Single-Site Cobalt-Catalyst Ligated with Pyridylimine-Functionalized Metal–Organic Frameworks for Arene and Benzylic Borylation

Rajashree Newar, Wahida Begum, Neha Antil, Sakshi Shukla, Ajay Kumar, Naved Akhtar, Balendra, and Kuntal Manna*

ABSTRACT: We report a highly active single-site heterogeneous cobalt-catalyst based on a porous and robust pyridylimine-functionalized metal–organic frameworks (pyrim-MOF) for chemoselective borylation of arene and benzylic C–H bonds. The pyrim-MOF having UiO-68 topology, constructed from zirconium-cluster secondary building units and pyridylimine-functionalized dicarboxylate bridging linkers, was metalated with CoCl₂ followed by treatment of NaEt₃BH to give the cobalt-functionalized MOF-catalyst (pyrim-MOF-Co). Pyrim-MOF-Co has a broad substrate scope, allowing the C–H borylation of halogen-, alkoxy-, alkyl-substituted arenes as well as heterocyclic ring systems using B₂pin₂ or HBpin (pin = pinacolate) as the borylating agent to afford the corresponding arene- or alkyl-borate esters in good yields. Pyrim-MOF-Co gave a turnover number (TON) of up to 2500 and could be recycled and reused at least 9 times. Pyrim-MOF-Co was also significantly more robust and active than its homogeneous control, highlighting the beneficial effect of active-site isolation within the MOF framework that prevents intermolecular decomposition. The experimental and computational studies suggested (pyrim•−CoI(THF)) as the active catalytic species within the MOF, which undergoes a mechanistic pathway of oxidative addition, turnover limiting σ-bond metathesis, followed by reductive elimination to afford the boronate ester.

1. INTRODUCTION

Organoboranes are versatile synthetic intermediates for carbon–carbon and carbon–heteroatom bond formations. Among many methods, transition-metal-catalyzed borylation of C–H bonds is the most efficient and atom economic for direct formation of organoboron compounds. Although significant progress has been made using precious-metal-catalyzed C–H borylation, the development of catalysts with cheap and nontoxic earth-abundant metals is of greater interest. Recently, iron-, cobalt-, and nickel-based catalysts have been developed for C–H borylation. Transition-metal catalysts generally favor C(sp³)–H sites due to the kinetic preference of oxidative addition. Therefore, chemoselective C(sp³)–H borylation in the presence of C(sp²)–H bonds is far less common. The regioselectivity of the nondirected borylation of C(sp³)–H bonds strongly favors at primary C–H bonds, making the functionalization of secondary C–H bonds challenging. Recently, cobalt- and nickel-catalyzed borylation of secondary benzylic C–H bonds has been reported.

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However, significant challenges remain for its practical applicability such as chemoselectivity, low catalyst loading, recyclability of the catalysts, and ease of purification of the products. In addition, the lack of a report of chemoselective borylation of secondary or tertiary C(sp$_3$)$-\text{H}$ bonds in the presence of C(sp$_2$)$-\text{H}$ and primary C(sp$_3$)$-\text{H}$ bonds requires further catalyst development for these challenging transformations.

