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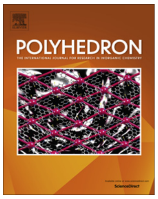

Organocatalysis by site-isolated N-heterocyclic carbenes doped into the UIO-67 framework

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ABSTRACT

Two imidazolium-tagged biphenyldicarboxylates were synthesized and incorporated into the UiO-67 framework. Post synthetic exchange did not prove a useful route to these materials. Alternatively, mixed-linker synthesis of the solid afforded materials loaded with 6–7% imidazolium linker, corresponding to fewer than one active site per cage. Powder X-ray diffraction patterns for the doped metal–organic frameworks (MOFs) revealed that they were isostructural with UiO-67. Once activated, the N-heterocyclic carbene (NHC) containing MOF was found to catalyze the transesterification of vinyl acetate with benzyl alcohol in good yield. The catalyst could be recycled with a modest drop in conversion. This is the first report of a NHC-doped MOF acting as an organocatalyst.

1. Introduction

The discovery of the first stable N-heterocyclic carbenes (NHCs) over 20 years ago led to a wide range of research using them as ligands and catalysts [1–3]. Their facile tunability, both sterically and electronically, has contributed to their successful application to a range of homogenous catalytic reactions [3]. Incorporation of these catalysts into porous frameworks would offer the advantages of heterogeneous catalysts, such as ease of product isolation and catalyst recyclability, while maintaining the tunability that made them successful in homogenous catalysis.

Metal–organic frameworks (MOFs) are synthesized using organic linkers and metal nodes yielding predictable structures with tunable porosity. In fact, they are an ideal platform for constructing heterogenous catalysts as the organic linker can be modified to incorporate a wide range of known catalysts [4,5]. Not surprisingly, NHCs have been incorporated into a number of MOFs using a variety of metal nodes including: Cd, Co, Cu, Zn, and Zr ions [6–14]. Typically, the NHC is incorporated by grafting an imidazolium or benzimidazolium salt into the organic linker. The azolium salts have been incorporated as a central structural component of the linker or as appendages to known organic linkers as demonstrated in a few examples (Fig. 1). These azolium salts were then combined with a variety of metal nodes. Treatment of the azolium containing MOFs with an appropriate base would then form the NHC. The linker syntheses are fairly linear making the creation of a diverse set of NHC precursors with varying steric and electronic properties cumbersome. Hupp and coworkers (**3**), on the other hand, have a more flexible synthesis where the imidazolium component is incorporated near the end of the linker synthesis via a simple S_N2 reaction [13]. This synthesis should allow a diverse set of N-alkyl and N-aryl groups to be incorporated onto the imidazolium ring opposite the diacid linker although, to date, only the synthesis of a linker containing an N-methyl was reported, likely due to the difficulty making MOF solids with linkers that are too bulky.

Bulky NHC precursors are potentially problematic when used as the sole organic linker as they can lead to a dramatic reduction in the solid's porosity. However, it has been demonstrated that large transition-metal containing groups can be incorporated into MOFs by either post-synthetic exchange or by a doping synthesis in which the metal-tagged linker is combined with a traditional linker in the MOF synthesis [7,15–18]. In either of these cases a relatively small percentage of the bulky linkers are incorporated into the solid resulting in overall larger pore sizes making them better candidates for applications such as catalysis. One example demonstrating this possibility involved the incorporation of an Ir-NHC linker into UIO-68 by both post synthetic exchange and doping at 27% and 17% respectively [7].

Although a variety of NHC containing MOFs have been synthesized [10], only a few have actually resulted in useful catalysis.

