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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.6b00849 • Publication Date (Web): 11 Feb 2016

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Metal-Organic Frameworks Stabilize Solution-Inaccessible Cobalt Catalysts for Highly Efficient Broad-Scope Organic Transformations

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ABSTRACT: New and active earth-abundant metal catalysts are critically needed to replace precious metal-based catalysts for sustainable production of commodity and fine chemicals. We report here the design of highly robust, active, and reusable cobalt-bipyridine and cobalt-phenanthroline based metal-organic framework (MOF) catalysts for alkene hydrogenation and hydroboration, aldehyde/ketone hydroboration, and arene C-H borylation. In alkene hydrogenation, the MOF catalysts tolerated a variety of functional groups and displayed unprecedentedly high turnover numbers of $\sim 2.5 \times 10^6$ and turnover frequencies of $\sim 1.1 \times 10^5 \text{ h}^{-1}$. Structural, computational, and spectroscopic studies show that site isolation of the highly reactive (bpy)Co(THF)₂ species in the MOFs prevents intermolecular deactivation and stabilizes solution-inaccessible catalysts for broad-scope organic transformations. Computational, spectroscopic, and kinetic evidences further support a hitherto unknown (bpy)Co(THF)₂ ground state that coordinates to alkene and dihydrogen, then undergoing σ -complex assisted metathesis to form (bpy)Co(alkyl)(H). Reductive elimination of alkane followed by alkene binding completes the catalytic cycle. MOFs thus provide a novel platform for discovering new base-metal molecular catalysts and exhibit enormous potential in sustainable chemical catalysis.

Introduction

The discovery of new earth-abundant base-metal catalysts is becoming increasingly critical for sustainable and economical production of commodity and fine chemicals owing to the scarcity of precious metals such as Rh, Pd, and Pt. The most common and successful strategy for developing homogeneous base-metal catalysts requires sterically demanding chelating ligands to protect highly active metal centers from intermolecular deactivation into oligomeric species or metal/metal oxide nanoparticles.¹ Such a steric protection strategy can indeed enhance the stability of base-metal catalysts, but often at the expense of their catalytic activities.² Overly elaborate designs of sterically hindered chelating ligands also make them prohibitively expensive, further reducing the practicality of many elegantly designed homogeneous base-metal catalysts.³ Alternative strategies are needed for the discovery and development of earth-abundant metal catalysts for sustainable chemical synthesis.

Constructed from metal cluster secondary building units (SBUs) and organic linkers, metal-organic frameworks (MOFs) have emerged as a class of tunable molecular materials with great potential in many applications, including gas storage,⁴ separations,⁵ sensing,⁶ drug delivery,⁷ and biomedical imaging.^{7b} In particular, MOFs have served as a powerful platform for developing recyclable and reusable single-site solid catalysts.⁸ In select examples, MOF catalysts even showed enhanced activities over their homogeneous counterparts.⁹ In this paper, we report the first structural and spectroscopic evidence for the generation of solution-inaccessible base-metal catalysts, achieved by eliminating intermolecular decomposition pathways as a result of active site isolation within a MOF (Figure 1). We show that MOFs can stabilize base metal homogeneous catalytic species which cannot be prepared in solution, leading to highly active and reusable single-site solid catalysts for a wide range of organic transformations. Our work thus reveals a new MOF-based strategy to discover nov-

el base-metal based molecular catalysts, and has significant implications in enabling sustainable production of commodity and fine chemicals.

Results and Discussion

MOF Synthesis and Postsynthetic Metalation with CoCl₂. 2,2'-bipyridyl (bpy) and derivatives are widely used as chelating ligands with strong binding affinity to base metals, but they do not offer adequate steric protection around the metal centers to afford efficient base-metal catalysts. Inspired by recent reports on precious metal-bpy complex based MOF catalysts,^{9a, 10} we surmised that the orthogonal bpy-type ligands composing the MOF struts are site-isolated and can stabilize base-metal complexes for catalytic organic transformations. Two bpy-containing UiO MOFs, bpy-MOF and bpyv-MOF (bpyv = 5,5'-bis(carboxyethenyl)-2,2'-bipyridyl), and the mixed ligand MOF, mPT-MOF (PT = 3,8-bis(4-carboxyphenyl)phenanthryl), were prepared as described previously.^{9a, 10e, 11} The new mixed ligand MOF, mBPP-MOF, was synthesized by heating a mixture of ZrCl₄, 4,4'-(2,2'-bipyridyl-5,5'-diyl)dibenzoic acid (H₂BPP, functionalized ligand), and 4,4'-bis(carboxyphenyl)-2-nitro-1,1'-biphenyl (H₂TPHN, spectator ligand) in the presence of trifluoroacetic acid in dimethylformamide (DMF) at 100 °C. The structure of mBPP-MOF was established by comparison of its PXRD to that of mPT-MOF and TPHN-MOF.^{10e} For bpyv-MOF, appearance of several weak extra peaks suggests structure distortion in the powder samples, which has been observed in other nanoscale MOFs.¹² The molar ratios of functionalized and spectator bridging linkers in mPT-MOF and mBPP-MOF were determined to be approximately 1:2 by ¹H NMR spectra of the MOF digests in a mixture of K₃PO₄/D₂O/DMSO-*d*₆, consistent with the ratios in the synthesis (Figure S1, SI).^{10e} The TPHN spectator ligand was introduced into mPT-MOF and mBPP-MOF to increase their open channel sizes to facilitate substrate and product diffusion.