We are interested to develop robust and recyclable first-row transition-metal catalysts having open metal sites for C$-\text{H}$ borylation of sterically congested C$-\text{H}$ bonds using bidentate Schiff base ligands due to their ease of synthesis and redox noninnocent properties. Schiff bases, synthesized from amino and carbonyl compounds, are an important class of chelating ligands in coordination chemistry, and their base-metal complexes have been widely used as catalysts in many important organic transformations such as epoxidation, hydrogenation, hydroelementation, and aldol reactions.9 Bidentate redox-active Schiff base ligands such as pyridylimine and salicylaldimine can influence the breaking and making of chemical bonds in a catalytic process by tuning the electronic properties of the metal and also allow multielectron transformations. However, their metal complexes readily undergo decomposition due to the weak ligand–metal bonding as well as deleterious intermolecular interaction.10 Robust base metal catalysts with such bidentate Schiff base ligands have been afforded via active-site isolation in porous solid supports without relying on bulky substituents.11 Unlike traditional supported catalysts, metal–organic framework-based single-site solid catalysts combine both the advantages offered by heterogeneous catalysts such as facile catalyst separation and recovery, high stability, less leaching, as well as those offered by their homogeneous counterparts such as homogeneity of active sites, reproducibility, and selectivity.12 Herein, we report a robust and recyclable single-site cobalt-catalyst ligated with redox noninnocent pyridylimine-functionalized metal–organic frameworks for arene and benzylic C$-\text{H}$ bonds. The MOF-catalyst is also enabled to catalyze unprecedented nondirected and chemoselective borylation of the secondary or tertiary C(sp$_3$)$-\text{H}$ bond in the presence of C(sp$_2$)$-\text{H}$ and primary C(sp$_3$)$-\text{H}$ bonds.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Pyridylimine-Functionalized MOF and Its Postsynthetic Metalation with Cobalt. The MOF-cobalt-catalyst was prepared by the metalation of pyridylimine-functionalized zirconium-MOF (pyrim-MOF) with CoCl$_2$ followed by treatment of NaEt$_3$BH. Pyrim-MOF was constructed from Zr-cluster nodes and pyridylimine-functionalized dicarboxylate bridging linkers (pyrim-TPDC) to afford a UiO-type framework of Zr$_6$O$_4$(OH)$_4$(pyrim-TPDC)$_6$.13 The dicarboxylic acid linker (H$_2$pyrim-TPDC) was synthesized by the condensation between amino-triphenyldicarboxylic acid (NH$_2$-TPDC) and 2-pyridinecarboxaldehyde in 56% yield. The solvothermal reaction between ZrCl$_4$ and H$_2$pyrim-TPDC in the presence of benzoic acid in DMF at 80 ºC afforded pyrim-MOF as an off-white solid (Figure 1a). Alternatively, pyrim-MOF was also prepared by the treatment of 2-pyridinecarboxaldehyde and amino-functionalized UiO-68-MOF in DMF.14
similarity of its PXRD pattern with that of UiO-68-MOF (Figure 1b). The presence of the pyridylimine moiety in the MOF was confirmed by 'H NMR of the digested pyrim-MOF, which made evident the presence of the ~100% intact pyridylimine moiety within the MOF (Figure S1, SI). The nitrogen sorption experiment indicated that pyrim-MOF is highly porous with a BET surface area of 2042 m²/g and pore size of 2.5 nm.

The metalation of pyrim-MOF with anhydrous CoCl₂ in THF at room temperature gave Co-functionalized pyrim-MOF (pyrim-MOF-CoCl₂) as a green solid. The DFT calculation suggested a five-coordinate cobalt(II) species of (pyrim)CoCl₂(THF) within the MOF in the ground state (Figures S17 and S22, SI). The liberation of 1 equiv of THF with respect to Co was also detected in the 'H NMR spectrum upon heating a mixture of (pyrim)CoCl₂(THF) and D₂O in CDCl₃ (Figure S8, SI). The crystallinity of the MOF was maintained after metalation as made evident by the similarity of the PXRD pattern with that of pyrim-MOF (Figure 1b). Inductively coupled plasma optical emission spectroscopy (ICP-OES) of the digested metalated MOF showed the Co-loading of 41% with respect to the pyridylimine moiety. The particles of pyrim-MOF-CoCl₂ are of an octahedral shape and have a diameter of 0.8−1.0 μm as shown by the TEM image (Figure 1c). TEM-EDX analysis of pyrim-MOF-CoCl₂ exhibited the presence of Zr, Co, and Cl atoms within MOF (Figure S5b, SI). Pyrim-MOF-CoCl₂ has a BET surface area of 1450 m²/g and pore size of 2.1 nm. The decrease in the surface area and pore size of pyrim-MOF after metalation is attributed to the partial filling of the void space of MOF with the cobalt chloride moiety (Figure 1d).

