JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
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Improved Catalytic Activity and Stability of a Palladium Pincer Complex by Incorporation into a Metal−Organic Framework

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Supporting Information

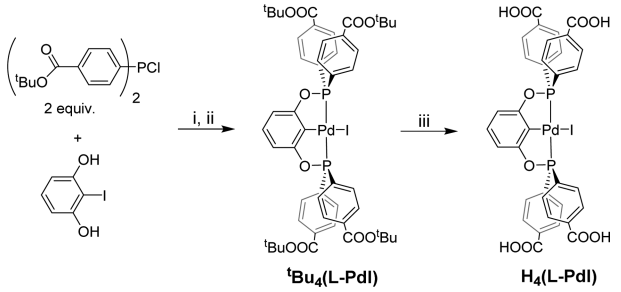
ABSTRACT: A porous metal−organic framework $Zr_6O_4(OH)_4$(L-PdX)$_3$ (**1-X**) has been constructed from Pd diphosphinite pincer complexes ([L-PdX]$^{4-}$ = [(2,6-$(OPAr_2)_2C_6H_3$)PdX]$^{4-}$, Ar = *p*-$C_6H_4CO_2^-$, X = Cl, I). Reaction of **1-X** with $PhI(O_2CCF_3)_2$ facilitates I^-/$CF_3CO_2^-$ ligand exchange to generate **1-TFA** and I_2 as a soluble byproduct. **1-TFA** is an active and recyclable catalyst for transfer hydrogenation of benzaldehydes using formic acid as a hydrogen source. In contrast, the homogeneous analogue **^{t}Bu(L-PdTFA)** is an ineffective catalyst owing to decomposition under the catalytic conditions, highlighting the beneficial effects of immobilization.

Metal−organic frameworks (MOFs) are a burgeoning class of porous materials with structural and functional diversity arising from a vast scope of potential organic and inorganic building blocks. This diversity offers an avenue for the design and study of hybrid materials that embody the activity and selectivity of homogeneous catalysts and provide the ease of product separation and recyclability associated with heterogeneous catalysts. In this regard, catalytically active transition metal complexes have been immobilized in MOFs via guest encapsulation and covalent grafting as well as incorporated as linkers using postsynthetic exchange or direct assembly routes.[1] The latter approach is particularly appealing owing to the uniformity of catalytic sites in the resulting materials and the decreased likelihood of leaching. Consequently, catalytically active MOFs have been assembled from linkers based on metal salen,[2] porphyrin,[3] bipyridine,[4] and phenylpyridine[5] complexes as well as others.[6] Despite the ubiquity of phosphine ligands in homogeneous catalysis, there are relatively few examples of MOFs constructed from phosphine-containing linkers.[7] Recently, Lin et al. reported asymmetric catalysis with a Zr MOF containing Rh(I) and Ru(II) BINAP-based (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) linkers.[8] Remarkably, the activity and enantioselectivity of the MOF-supported BINAP complexes were comparable to or exceeded those of the homogeneous analogues.

Diphosphine pincer ligands have been widely used in homogeneous catalysis owing to their rigid coordination, tunability, and stability.[9] In particular, palladium diphosphine pincer complexes have been shown to be catalysts or precatalysts for a number of transformations including C−C cross coupling,[10] aldol and Michael reactions,[11] allylation of aldehydes and imines,[12] and hydrogenation.[13] Herein we report the synthesis of a Zr MOF constructed from linkers based on palladium aryl diphosphinite (POCOP) pincer complexes. Initial studies reveal that immobilization has a profound effect on the catalytic activity of the Pd-POCOP complex. While the homogeneous complex exhibits poor activity for transfer hydrogenation of aldehydes, the MOF demonstrates good catalytic activity owing to the inhibition of decomposition pathways.