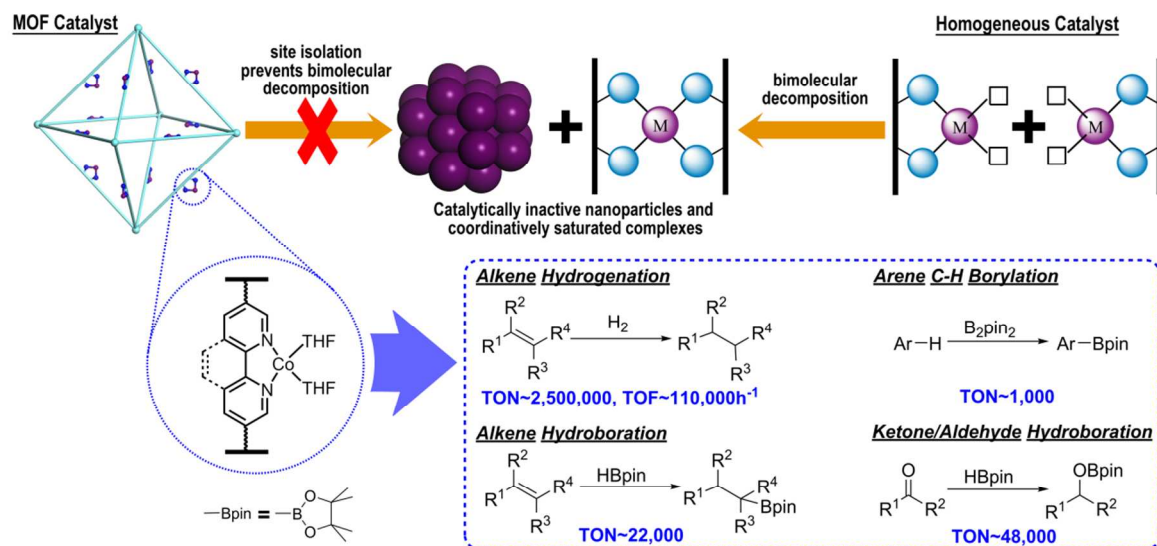


Figure 1. Schematic showing the beneficial effects of active site-isolation in MOFs: while homogeneous catalysts undergo intermolecular deactivation via ligand disproportionation/decomposition reactions, such pathways are completely shut down in MOFs due to active site isolation. MOFs thus provide a new platform for discovering novel base-metal molecular catalysts.

Post-synthetic metalation of the MOFs with 8 equiv. of CoCl_2 afforded MOF- CoCl_2 materials as blue-green solids (Figures 2a-c). PXRD patterns showed that all MOF- CoCl_2 materials remained crystalline (Figures 2d, S3, S6a, and S12, SI), whereas inductively coupled plasma-mass spectrometry (ICP-MS) analyses of the digested metalated MOF samples revealed Co loading of 86%, 92%, 63% and 36% relative to the functionalized bridging ligands for bpy-MOF- CoCl_2 , bpyv-MOF- CoCl_2 , mBPP-MOF- CoCl_2 , and mPT-MOF- CoCl_2 , respectively. Nitrogen sorption experiments gave BET surface areas of 764, 768, and 1192 m^2/g for bpy-MOF- CoCl_2 , mBPP-MOF- CoCl_2 and mPT-MOF- CoCl_2 , which are smaller than those of the unmetalated MOFs. However, bpyv-MOF and bpyv-MOF-Co exhibited unexpectedly low BET surface areas of 373 and 294 m^2/g , respectively, which is likely caused by framework distortion upon solvent removal, due to the highly bent nature of the bpyv ligand. Upon metalation, the pore sizes also decreased slightly. The reductions in surface areas and pore sizes of the metalated MOFs are consistent with the presence of Co centers and associated ligands in the MOF cavities.

Although earlier reports suggested that the metalated bpy-MOF can adopt ordered structure in a lower-symmetry space group,^{10d} this was not observed in our cases which can be attributed to our mild metalation conditions. Intrinsic disorder and incomplete metalation prevent us from characterizing the MOF- CoCl_2 materials by single crystal X-ray diffraction. Instead, we used X-ray absorption spectroscopy (XAS) to investigate the Co coordination environments. Fitting the extended X-ray absorption fine structure (EXAFS) regions of bpy-MOF- CoCl_2 , bpyv-MOF- CoCl_2 , mBPP-MOF- CoCl_2 , and mPT-MOF- CoCl_2 , X-ray absorption spectra confirmed that the Co centers in the MOFs adopt tetrahedral coordination environments like the model complex $\text{Co}^{(\text{Me}_2\text{bpy})}\text{Cl}_2$ (Figures 2e, S29-32, SI, $\text{Me}_2\text{bpy} = 6,6'$ -dimethyl-2,2'-bipyridyl).¹³

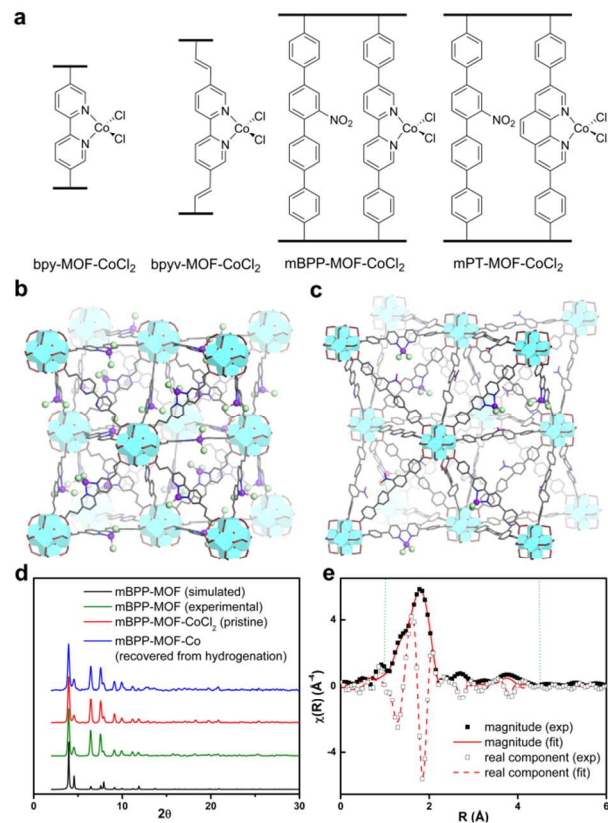


Figure 2. a) Schematic structures of the MOF- CoCl_2 precatalysts; b, c) Idealized structures of bpyv-MOF- CoCl_2 (b) and mBPP-MOF- CoCl_2 (c); d) The Similarity of the PXRD pattern simulated from the CIF file of TPHN-MOF (black) and the PXRD patterns of mBPP-MOF (green), mBPP-MOF- CoCl_2 (red), and mBPP-MOF-Co recovered from hydrogenation of 1-octene (blue) indicates the retention of mBPP-MOF crystallinity after post-synthetic metalation and catalysis; e) EXAFS spectra and the fits in R-space at the Co K-edge of bpyv-MOF- CoCl_2 showing the magnitude (solid squares, solid line) and real component (hollow squares, dashed line).