2.2. Pyrim-MOF-Co-Catalyzed Borylation of Arene C−H Bonds. Upon the treatment of NaEt₃BH in THF, pyrim-MOF-Co material became an active catalyst for the dehydrogenative borylation of C−H bonds of various activated as well as unactivated arenes and heterocyclic compounds using B₂pin₂ or HBpin (pin = pinacolate) as the borylating agent (Table 1). In the optimized conditions, the catalytic borylation reactions were performed at 110 °C either in neat arene substrates or using heptane as a solvent. With 0.5 mol % of Co-loading, pyrim-MOF-Co gave complete conversions in 2 days and afforded arylboronate esters from toluene and xylenes in 73−94% isolated yields (Table 1, entries 2−6). Importantly, a turnover number (TON) of 2500 was obtained for the borylation of o-xylene. Notably, pure boronate ester products were obtained by simply removing the catalyst via centrifugation followed by removal of the volatiles. Pyrim-MOF-Co-catalyzed borylation reactions have a broad substrate scope with good regioselectivity allowing the C−H borylation of halogen- and alkoxy-substituted arenes (Table 1, entries 8−13) as well as heterocyclic ring systems (Table 1, entries 14−18). However, pyrim-MOF-Co displayed a higher TOF for electron-rich arenes having electron-donating substituents compared to that for arenes bearing electron-withdrawing groups. The borylation of heterocycles such as indole, 2,3-benzofuran, 2-methylindole, and quinoline proceeded smoothly under the reaction conditions to give the corresponding monoborylated products in good yields (Table 1, entries 15−18). The C−H borylation occurred at the least sterically hindered position of the unactivated arenes (Table 1, entries 2−14) and at the 2-position of heteroarenes such as indole and benzofuran (Table 1, entries 15 and 16). In the case of borylation of N,N-dimethylaniline, N⁴,N⁴,N⁴⁴ tetramethyl-[1,1'-biphenyl]-4,4'-diamine was formed as the major product presumably due to pyrim-MOF-Co-catalyzed tandem C−H borylation to give N,N-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline and its subsequent homocoupling (Table 1, entry 20).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Arene</th>
<th>Product</th>
<th>%Conversion (yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Ar-H</td>
<td>Bpin</td>
<td>71 (57)</td>
</tr>
<tr>
<td>2b</td>
<td>Ar-H</td>
<td>Bpin</td>
<td>100 (90; m: n 3:7)</td>
</tr>
<tr>
<td>3b</td>
<td>Ar-H</td>
<td>Bpin</td>
<td>100 (73)</td>
</tr>
<tr>
<td>4b</td>
<td>Ar-H</td>
<td>Bpin</td>
<td>100 (93)</td>
</tr>
<tr>
<td>5b</td>
<td>Ar-H</td>
<td>Bpin</td>
<td>100 (95)</td>
</tr>
<tr>
<td>6b</td>
<td>Ar-H</td>
<td>Bpin</td>
<td>100 (94)</td>
</tr>
<tr>
<td>7b</td>
<td>Ar-H</td>
<td>Bpin</td>
<td>100 (100; m:n 9:1)</td>
</tr>
<tr>
<td>8</td>
<td>Cl</td>
<td>Bpin</td>
<td>64 (40)</td>
</tr>
<tr>
<td>9</td>
<td>MeO</td>
<td>Bpin</td>
<td>35 (33)</td>
</tr>
<tr>
<td>10</td>
<td>MeO</td>
<td>Bpin</td>
<td>100 (100; m:n 2.5:7.5)</td>
</tr>
<tr>
<td>11</td>
<td>MeO</td>
<td>Bpin</td>
<td>100 (94)</td>
</tr>
<tr>
<td>12</td>
<td>MeO</td>
<td>Bpin</td>
<td>100 (82; m:n 8:1)</td>
</tr>
<tr>
<td>13</td>
<td>MeO</td>
<td>Bpin</td>
<td>76 (52)</td>
</tr>
<tr>
<td>14</td>
<td>MeO</td>
<td>Bpin</td>
<td>73 (39)</td>
</tr>
<tr>
<td>15</td>
<td>N</td>
<td>Bpin</td>
<td>100 (62)</td>
</tr>
<tr>
<td>16</td>
<td>N</td>
<td>Bpin</td>
<td>100 (72)</td>
</tr>
<tr>
<td>17</td>
<td>N</td>
<td>Bpin</td>
<td>72 (45)</td>
</tr>
<tr>
<td>18</td>
<td>N</td>
<td>Bpin</td>
<td>100 (56)</td>
</tr>
<tr>
<td>19</td>
<td>MeO</td>
<td>Bpin</td>
<td>20 (20)</td>
</tr>
<tr>
<td>20</td>
<td>MeO</td>
<td>Bpin</td>
<td>100 (67)</td>
</tr>
</tbody>
</table>