The Pd-POCOP pincer complex **H_4(L-PdI)** was synthesized as shown in Scheme 1. A mixture of **H_4(L-PdI)** and $ZrCl_4$ in 4/1 (v/v) dimethylformamide (DMF)/acetic acid was sealed in a 20 mL vial and heated at 120 °C for 12 h resulting in formation of **1-X** as an off-white microcrystalline powder (Scheme 2). The structure of **1-X** has been determined from synchrotron powder X-ray diffraction (PXRD) data (Figure 1 and Supporting Information (SI)). Indexing provided a cubic unit cell (*a* =

Scheme 1. Synthesis of H_4(L-PdI)[a]



[a]Reagents: (i) Et_3N, Et_2O; (ii) $Pd(PPh_3)_4$, Et_2O; (iii) CF_3COOH, CH_2Cl_2.

Scheme 2. Solvothermal Synthesis of 1-X

H_4(L-PdI) —$ZrCl_4$ (2.7 equiv.), DMF/AcOH (4:1), 120 °C, 12 h→ $Zr_6O_4(OH)_4$[L-PdX]$_3$, X = Cl (40%), I (60%) (**1-X**)

Received: November 25, 2015
Published: January 27, 2016

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DOI: 10.1021/jacs.5b12366
J. Am. Chem. Soc. 2016, 138, 1780−1783

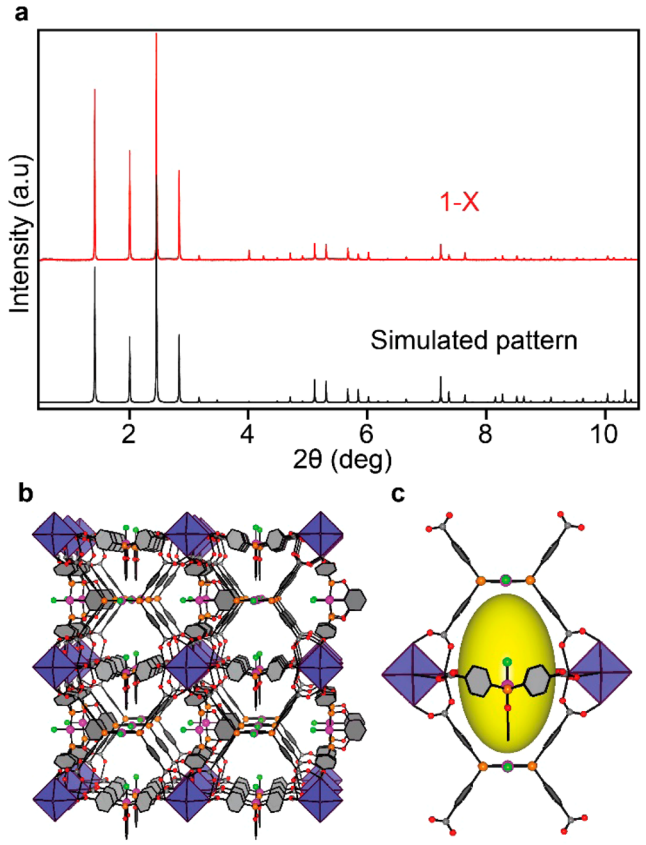


Figure 1. (a) Experimental and simulated PXRD patterns of **1-X** (synchrotron radiation, λ = 0.413959 Å). (b) Framework structure of **1-X**. Linker disorder has been omitted for clarity. (c) View of a portion of the framework showing ovoidal pores. Blue octahedra represent $[Zr_6O_4(OH)_4]^{12+}$ building units.

16.724 Å) with *Pm*-3 as the most likely space group. The structural model of **1-X** shows $[Zr_6O_4(OH)_4]^{12+}$ octahedra connected by $[L\text{-}PdX]^{4-}$ linkers that span each face of the cubic unit cell, generating ovoidal pores ~16 × 10 Å in diameter. Moreover, in the *Pm*-3 space group, the $[L\text{-}PdX]^{4-}$ linkers are four-fold disordered as a consequence of the crystallographic mirror plane normal to the *a*-axis and the C_{2v} molecular symmetry of the linker which gives rise to noncrystallographic rotational disorder (Figure S1).