squares, dash line) of the Fourier transform. The fitting range is 1 – 4.5 Å in R space (within the green dot lines).

MOF-Co Materials for Catalytic Alkene Hydrogenation with Unprecedentedly High Activity. Upon treatment with NaBEt₃H, MOF-Co materials became highly active catalysts for the hydrogenation of a range of olefins at room temperature (Fig 3a and Table 1).¹⁴ Mono-substituted alkenes such as 1-octene, styrene, and 4-allylanisole were readily hydrogenated within 24 h in quantitative yields using 0.1-0.01 mol % catalysts (entries 1-4 and 8-14, Table 1). At 0.1 mol % Co-loading, bpy-MOF-Co and bpyv-MOF-Co catalyzed hydrogenation of 1,1-, *cis*-1,2-, and *trans*-1,2-disubstituted alkenes in 88-100% yields (entries 15-25, Table 1). Additionally, dialkenes such as 1,7-octadiene, and tri-substituted alkenes such as α -terpinene, *trans*- α -methylstilbene and 1-methyl-1-cyclohexene were completely hydrogenated by mBPP-MOF-Co in excellent yields (entries 29, 31-34, Table 1; Table S10, SI). In general, the order of catalytic activity of MOF-catalysts in hydrogenation was mBPP-MOF-Co > mPT-MOF-Co > bpyv-MOF-Co > bpy-MOF-Co (Table S9, SI), due to the decreasing channel sizes in the series. TONs of 2.0×10^5 and 2.1×10^5 were observed for bpyv-MOF-Co and mPT-MOF-Co with 1-octene as the substrate (entries 5-6, Table 1), which are higher than those of previously reported Fe- and Co-functionalized salicylaldehyde-based MOF catalysts.^{9b} Remarkably, mBPP-MOF-Co displayed a TON of 2.5×10^6 in hydrogenation of 1-octene, which is the highest TON that has ever been reported for Co-catalyzed olefin hydrogenation (entry 7, Table 1). In this case, a turnover frequency of $1.1 \times 10^3 \text{ h}^{-1}$ per cobalt center was achieved in the first 9 hours, and after simple filtration, the *n*-octane product contained only 0.26 ppb Co and 1.34 ppb Zr. Moreover, mBPP-MOF-Co catalyzed hydrogenation of tri-substituted alkenes also proceeded efficiently under milder reaction conditions of 4 atm of H₂ and 22 °C (Table S10, SI). MOF-Co catalysts are also tolerant of carbonyl group. Functionalized alkenes such as allyl acetate, dimethylitaconate and 2-vinylpyridine were hydrogenated selectively to propyl acetate, dimethyl-2-methylsuccinate, and 2-ethylpyridine, respectively, in good yields (entries 35-38, Table 1). MOF catalysts were also active in hydrogenation of tetrasubstituted alkenes, with a TON of 170 observed for the hydrogenation of tetramethyl-ethylene by mBPP-MOF-Co (entry 40, Table 1).

Impressively, at 0.5 mol% Co loading, both bpy-MOF-Co and bpyv-MOF-Co catalysts can be recovered and reused for at least 16 times for the hydrogenation of 1-octene without loss of catalytic activity (Figures S40-42, SI). Complete conversion was observed in every run without olefin isomerization or formation of other byproducts. PXRD patterns of the MOF catalysts after catalysis were identical to those of the pristine MOF catalysts, indicating the stability of the framework under catalytic conditions (Figures 2d, S3, S6 and S12, SI). Additionally, ICP-MS analyses of the organic product showed a negligible metal leaching after the 1st run, with the leaching of 0.0004% Co and 0.001% Zr for bpy-MOF-Co, 0.0005% Co and 0.002% Zr for bpyv-MOF-Co, and 0.08% Co and 0.1% Zr for mPT-MOF-Co, respectively. A “cross” test further confirmed the heterogeneity of MOF-catalysts: after completely hydrogenating styrene in 6 h, bpyv-MOF-Co was separated from the supernatant. An equal amount of 1-octene was added to the solid and supernatant, respectively. After 18 h under hydrogen atmosphere, 1-octene was completely converted to *n*-octane in presence of the MOF solid but no conversion was observed in presence of the supernatant. This

experiment proved that the MOF-Co, not the leached species, was the active catalyst for hydrogenation. Comparisons of the activities of MOF-Co catalysts with those of Co(^{Me2}bpy)Cl₂ activated with NaBEt₃H and mercury poisoning experiments support that MOF-Co materials are truly single-site solid catalysts with activities several orders of magnitude higher than their homogeneous counterparts (Table S8, SI). In addition, mBPP-MOF-Co gave higher conversion of styrene compared to the analogous bulkier alkene, 4-*tert*-butylstyrene under identical conditions, which demonstrates that catalysis is facilitated by Co-sites both inside the pores and on the outside of the MOFs not the framework surface alone (Section 7.7, SI).

