spectrum of **1**, with additional minor components ascribed to either small Cu deposits on the Zr clusters or inadvertent partial oxidation of **3** during sample manipulation for XPS analysis (Figure S3).

In line with the activity of molecular $[CuTpm]^+$ complexes,[49,56] **3** is an efficient heterogeneous catalyst for olefin cyclopropanation. Slow addition of a CH_2Cl_2 solution of ethyl diazoacetate (EDAA) to a suspension of **3** and an olefin substrate in CH_2Cl_2 under inert atmosphere produces cyclopropanes in yields comparable to molecular catalysts (Table 1). A control reaction using **2**, the demetalated version of **3**, as catalyst showed no detectable catalytic activity (less than 0.1% yield by ^1H NMR spectroscopy).

Table 1. Olefin Cyclopropanation Reactivity with 3[a]



entry	substrate	yield (%)[b]
1	styrene	95[c]
2[d]	styrene	83[c]
3	1-octene	81[c]
4	cyclohexene	64[e]
5	2,5-dimethyl-2,4-hexadiene	84[c]
6	methyl 2-furoate	32[c]

[a] 40 μM EDAA in 6 mL CH_2Cl_2 was added into a mixture of 4 mg **3**, 2 mL CH_2Cl_2 and 2.4 mmol substrate over 5 h. The mixture was stirred for another 9 h before analysis by ^1H NMR and GC. [b] Combined yield of *trans* and *cis* (*endo* and *exo*) diastereomers, calculated based on amount of EDAA. [c] Determined by ^1H NMR spectroscopy. [d] The reaction was stopped 1 h after the addition of EDAA. [e] Determined by GC-FID.

Furthermore, using Cu(I)-metalated NU-1000 as catalyst, where the only possible Cu^I species are those attached to the Zr SBUs, produced a yield of only 12% after 14 h (SI), compared to 95% for **3** under identical conditions. The heterogeneous nature of **3** was confirmed by a hot filtration experiment (Figure S10), which indicated that no catalytically competent Cu species are leached into the supernatant. In addition, the solid recovered after reaction retained its crystallinity (Figure S5), confirming the structural integrity of **3** under catalytic conditions. Compared with other copper-based solid catalysts for cyclopropanation,[57−60] **3** uniquely combines the merit of high productivity with uniform, well-defined active sites. Importantly, and portending to other potential applications in catalysis, **3** efficiently promotes carbene insertion into C−H bonds in cyclohexane, producing ethyl cyclohexylacetate in 67% yield, surpassing the activity of the analogous homogeneous catalyst, which produces a yield of only 30% under comparable conditions.[49]

In summary, a tricarboxyl-trispyrazolylmethane metalloligand produces a MOF where neutral scorpionate-like moieties can be demetalated and remetalated readily, with preservation of crystallinity and porosity. The utility of this first example of a Tpm-like environment in a MOF was demonstrated through cyclopropanation catalysis enabled by Cu^I species installed postsynthetically into the MOF. Ongoing studies suggest that the same strategy is effective for installing other first row transition metals into this MOF, which will prove especially useful for metal ions that prefer to form homoleptic bis-Tpm complexes under homogeneous conditions. This work therefore represents a blueprint for heterogenizing other Tpm-based homogeneous catalysts that could benefit from site-isolation, and may find further applications in gas separations, where open metal sites are often required for selective adsorption.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b11085.

Experimental details, Figures S1−S11, Tables S1 and S2 (PDF)

Crystallographic data for **1** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported through a Research Agreement with Saudi Aramco, a Founding Member of the MIT Energy Initiative. The high-resolution PXRD was collected at beamline 11-BM of the Advanced Photon Source, Argonne National Laboratory, which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We thank R. McGillicuddy and Prof. J. Mason for assistance with TGA measurements. We also thank Y. Zhou, H. Zhang, and Prof. S. Buchwald for assistance with GC measurements. M. Korzyński is acknowledged for providing NU-1000. We thank Dr. C. Brown for discussions on the Rietveld refinement.

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