*Reaction conditions: 0.5 mol % Co, B₂pin₂ (0.134 mmol), arene (0.28 mmol), 2.0 mL of heptane, 110 °C, 48 h. †Isolated yield in the parentheses, regioselectivity was determined by GC−MS. ‡Reaction was performed at 85 °C. §Neat arene was used. ‖1.0 mol % Co, 20 h. ‡GC yield. ‡‡HBpin was used as the borylating reagent. ‡‡‡72 h.
2.3. Effect of Pore Sizes and Comparison Studies with Homogeneous Control. The effect of pore sizes of MOF in borylation reactions was further studied by comparing the catalytic activity of pyrim-MOF-Co with pyrim-Uio-66-Co MOF having similar UiO-topology but smaller pore sizes (Figure 2a). Pyrim-Uio-66-Co MOF having UiO-66 topology was synthesized via postsynthetic modification of UiO-66-NH₂-MOF with pyridinecarboxaldehyde, followed by metatation with CoCl₂ to afford a bluish-green crystalline solid. Under identical reaction conditions, pyrim-MOF-Co was almost 5 times more active than pyrim-Uio-66-Co in the C–H borylation of toluene, indicating that the catalysis facilitated by pyrim-Co sites was both on the surface and inside the pores (Figure S15, SI). Interestingly, pyrim-MOF-Co was also significantly more active than its homogeneous control ([Ph(pyrim)(PhCO₂Me)₂]Co) (Figure S12, SI). The homogeneous control was prepared by the condensation reaction between dimethyl-2′-aminopyrimidine and Ph(pyrim)-(PhCO₂Me)₂ ligand due to the lack of steric protection around the Co-center for shutting down the intermolecular decomposition pathways.

2.4. Heterogeneity Test. We have performed several experiments to test the heterogeneous nature of the pyrim-MOF-Co-catalyst. The rate of borylation was unchanged in the presence of metallic mercury, ruling out the role of any in situ generated Co-particles or leached Co-particles during the reactions (Figure S10, SI). In addition, no further conversion was detected after the removal of the MOF-catalyst during the course of the borylation reaction (Figure S9, SI). Furthermore, at 0.5 mol % Co-loading, pyrim-MOF-Co was recovered and reused at least 9 times without significant loss of catalytic activity (Figure 2b). The leaching of Co and Zr in the supernatant for the first run was only 0.05% and 1.9%, respectively, and that for the fourth run was 0.1% and 3.01%, respectively (Table S2, SI). The PXRD pattern of pyrim-MOF-Co after the borylation reaction remained unchanged, indicating the robustness of the MOF frameworks under the catalytic conditions (Figure 1b).

2.5. Pyrim-MOF-Co-Catalyzed Borylation of Benzylic C–H Bonds. Pyrim-MOF-Co also catalyzes regioselective borylation of secondary or tertiary C(sp³)−H bonds at the benzylic position over arene groups. Heating the mixture of pyrim-MOF-Co (0.5 mol % Co) and B₂pin₂ in neat alkylarenes at 110 °C gave the corresponding benzylic boronate esters in 100% conversion with good selectivity. Due to significant loss of yields of benzylic boronates during isolation (Table S1, SI), the crude products were directly oxidized, and the final products were isolated as the corresponding benzyl alcohols in high yields. The borylation of mesitylene occurred selectively at the benzylic position presumably due to the steric factor (Table 2, entry 1). 2,4,6-Trimethylbenzyl alcohol was afforded after oxidation of the corresponding boronate ester in 82% yield, and no aryl boronate ester was detected. In the case of borylation of ethylbenzene, 1-ethyl-4-methoxybenzene, 1-ethyl-4-chlorobenzene, and cumene, good selectivities of borylation were also observed in favor of benzylic C–H bonds over aryl C–H bonds, affording high yields of the corresponding benzyl alcohols (Table 2, entries 2–5). Interestingly, in the case of p-cymene, the regioselectivity of borylation strongly favored at tertiary C–H bonds over arene C(sp³)−H or primary C(sp³)−H bonds, and 2-(p-tolyl)propan-2-ol was obtained in 89% yield (Table 2, entry 6).