Stabilization of Bpy-Co(solvent)₂ Species in the MOFs Is Responsible for Catalytic Alkene Hydrogenation. The catalytically active species generated after NaBEt₃H treatment of MOF-CoCl₂ materials were investigated by comparison with homogeneous analogs using structural, spectroscopic, and computational techniques. Treatment of Co(^{Me2}bpy)Cl₂ with 2.0 equiv. of NaEt₃BH in THF under dinitrogen atmosphere at room temperature afforded a deep blue solution of Co(^{Me2}bpy)₂ (0.5 equiv) with the concomitant formation of one equiv. of H₂ and Co nanoparticles as a black precipitate (Figure 3b). Co(^{Me2}bpy)₂·1/3THF was crystallized from a concentrated THF/Et₂O solution as a paramagnetic bluish-black solid, whose structure was determined by single crystal X-ray diffraction (Figure S16, SI). Presumably, the reductive elimination of H₂ from the transient ^{Me2}bpy-cobalt dihydride generates the reduced ^{Me2}bpy-Co species, which undergoes intermolecular ligand-disproportionation to furnish the observed Co(^{Me2}bpy)₂ and Co nanoparticles. In a related precedent, the treatment of bulky aryl-substituted bis(imino)pyridine (^APDI)-ligated Co-dichloride complex with NaBEt₃H resulted in neutral Co-dinitrogen complex (^APDI)Co(N₂) via reductive elimination of H₂ from the putative cobalt(II) dihydride intermediate.¹⁵ The steric protection around the Co center in (^APDI)Co(N₂) is key to stabilizing the reduced Co compound from undergoing intermolecular decomposition. Co(^{Me3}bpy)₂ showed broad UV-vis peaks in THF at 635 nm and 688 nm, indicating a strong metal-to-ligand charge-transfer (MLCT) transition in this low valence Co species.¹⁶ However, Co(^{Me2}bpy)₂ is EPR silent even at 77 K, possibly due to rapid relaxation processes.

Treatment of bpyv-MOF-CoCl₂ with NaBEt₃H in THF gave bpyv-MOF-Co as a bluish-black solid which was characterized by EXAFS to contain (bpy)Co(THF)_x (93%) and a trace amount of Co nanoparticles (7%). The EXAFS spectrum showed contributions from both Co-N and Co-Co scattering paths, with their bond lengths fitted at 1.96 ± 0.04 Å and 2.45 ± 0.05 Å, respectively (Figure 3c). These bond lengths are consistent with those of Co(^{Me2}bpy)₂ and metallic Co, respectively. The ratio for Co-N and Co-Co scattering paths was fitted to be 2:0.9, indicating ~7% contribution from Co nanoparticles (assuming an average coordination number of 12 as in metallic Co). We believe that the small amounts of Co nanoparticle formed from CoCl₂ trapped in the MOF at the metalation step. Control experiments ruled out significant contribution of catalytic activity from the trapped Co nanoparticles (Section 4.4, SI).

Table 1. Catalytic hydrogenation of olefins.^a

Entry	Substrate	MOF-Co (mol % Co)	Time	Yield (%) ^b	TONs
1		bpy-MOF-Co (0.1)	20 h	100	>1000
2		bpyv-MOF-Co (0.1)	20 h	100	>1000
3		bpy-MOF-Co (0.01)	20 h	23	2300
4		bpyv-MOF-Co (0.01)	20 h	100	>10000
5		bpyv-MOF-Co (4×10 ⁻⁴)	168 h	78	2.0×10 ⁵
6		mPT-MOF-Co (3.1×10 ⁻⁴)	216 h	66	2.1×10 ⁵
7		mBPP-MOF-Co (2.5×10 ⁻⁵)	144 h	64	2.5×10 ⁶
8		bpy-MOF-Co (0.1)	20 h	100	>1000
9		bpyv-MOF-Co (0.1)	20 h	100	>1000
10		bpy-MOF-Co (0.01)	20 h	15	1500
11		bpyv-MOF-Co (0.01)	20 h	100	>10000
12		mBPP-MOF-Co (0.001)	30 h	100 (91)	>1.0×10 ⁵
13		bpyv-MOF-Co (0.01)	48 h	100	>10000
14		mPT-MOF-Co (0.01)	96 h	100 (100)	>10000
15		bpy-MOF-Co (0.1)	20 h	100	>1000
16		bpyv-MOF-Co (0.1)	20 h	100 (95)	>1000
17		mPT-MOF-Co (0.01)	3 h	36	3600
18		mBPP-MOF-Co (5×10 ⁻⁴)	32 h	96	1.92×10 ⁵
19		mBPP-MOF-Co (0.1)	35 h	100 (99)	>1000
20		bpy-MOF-Co (0.1)	20 h	100	>1000
21		bpyv-MOF-Co (0.1)	20 h	100 (92)	>1000
22		bpy-MOF-Co (0.1)	20 h	88	880
23		bpyv-MOF-Co (0.1)	20 h	100	>1000
24		bpy-MOF-Co (0.1)	20 h	100	>1000
25		bpyv-MOF-Co (0.1)	20 h	100	>1000
26		mBPP-MOF-Co (0.005)	72 h	100	>20000
27		bpyv-MOF-Co (0.01)	48 h	100	>10000
28		mPT-MOF-Co (0.01)	48 h	100	>10000
29		mBPP-MOF-Co (0.005)	48 h	100 (82)	>20000
30		bpyv-MOF-Co (0.1)	24 h	53	530
31		mBPP-MOF-Co (0.1)	36 h	100 (89)	>1000
32		mBPP-MOF-Co (0.1)	96 h	95 (89)	890
33 ^c		mBPP-MOF-Co (0.1)	32 h	100 (94)	>1000
34 ^c		mBPP-MOF-Co (0.02)	66 h	82	8200
35		bpy-MOF-Co (0.1)	70 h	15	150
36		bpyv-MOF-Co (0.1)	70 h	66	660

37	mBPP-MOF-Co (0.1)	36 h	100	>1000
38	mBPP-MOF-Co (0.1)	36 h	92	920
39 ^d	mBPP-MOF-Co (1.0)	24 h	76	76
40 ^d	mBPP-MOF-Co (0.1)	60 h	17	170

^aReaction conditions: 2-3 mg of MOF-CoCl₂, 8 equiv of NaBEt₃H (1.0 M in THF) w.r.t. Co, alkene, THF, 40 bar H₂, 23 °C. ^bYields were determined by ¹H NMR with mesitylene as the internal standard. Isolated yield in the parenthesis. ^cReaction was performed at 70 °C under 50 bar H₂. ^dReaction was performed at 50 °C.