Similar to other Zr-based MOFs, **1-X** displays exceptional chemical stability.[14] The material is stable for weeks under ambient conditions and retains crystallinity upon exposure to strong acid (1 M HNO_3) and base (0.1 M NaOH) (Figure S2). In line with the predicted porous structure of **1-X**, thermogravimetric analysis shows ~25 wt % mass loss at 250 °C arising from occluded solvent (Figure S3). A sample of **1-X** was activated by heating in vacuum (10^{-4} Torr) at 150 °C for 12 h, and an apparent Brunauer–Emmett–Teller (BET) surface area of 1164 $m^2\ g^{-1}$ was calculated from a N_2 adsorption isotherm measured at 77 K (Figure S4). Elemental analysis (EA) of an activated sample of **1-X** revealed the presence of a significant amount of Cl (1 wt %) and a lower than expected I content (6.5 wt % versus 15 wt %) based on the presence of $[L\text{-}PdI]^{4-}$ linkers. Thus, the use of $ZrCl_4$ in the solvothermal synthesis appears to result in partial ligand exchange at Pd and a halide occupancy of ~60% I and ~40% Cl. Attempts to circumvent halide disorder by using a Cl-exchanged linker, H_4(L-PdCl), were unsuccessful as no crystalline products could be obtained. The MAS ^{31}P NMR spectrum of **1-X** shows a major resonance (96%) centered at 150 ppm, close to that observed for $\mathbf{H_4(L\text{-}PdI)}$ (149 ppm) in DMSO-d_6 solution (Figure 2). The halide disorder in the linkers

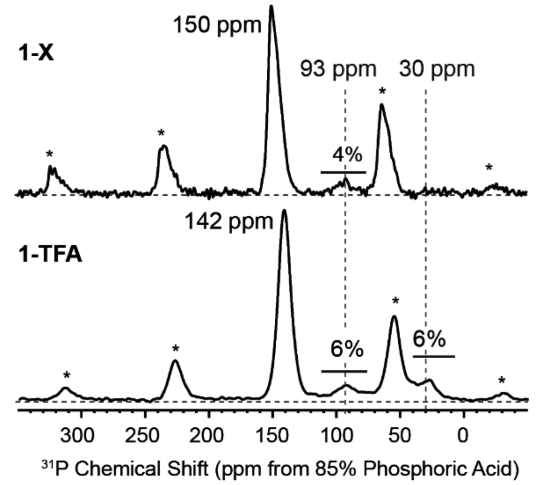


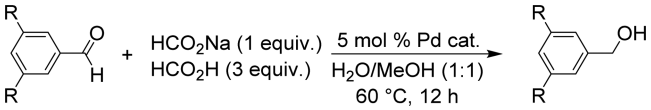
Figure 2. MAS ^{31}P NMR spectra of **1-X** and **1-TFA**. Asterisks (*) are used to denote spinning side bands.

is corroborated by the asymmetry of the main resonance which suggests overlap of two signals with similar chemical shift (Figure S5). The spectrum also shows the presence of an unidentified species giving rise to a small resonance (4%) centered at 93 ppm.

Catalytic transfer hydrogenation of organic substrates with sacrificial hydrogen donors such as alcohols or formic acid is a mild and convenient alternative to direct hydrogenation with H_2.[15] Pd diphosphine pincer complexes have recently been shown to catalyze chemoselective transfer hydrogenation of α,β-unsaturated ketones using *n*-butanol as a hydrogen source.[13a,b] Consequently, we decided to investigate the activity and recyclability of **1-X** as a catalyst for transfer hydrogenation. Given the chemical stability exhibited by **1-X**, transfer hydrogenation reactions were tested in aqueous solvent mixtures with formic acid as the hydrogen source. Unfortunately, initial catalyst screening with benzaldehyde as a substrate afforded low yields (<20%) of benzyl alcohol (Table 1). We considered that the presence of strongly bound I^- ligands might hinder reactivity at the Pd sites of **1-X** and sought to exchange the halide for a more weakly coordinating anion. The use of common halide abstraction reagents such as Ag or Tl salts is complicated by precipitation of the MX byproducts with the MOF. Therefore, we required a reagent that would facilitate ligand exchange and generate fully soluble byproducts. Consequently, when a suspension of **1-X** in CH_2Cl_2 was treated with $PhI(TFA)_2$ (TFA = CF_3CO_2), the supernatant solution gradually turned red-purple over the course of 12 h, signaling the formation of I_2 and I^- ligand replacement with TFA^- (Scheme 3). After washing with CH_2Cl_2, the PXRD pattern of the resulting solid (**1-TFA**) was largely unchanged from that of the starting material (Figure S6). EA of **1-TFA** showed the presence of I, Cl, and F. Based on the observed ratios of these halides, the ligand occupancy at the Pd sites is estimated to be 0.17 I^-, 0.39 Cl^-, and 0.44 CF_3COO^-, suggesting that I^-/CF_3COO^- ligand exchange proceeds in ~72% yield and ligand substitution does not occur at the Pd–Cl sites. The MAS ^{13}C NMR spectrum of **1-TFA** displays a partially resolved quartet at 116.6 ppm ($-CF_3$, J_{C-F} = ~280 Hz) as well as a new resonance at 163 ppm assigned to the carbonyl group of TFA (Figure S7). The MAS ^{31}P NMR spectrum shows an upfield