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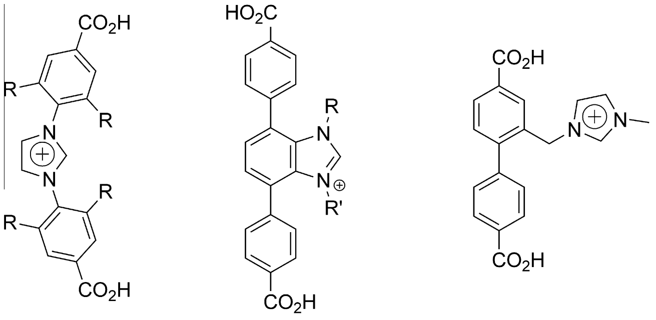

1a R=H
1b R=^{i}Pr

2a R=R'=CH_3
2b R=Bu, R'=$C(CH_3)_2OH$

3

Fig. 1. Representative NHC precursor linkers.

Reactions include the Ir-catalyzed isomerization of allyl alcohols [7], copper-catalyzed hydroboration of CO_2 [6], and Pd-catalyzed Suzuki–Miyaura and Heck reactions. [11] To date no organocatalysis has been reported using NHC-containing MOF's although NHC's are known to catalyze a variety of organocatalytic reactions [1,19].

Herein, we report the synthesis of two new building blocks that include an NHC precursor and investigate two strategies for incorporating these linkers into UIO-67. We demonstrate that using a mixed ligand synthesis results in an ideal doping level of around 8%. This doping level should correspond to approximately one NHC per large cavity and, therefore, afford site-isolated catalysts. Finally, these solids are probed for their ability to catalyze the transesterification of vinyl acetate with benzyl alcohol.

2. Experimental

2.1. Measurement and materials

All reagents were of analytical grade and used as received. UiO-67 was synthesized as previously described [20]. N-arylimidazoles were synthesized using a published procedure [21].

The ^{1}H and ^{13}C NMR spectra were collected at 400 and 100 MHz respectively on an Agilent MercuryPlus 400 AS instrument. Mass spectra were collected by the Mass Spectrometry Facilities in the Department of Chemistry and Biochemistry at UC San Diego. X-ray powder diffraction patterns were collected using Cu Kα (λ = 1.5418 Å) radiation on a Bruker D8 Advance diffractometer equipped with a LynxEye detector.

2.2. Preparation of complexes

2.2.1. Me_2BPDC-ME (**4**)

Methyl-4-bromo-3-methylbenzoate (2.06 g, 9 mmol) and 4-Methoxycarbonyphenylboronic acid (1.62 g, 9 mmol) were added to a round-bottom flask and pumped into a glove box. Dry DMF (40 mL) was added along with $Pd(PPh_3)_4$ (312 mg, 0.27 mmol) and cesium carbonate (4.40 g, 13.5 mmol). The flask was fitted with a septa, placed in an oil bath at 80 °C, and stirred overnight. The flask was removed from the oil bath and allowed to cool to room temperature at which time water (20 mL) and ethyl acetate (20 mL) were added and a white precipitate was removed by vacuum filtration. The filtrate was washed with brine (3 × 50 mL) and dried over sodium sulfate. The volatiles were removed *in vacuo* and the crude residue was purified by silica gel column chromatography using hexanes and ethyl acetate as eluent. The product **4** was isolated as a white solid (1.77 g, 69%). The NMR spectra matched that of the known compound.

2.2.2. Me_2BPDC-MeBr (**5**)

Me_2BPDC-ME (**4**) (1.14 g, 4 mmol), NBS (784 mg, 5.1 mmol), and benzoyl peroxide (96 mg, 0.4 mmol) were combined in a pressure tube. Benzene (24 mL) was added and the reaction was placed in an oil bath at 85 °C overnight. The reaction was allowed to cool and the volatiles were removed *in vacuo*. The crude residue was purified via silica gel column chromatography using hexanes and ethyl acetate as the eluent. Compound **5** was isolated as a white solid (800 mg, 55%). The NMR spectra matched that of the known compound.