The bpyv-MOF-Co suspension in THF showed broad absorption peaks at ~420 nm and ~700 nm over the scattering background (Figure 3d). Treatment of bpyv-MOF-Co with 2 equiv of 2,2'-bipyridine in THF blue-shifted the absorption peaks to the positions very close to those of the homogeneous Co(^{Me}₂bpy)₂ complex. Consistent with this, the bpy-stabilized MOF showed greatly reduced activity towards olefin hydrogenation (<17%) and hydroboration (<8%) compared to the original MOF catalyst (Section 4.3, SI). In addition, no characteristic band of N≡N was observed in infrared spectroscopy, which rules out the coordination of dinitrogen to Co centers in MOFs. We thus infer the Co coordination environment of (bpy)Co(THF)₂ in the MOF-Co material. Density functional theory (DFT) calculations and natural charge analyses were performed with the 6-311+G**/B3LYP basis set on (bpy)Co(THF)₂ and Co(^{Me}₂bpy)₂, which show high positive charge distributions on the Co atoms (0.6 and 0.9, Figure 3e), suggesting a (bpy)Co^I(THF)₂ ground state.^{16a} XANES spectra show that Co K-edge positions of bpyv-MOF-Co and (^{Me}₂bpy)₂Co are close to that of Co(^{Me}₂bpy)Cl₂, but at significantly higher energy (by 7-8 eV) than that of metallic Co. These results indicate the Co centers in bpyv-MOF-Co(THF)₂ and Co(^{Me}₂bpy)₂ have higher oxidation states than formally assigned zero valence, consistent with the DFT results. Similar behaviors have been observed for other low-valence transition metal complexes with redox non-innocent ligands.¹⁷

The spectroscopic, structural, and DFT calculation results indicate that (bpy)Co(THF)₂ is likely the active catalyst for hydrogenation reactions. To further investigate the mechanism, the empirical rate law was determined by the method of initial rates (<10% conversion), which shows that the hydrogenation of styrene by mBPP-MOF-Co has a first-order dependence on the catalyst and hydrogen concentrations, and a zeroth-order dependence on the alkene concentration (Figures 3f and S44, SI). Further DFT calculations were performed to propose a possible catalytic cycle (Figure 3g). In the calculated mechanism, (bpy)Co(THF)₂ first binds the alkene reversibly to form a Co(bpy)(alkene) complex. Hydrogen then coordinates to the Co center to form a σ-H₂ complex, which undergoes σ-complex assisted metathesis¹⁸ to form the (bpy)Co(H)(R) species (Figure 3g). Reductive elimination of (bpy)Co(H)(R) in THF forms the alkane product and regenerates the (bpy)Co(THF)₂ catalyst. Computation attempts on identifying the transition states gave a five-member ring transition states for the σ-complex assisted metathesis step with a ΔG[‡] = 13.2 kcal/mol (Figure S38-S39, SI), while well-defined transition state of the H₂ binding step was not found. Based on the kinetic and computational results, it can be proposed that the bpyCo(alkene) and bpyCo(alkene)(H₂) intermediates are in

pre-equilibrium with the σ-complex assisted metathesis as the turn-over limiting step.

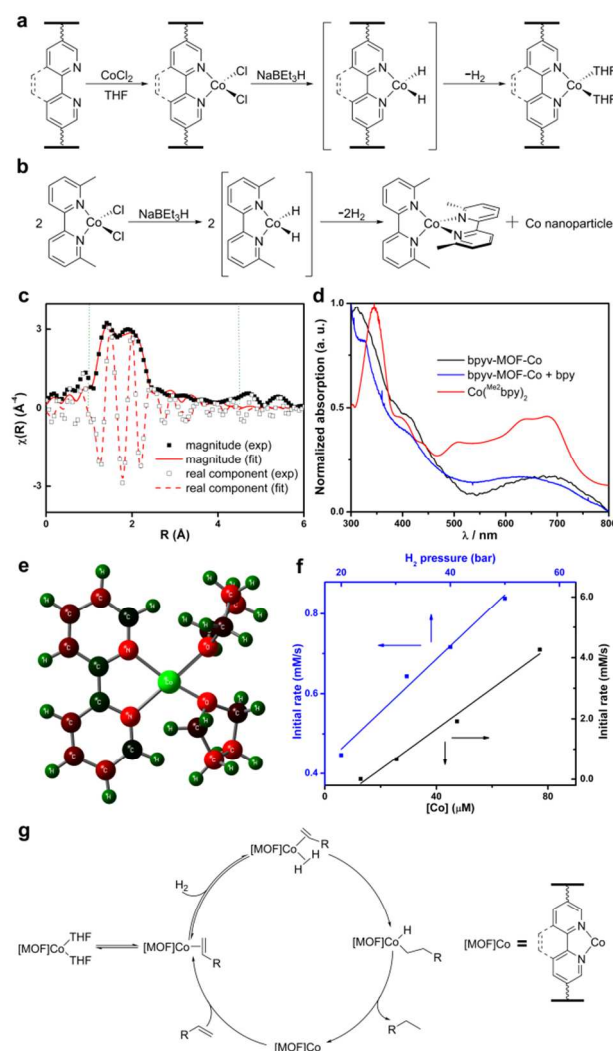


Figure 3. a) Scheme showing the synthesis of MOF-CoCl₂ precatalysts and their reduction by NaBEt₃H to form MOF-Co(THF)₂ catalysts; b) Scheme showing the reduction of Co(^{Me}₂bpy)Cl₂ to the putative (^{Me}₂bpy)Co(H)₂ which quickly disproportionates to form Co(^{Me}₂bpy)₂ and Co nanoparticles in solution; c) EXAFS spectra and the fits in R-space at the Co K-edge of bpyv-MOF-Co(THF)_x showing the magnitude (solid squares, solid line) and real component (hollow squares, dash line) of the Fourier transform. The fitting range is 1 – 4.5 Å in R space