2.6. Stabilization of Catalytically Active (Pyrim⁺)-Co(THF) Species within MOF. We then investigated the mechanism of the pyrim-MOF-Co-catalyzed C–H borylation of arenes by the characterization of the active cobalt species, kinetics, and computational studies. The reaction between pyrim-MOF-CoCl₂(THF) and NaEt₃BH in THF resulted in a black MOF-material and 1 equiv of H₂ with respect to cobalt. In a related bis(imino)pyridine (6PDI) system, the treatment of 2 equiv of NaEt₃BH with (6PDI)CoCl₂ produced the Co-
Table 2. Pyrim-MOF-Co-Catalyzed Benzylic C–H Borylation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Arene</th>
<th>Product</th>
<th>% Isolated yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ArH</td>
<td>ArOBpin</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>ArH</td>
<td>ArOBpin</td>
<td>85 (96:4)</td>
</tr>
<tr>
<td>3</td>
<td>MeO-ArH</td>
<td>MeO-ArOBpin</td>
<td>73 (85:15)</td>
</tr>
<tr>
<td>4c</td>
<td>Cl-ArH</td>
<td>Cl-ArOBpin</td>
<td>81 (90:10)</td>
</tr>
<tr>
<td>5</td>
<td>ArH</td>
<td>ArOBpin</td>
<td>65 (89:11)</td>
</tr>
<tr>
<td>6</td>
<td>ArH</td>
<td>ArOBpin</td>
<td>89 (96:4)</td>
</tr>
</tbody>
</table>

*Reaction conditions: (i) borylation; 0.5 mol % Co, B2pin2 (0.134 mmol), neat arene, 110 °C, 2 days, 100% conversion; (ii) oxidation; 2 M NaOH, 30% H2O2, room temperature, 2 h. The ratio of benzyl- and aryl-boronate ester in the crude product obtained after borylation reaction as determined by GC-MS is mentioned in the parentheses. Heptane was used as the solvent.

2.7. Investigation of the Mechanism of MOF-Co-Catalyzed C–H Borylation. The reaction pathway was further characterized by kinetic studies. The empirical rate law was determined by the investigations of instantaneous rate dependence on product concentration for the first 3–15% conversion of o-xylene. The concentration of the boronate ester was monitored by GC-MS throughout the catalytic conversion. The average initial substrate conversion rates increase linearly with initial concentrations of o-xylene and cobalt, indicating a first-order rate dependence on both substrate and catalyst concentrations (Figure 3c). However, the initial rate of the C–H borylation of o-xylene showed a zeroth-order dependence on B2pin2 concentration (Figure 3d). Besides, a significant enhancement of reaction rate was observed upon the addition of 10–30 equiv of THF with respect to Co, indicating the potential coordination of THF to the catalytic intermediates in the favorable pathway (Table S3, SI).

Based on the spectroscopic and kinetic studies, two plausible pathways are proposed (Figure S16, SI). According to A-pathway, the oxidative addition of B2pin2 to cobalt of (pyrim)Co(THF) would give (pyrim)Co(Bpin)2[INT-1(A)], which undergoes turnover limiting σ-bond metathesis with the arene C–H bond to generate (pyrim)Co(H)(Bpin)[INT-2(A)] and arylboronate. Subsequent coordination of THF to the cobalt of INT-2(A) followed by reductive elimination would lead to the regeneration of the active state of the Co-catalyst and completes the catalytic cycle. Alternatively, the rate-limiting oxidative addition of the arene C–H bond followed by σ-bond metathesis with B2pin2 would give INT-3(B), which undergoes reductive elimination to regenerate the Co-catalyst and arylboronate (B-pathway, Figure S16, SI).