2.2.3. H_2BPDC-DiPPI (**6a**)

Compound **5** (268 mg, 0.80 mmol) was added to a pressure tube along with 1-(2,6-diisopropylphenyl)imidazole (200 mg, 0.88 mmol). Freshly distilled THF (2 mL) was added, and the reaction was heated to 70 °C overnight. The precipitate was collected via vacuum filtration and was dried *in vacuo* yielding a fluffy white solid (341 mg, 72%). A portion of this solid (180 mg, 0.30 mmol) was then added to a round bottom flask along with 20 mL 0.1 M LiOH and 4 mL of methanol. The reaction stirred at room temperature overnight. The solution was acidified with 10% HCl and white solids precipitated from the reaction mixture. The solids were collected via vacuum filtration and were dried *in vacuo*. **6a** (154 mg, 98%) was isolated as a white solid. ^{1}H NMR (DMSO-d_6): 1.14 (6H, d, *J* = 6.8 Hz), 1.16 (6H, d, *J* = 6.8 Hz), 2.21 (2H, sep, *J* = 6.8 Hz), 5.75 (2H, s), 7.46 (2H, d, *J* = 7.6 Hz), 7.58 (1H, d, *J* = 7.6 Hz), 7.64 (3H, m), 7.73 (1H, s), 7.97 (1H, s), 8.11 (4H, m), 9.60 (1H, s); ^{13}C NMR (DMSO-d_6): 24.55, 24.67, 29.04, 51.66, 124.88, 125.24, 126.20, 129.60, 129.90, 130.55, 130.62, 131.34, 131.46, 131.84, 131.94, 132.38, 133.33, 139.27, 143.61, 145.11, 145.92, 167.47, 167.81; ESI-MS (M-Cl) 483.

2.2.4. H_2BPDC-DEPI (**6b**)

Compound **5** (153 mg, 0.46 mmol) was added to a pressure tube along with 1-(2,6-diethylphenyl)imidazole (100 mg, 0.50 mmol). Freshly distilled THF (2 mL) was added, and the reaction was heated to 70 °C overnight. The precipitate was collected via vacuum filtration and was dried *in vacuo* yielding a fluffy white solid (200 mg, 78%). A portion of this solid (200 mg, 0.35 mmol) was then added to a round bottom flask along with 25 mL 0.1 M LiOH and 4 mL of methanol. The reaction stirred at room temperature overnight. The solution was acidified with 10% HCl and white solids precipitated from the reaction mixture. The solids were collected via vacuum filtration and were dried *in vacuo*. **6b** (155 mg, 90%) was isolated as a white solid. ^{1}H NMR (DMSO-d_6): 1.07 (6H, t, *J* = 7.2 Hz), 2.23 (4H, m), 5.73 (2H, s), 7.39 (2H, d, *J* = 7.6 Hz), 7.59 (4H, m), 7.87 (2H, d, *J* = 8.4 Hz), 8.04 (1H, s), 8.10 (3H, m), 9.45 (1H, s); ^{13}C NMR (DMSO-d_6): 15.67, 24.34, 51.80, 124.61, 125.75, 127.92, 129.82, 130.46, 130.61, 130.79, 131.85, 132.04, 132.88, 133.10, 139.08, 140.54, 141.28, 143.57, 145.07, 167.68, 167.98; ESI-MS (M-Cl): 455.

2.3. Preparation of solids

2.3.1. $[Zr6(\mu_3\text{-}O)4(\mu_3\text{-}OH)_4(BPDC)_{5.4}(6a)_{0.6}]$ (**MOF-1**)

$ZrCl_4$ (120 mg, 0.514 mmol) and benzoic acid (1.88 g, 30 equiv.) were added to a 120 mL jar containing 20 mL of anhydrous DMF. The solution was sonicated until all solids dissolved. The linkers bpdc (62 mg, 0.26 mmol) and **6a** (133 mg, 0.26 mmol) were added and the solution sonicated for 5 min. The solution was heated to 120 °C over 4 h, kept at that temperature for 24 h, and cooled to room temperature over 4 h. The solids were washed with DMF (3 × 10 mL) followed by EtOH (3 × 10 mL) and THF (5 × 10 mL).