(within the green dot lines); d) UV-vis spectrum of $\text{Co}(\text{Me}_2\text{bpy})_2$ (red) and bpyv-MOF-Co (black) and $\text{bpyv-MOF-Co}(\text{bpy})$ (blue); e) Atomic charge distribution of $\text{Co}(\text{bpy})(\text{THF})_2$ as calculated by NBO population analysis, atoms bearing positive and negative charges are denoted by green and red colors, respectively. The NBO population analysis suggests a $(\text{bpy}^-)\text{Co}^+(\text{THF})_2$ ground state; f) Kinetic plots of initial rates ($d[\text{ethylbenzene}]/dt$) for hydrogenation of styrene versus catalyst concentration and hydrogen pressure for the first 120 seconds, showing first-order dependence on both components; g) According to the kinetic and computational studies, MOF-Co-catalyzed hydrogenation of alkenes likely proceeds via reversible addition of H_2 to $\text{bpyCo}(\text{alkene})$ followed by turnover-limiting σ -complex assisted metathesis (σ -CAM).

MOF-Co Materials for Catalytic Hydroboration of Alkenes and Ketones/Aldehydes and Dehydrogenative C-H Borylation of Arenes. MOF-Co materials were also investigated in catalytic hydroboration of alkenes¹⁹ or dehydrogenative C-H borylation of arenes²⁰ to afford alkyl or arylboronates, which are versatile reagents in organic synthesis. Alkene hydroboration reactions were performed

with 0.1-0.01 mol % MOF-Co in a neat mixture of alkene and pinacolborane (HBpin, 1:1.4 molar ratio) at room temperature to afford the desired products in high yields (Table 2). At a 0.1 mol % Co loading, bpyv-MOF-Co gave complete conversion of 1-octene within 16 h to furnish a mixture as 1-decene, 5-methyl-1-hexene and 6-chloro-1-hexene occurred selectively in the anti-Markovnikov fashion to afford corresponding alkylboronates in excellent yields with 0.1-0.01 mol % mPT-MOF-Co. mPT-MOF-Co was also active in catalytic hydroboration of internal alkene and 1,1-disubstituted alkene such as 2-methyl-2-butene and α -methyl-styrene. Importantly, mPT-MOF-Co can be recycled at least six times without any loss of activity in hydroboration of 1-octene. A negligible amount of leaching was observed for Co (0.01%) and Zr (0.03%). No additional hydroboration product was observed after removal of mPT-MOF-Co from the reaction mixture, which rules out any role of leached cobalt species in catalyzing hydroboration. Additionally, Co-nanoparticles and $\text{Co}(\text{Me}_2\text{bpy})\text{Cl}_2/\text{NaBEt}_3\text{H}$ are barely active in catalyzing hydroboration reactions (entries 7-8, Table 2)

Table 2. MOF-Co-catalyzed hydroboration of alkenes^a

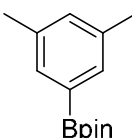
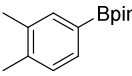
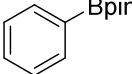
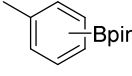
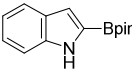
Entry	Substrate	Product	MOF-Co (mol % Co)	Time	% Yield ^b (TONs)
1			bpyv-MOF-Co (0.1)	16 h	66 (660)
2			mBPP-MOF-Co (0.1)	18 h	98 ^c
3			mBPP-MOF-Co (0.0015)	120 h	81 (54000)
4			mPT-MOF-Co (0.1)	16 h	100 (>1000)
5			mPT-MOF-Co (0.01)	72 h	94 ^c (10000)
6 ^d			mPT-MOF-Co (0.0025)	144 h	55 (22000)
7			Co nanoparticle (0.1)	20 h	0
8			$\text{Co}(\text{Me}_2\text{bpy})\text{Cl}_2$ (0.1)	20 h	37
9			mBPP-MOF (0.1)	24 h	0
10			mPT-MOF-Co (0.1)	16 h	98 ^c (>1000)
11			mPT-MOF-Co (0.1)	16 h	92 ^c (>1000)
12			mPT-MOF-Co (0.01)	96 h	100 (10000)
13			mPT-MOF-Co (0.1)	48 h	86 (860)
14			mPT-MOF-Co (0.1)	18 h	100 (>1000)
15			mBPP-MOF-Co (0.1)	18 h	100 (>1000)
16 ^e			mPT-MOF-Co (1.0)	36 h	82 ^c

^aReaction conditions: 0.1-0.01 mol % MOF-CoCl₂, 10 equiv NaBEt₃H (1.0 M in THF), alkene, pinacolborane (1.3 equiv w.r.t. alkene), 23 °C. ^bYields were determined by ¹H NMR with mesitylene as the internal standard. ^cIsolated yield. ^dReaction was performed at 40 °C. ^eReaction was performed at 60 °C.

The catalytic activity of MOF-Co catalysts in dehydrogenative borylation of aromatic C-H bonds was also investigated. While most efforts have focused on developing borylation catalysts based on Ir(I) complexes,²¹ bis(imino)pyridine- and bis(phosphino)pyridine-supported Co catalysts were recently shown to be active for arene C-H borylation.²⁰ mPT-MOF-Co was initially employed in C-H borylation reactions to optimize reaction conditions such as temperature, MOF activation, borylating agents, and solvents. The screening experiments revealed that the highest yields were obtained when the borylation reactions were performed in neat arene at 100 °C for liquid substrates or refluxed in *n*-heptane at 100 °C for solid substrates. mPT-MOF-Co catalyzed borylation of *o*- and *m*-xylene selectively at the least sterically hindered C-H bonds.