2.8. Computational Study and Catalytic Cycle. To further probe the mechanism of the borylation reaction, we performed DFT calculations, and the calculated energy profile of both pathways using the DFT method (B3LYP) and a basic set of 6-311G (d,p) on Gaussian 09 software suit as shown in Figure 4. In A-pathway, the catalytic cycle commences with (pyrim)Co(THF) and B2pin2, which undergoes oxidative addition via TS-1(A), requiring free energy of 6.5 kcal/mol. This step is exergonic and gives INT-1(A). Then, the σ-bond metathesis of Co–Bpin and arene C–H bond transforms INT-1(A) to INT-2(A) via TS-2(A), requiring an activation free energy of 20 kcal/mol. Subsequently, the coordination of THF leads to the formation of INT-3(A), which is 5.3 kcal/mol lower in energy than INT-2(A). Then, INT-3(A) undergoes reductive elimination to give (pyrim)Co(THF) and HBpin via...
Figure 3. (a) XANES spectra of (pyrim)CoCl₂(THF) and pyrim-MOF-Co(THF). (b) Atomic charge distribution of (pyrim)Co(THF) as calculated by NBO population analysis; atoms bearing positive and negative charges are denoted by green and red, respectively. (c) Kinetic plots of initial rates \( \frac{d[\text{product}]}{dt} \) for arene C–H borylation of o-xylene versus initial concentrations of cobalt and o-xylene for the first 12 h, showing the first-order dependence on both components. (d) Plot of initial rate \( \frac{d[\text{product}]}{dt} \) versus \([\text{B}_2\text{pin}_2]\)_{initial} for first 12 h (<10% conversion) in neat o-xylene showing the independence of initial rates on the \( [\text{B}_2\text{pin}_2] \) concentrations. (e) Proposed catalytic cycle based on kinetic and computational studies.
TS-3(A), and this step is endergonic by 13.3 kcal/mol (Figure 4). In the case of B-pathway, the oxidative addition of the arene C−H bond is disfavored by 6 kcal/mol compared to that of A-pathway. Furthermore, the subsequent σ-bond metathesis of the Co−H and B−B bond is associated with a step barrier of 29.5 kcal/mol, whereas the reductive elimination requires 10.5 kcal/mol. Therefore, the DFT-calculated energy profile of pyrim-MOF-Co(THF)-catalyzed C−H borylation reveals A-pathway as energetically favorable as compared to the B-pathway, and TS-2(A) is the turnover limiting step (Figure 3e). The DFT calculation identifies TS-2(A) as a four-member cyclic transition state involving σ-bond metathesis of Co−Bpin and the arene C−H bond (Figure S21). The first-order dependence on the concentrations of both cobalt and arene in the kinetic studies further supports the involvement of the arene C−H bond in the turnover limiting step. The proposed catalytic cycle (A-pathway) is thus in good agreement with our theoretical and kinetic studies (Figure 3e).

3. CONCLUSIONS

In conclusion, we have developed a highly active, robust, and recyclable cobalt-catalyst for arene and benzylic C−H borylation. This heterogeneous single-site cobalt-catalyst was prepared by metalation of easily synthesized pyridylimine-functionalized zirconium MOF with cobalt precursor. The MOF-Co-catalyst was significantly more active than its homogeneous control, highlighting the beneficial effect of active-site isolation within the MOF framework that prevents intermolecular decomposition. The experimental and computational studies showed that MOF stabilize highly reactive and solution-inaccessible (pyrim−)Co(THF) as the active catalytic species via site isolation. The proposed catalytic cycle of the borylation reaction has also been evaluated based on spectroscopic, kinetic, and computational studies. This work thus highlights the importance of MOF-ligated base-metal catalysis for the sustainable synthesis of fine chemicals.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00747.

- Synthesis and characterization of pyridylimine linkers, MOF, metalated MOF, and molecular analogue; procedures for catalytic reactions; and details for kinetics, GC analysis, and DFT calculations (PDF)

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**Notes**

The authors declare no competing financial interest.
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