1,2-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*m*-xylene were obtained from *o*- and *m*-xylene in 90 and 92% yield, respectively, with 0.1 mol % mPT-MOF-Co (entries 3 and 5, Table 3). Although only phenylboronate was afforded from benzene as a monoborylated product, the borylation of toluene furnished a mixture of *meta*- and *para*-substituted products in a 60:40 ratio. Interestingly, mPT-MOF-Co is at least 125 times more active in C-H borylation of arenes than its homogeneous control PT-CoCl₂ (PT = 1, 10-phenanthroline) in terms of TONs. 1.0 mol % of PT-Co afforded 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*m*-xylene from *m*-xylene in only 8% conversion in four days, after which no further conversion was observed with further heating. In contrast, the conversion of *m*-xylene proceeded with time until completion in the presence of 0.1 mol % mPT-MOF-Co (Figure S47, SI). The bpyv-MOF-Co and mBPP-MOF-Co materials were also active in arene borylation reactions, albeit with lower TONs than mPT-MOF-Co (entries 1-2, Table 3).

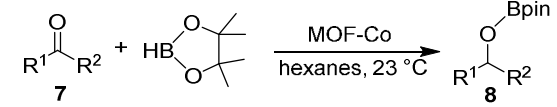
Table 3. MOF-Co-catalyzed C-H borylation of arenes^a

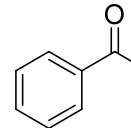
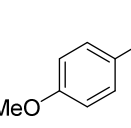
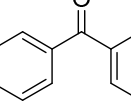
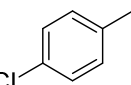
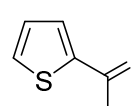
Entry	Product	MOF-Co (mol % Co)	Time	% Yield ^b
1		bpyv-MOF-Co (0.1)	10 d	46
2		mBPP-MOF-Co (0.5)	4 d	50
3		mPT-MOF-Co (0.1)	10 d	100 (92)
4		mPT-MOF-Co (1.0)	2.5 d	94
5		mPT-MOF-Co (0.1)	9 d	100 (90)
6		mPT-MOF-Co (1.0)	2.5 d	92
7		bpyv-MOF-Co (1.0)	11 d	85
8		mPT-MOF-Co (0.1)	8 d	100 (79)
9		mPT-MOF-Co (0.05)	12 d	51
10		mPT-MOF-Co (0.1)	6 d	90 (<i>o</i> : <i>m</i> : <i>p</i> = 0:60:40)
11		mPT-MOF-Co (0.25)	3 d	100
12		mPT-MOF-Co (0.1)	4.5 d	76

^aReaction conditions: 0.25-0.05 mol % MOF-CoCl₂, 10 equiv NaBEt₃H (1.0 M in THF), arene, B₂pin₂, 100 °C, reflux under N₂. [†]GC yield. ^bIsolated yield in the parenthesis.

The MOF-Co materials were also evaluated for catalytic hydroboration of ketones and aldehydes.²² The hydroboration reactions were performed by treating ketones or aldehydes with equimolar HBpin in presence of 0.05 – 0.01 mol % MOF-Co at room temperature (Table 4). 0.05 mol % bpyv-MOF-Co afforded borate ester products from a range of carbonyl substrates, including alkyl, halogenated, and alkoxy-functionalized aryl ketones and aldehydes in essentially quantitative yields. MOF-Co catalysts gave higher TONs in hydroboration of ketones compared to the analogous homogeneous catalysts (entries 9-10, Table 4). Impressively, a TON of 48,000 was obtained for hydroboration of acetophenone with mBPP-MOF-Co (entry 2, Table 4). Borate ester was also obtained from heterocyclic carbonyl compounds such as 2-acetylthiophene in excellent yields (entries 8-9, Table 4). Pure hydroboration products were obtained by simply removing the catalyst via centrifugation followed by removal of the organic volatiles. ICP-MS analyses showed that the amounts of Co and Zr leaching into the supernatant after hydroboration of 4-methoxyacetophenone were 0.02% and 0.008%, respectively, and after filtration, the borylated product contained only 4.2 ppm Co and 1.3 ppm Zr.

Table 4. MOF-Co catalyzed hydroboration of ketones and aldehydes.^a



Entry	Substrate	mol % Co	Time	% Yield ^b
1		0.05	1 d	100 (98)
2		0.001	4 d	48 ^c
3		0.05	1 d	100 (92)
4		0.0025	4 d	84
5		0.01	1 d	100 (96)
6		0.05	1.6 d	100
7		0.01	3 d	84
8		0.05	1 d	100 (96)
9		0.01	3 d	41
10		0.05	4 d	62 ^d

^aReaction conditions: bpyv-MOF-CoCl₂, 10 equiv. of NaBEt₃H, carbonyl substrate, hexanes, 23 °C. ^bYields were determined by ¹H NMR with mesitylene as the internal standard. Isolated yield

1 in the parenthesis. ^cReaction was done with mBPP-MOF-Co at 40
2 °C. ^dbpy-CoCl₂ was used as a precatalyst.

3 Conclusions

4 We have developed highly active, robust, and recyclable
5 single-site base-metal catalysts for alkene hydrogenation and
6 hydroboration, aldehyde/ketone hydroboration, and arene C-H
7 borylation reactions by simple post-synthetic metalation of
8 bipyridyl- and phenanthryl-based MOFs. The MOF catalysts
9 displayed unprecedentedly high turnover numbers (TONs) of
10 up to 2.5×10⁶ and turnover frequencies (TOFs) of up to 1.1 ×
11 10⁵ h⁻¹ for alkene hydrogenation. Structural, computational,
12 and spectroscopic studies provide the first direct evidence for
13 the stabilization of highly reactive and solution-inaccessible
14 (bpy)Co(THF)₂ species in MOFs via active site isolation
15 which shuts down intermolecular deactivation pathways.
16 Computational, spectroscopic, and kinetic evidences further
17 support a hitherto unknown (bpy)Co^I(THF)₂ ground state that
18 coordinates to alkene and then undergoes σ-complex assisted
19 metathesis with H₂ to initiate catalytic cycles for alkene hy-
20 drogenation. This work thus demonstrates for the first time
21 that MOFs enable an entirely new strategy for discovering
22 base-metal based molecular catalysts. This novel strategy lifts
23 the constraints placed on traditional homogeneous catalysis
24 and can lead to practical earth-abundant metal catalysts for
25 sustainable chemical catalysis.

26 Experimental Section

27 All of the reactions and manipulations were carried out un-
28 der nitrogen with the use of standard inert atmosphere and
29 Schlenk techniques or inside a nitrogen-filled glovebox. Cryst-
30 tal structures reported are deposited at the Cambridge Crystall-
31 lographic Data Centre (CCDC) under deposition numbers
32 1404664 [Co(^{Me2}bpy)₂]/3THF and 1404665 (bpyv-MOF).
33 The crystallographic files can be obtained free of charge. De-
34 tailed procedures for the ligand and MOFs synthesis are re-
35 ported in the Supplementary Information.

36
37
38 **Synthesis of MOFs and MOF-CoCl₂ precatalysts.** In a typi-
39 cal procedure, ZrCl₄ (10 mg), H₂BPP (6 mg) and 4,4'-
40 bis(carboxyphenyl)-2-nitro-1,1'-biphenyl (14 mg) were dis-
41 solved in 10 mL of DMF and 0.1 mL of trifluoroacetic acid
42 was added. The solution was heated at 100 °C for 5 days to
43 afford a pale yellow solid which was collected and washed
44 thoroughly with DMF and THF (17 mg, 45% yield). A THF
45 solution of CoCl₂ (6 mg) was added to the suspension of
46 mBPP-MOF in THF, and the resultant mixture was stirred
47 overnight, collected and washed with THF to afford the blue-
48 green mBPP-MOF-CoCl₂.

49
50 **General procedure for MOF-Co-catalyzed olefin hydro-**
51 **genation.** To a suspension of mBPP-MOF-CoCl₂ (1.0 mg, 0.1
52 mol % Co) in 1.0 mL THF was added NaBEt₃H (10 μL, 1.0 M
53 in THF), and the mixture was stirred for 1 h. The solid was
54 then centrifuged, washed with THF twice, and transferred to a
55 glass vial in 1.0 mL THF, followed by the addition of α-
56 isopropyl styrene (30 mg, 0.21 mmol). The vial was then
57 placed in a Parr reactor which was charged with 40 bar of
58 hydrogen. After stirring slowly at room temperature for 35 h,
59 the pressure was released, and the MOF catalyst was removed
60 from the reaction mixture via centrifugation and extracted

with hexanes twice. The combined organic extracts were con-
centrated *in vacuo* to afford pure 1-(3-methylbutan-2-
yl)benzene in a quantitative yield.

General procedure for MOF-Co-catalyzed hydroboration of alkenes. To a suspension of mBPP-MOF-CoCl₂ (1.0 mg, 0.1 mol % Co) in 1.0 mL THF was added 10 μL of NaBEt₃H in THF (1.0 M) and the mixture was stirred slowly for 1 h. The solid was centrifuged out of suspension and washed with THF twice. To the solid was added pinacolborane (34 μL, 0.22 mmol) and 1-octene (48 μL, 0.31 mmol). The resultant mixture was slowly stirred at room temperature for 18 h until complete conversion of 1-octene as monitored by GC. The solid was centrifuged out of suspension and extracted with hexane twice. The combined organic extracts were concentrated *in vacuo* to yield the pure product (52 mg, 0.216 mmol, 98%).

General procedure for MOF-Co-catalyzed C-H borylation of neat arenes. To a suspension of mPT-MOF-CoCl₂ (3.0 mg, 0.1 mol % Co) in 0.5 mL THF was added 20 μL of NaBEt₃H in THF (1.0 M) and the mixture was stirred slowly for 1 h. The solid was centrifuged out of suspension and washed with THF twice and with *m*-xylene once. B₂pin₂ (54.8 mg, 0.216 mmol) in 4.0 mL of *m*-xylene was added to the vial and the resultant mixture was transferred to a Schlenk tube. The tube was heated to reflux under nitrogen at 100 °C for 10 d. The reaction mixture was cooled to room temperature and the solid was centrifuged out of the suspension. The liquid was passed through a short plug of celite and then concentrated *in vacuo* to give pure 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*m*-xylene (92 mg, 0.396 mmol, 92%).

ASSOCIATED CONTENT

Supporting Information. Synthesis and characterization of ligands, MOFs, metalated MOFs and molecular analogs, procedures for all catalytic reactions, details for X-ray absorption spectroscopic analysis and DFT calculations, crystal structure figures and crystallographic files of Co(^{Me2}bpy)₂/3THF and bpyv-MOF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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ACKNOWLEDGMENT

This work was supported by the NSF (CHE-1464941) and startup funds from the University of Chicago. We thank Dr. Tianpin Wu, Dr. Trudy W. Bolin, C. Poon, Z. Lin, Dr. C. W. Abney, and P. Ji for experimental help. XAS analysis was performed at Beamline 9-BM, Advanced Photon Source (APS), Argonne National Laboratory (ANL). Use of the 9-BM beamline at the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. Single-crystal diffraction studies were performed at ChemMatCARS, APS, ANL. ChemMatCARS is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), NSF, under grant number NSF/CHE-

1346572. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE Office of Science by ANL, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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TOC Graphic