DOI: 10.1021/jacs.5b12366
J. Am. Chem. Soc. 2016, 138, 1780–1783

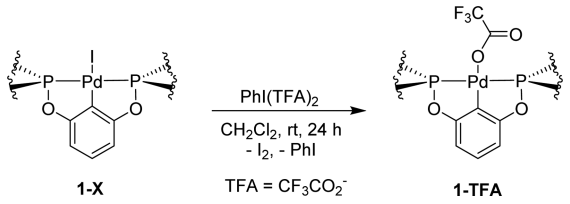
Table 1. Transfer Hydrogenation of Benzaldehydes[a]



entry	catalyst	substrate (R)	% conv.[b,c]	% yield[c]
1	**1-X**	H	19	16
2	**1-TFA**	H	100	84
3	UiO-67	H	0	0
4	**1-TFA** + Hg^0	H	95	76
5	**1-TFA**	OCH_3	100	89
6	**1-TFA**	OCH_2Ph	27	22
7	**1-TFA** (run 2)	H	96	78
8	**1-TFA** (run 3)	H	56	47
9	**^{t}Bu$_4$(L-PdTFA)**	H	6	<5

[a]Reaction conditions: substrate (0.2 mmol), catalyst (0.01 mmol), sodium formate (0.2 mmol), formic acid (0.6 mmol) in 1:1 H_2O/MeOH (2 mL), 12 h, 60 °C. [b]Based on conversion to benzylic alcohol. [c]Determined by ^{1}H NMR with respect to an internal standard (1,3,5-trimethoxybenzene) after work up. See SI for details.

Scheme 3. Ligand Exchange To Generate 1-TFA



shift of the major resonance to 142 ppm, consistent with that observed upon I^-/TFA^- ligand exchange of the homogeneous complex (Figure 2). The spectrum also shows the appearance of a small signal around 30 ppm. This chemical shift is close to that observed for diaryl phosphinate esters ($Ar_2P(O)OR$), suggesting a small amount of phosphine oxidation during the halide exchange reaction.[16] A N_2 adsorption isotherm measured for **1-TFA** after activation (100 °C, 10^{-4} Torr, 12 h) provided a BET surface area of 594 $m^2\ g^{-1}$ (Figure S8). The observed decrease in N_2-accessible surface area is consistent with exchange of I^- for larger trifluoroacetate anions.

1-TFA proved to be a more active transfer hydrogenation catalyst than **1-X**. Using catalyst loadings of 5 mol % based on Pd with benzaldehyde as the substrate and 3/1 HCO_2H/HCO_2Na as the hydrogen source, 19% and 100% conversion to benzyl alcohol was observed with **1-X** and **1-TFA**, respectively (Table 1, entries 1 and 2). When UiO-67[14a] was tested as a catalyst (entry 3), no conversion of benzaldehyde to benzyl alcohol was observed, indicating that the $Zr_6O_4(OH)_4(COO)_{12}$ SBUs are not responsible for catalysis. **1-TFA** exhibits good catalytic activity for transfer hydrogenation of a range of aromatic and aliphatic aldehydes (Table S1). However, decreased conversion was observed for substrates with strongly coordinating heteroatoms. The catalytic activity of **1-TFA** is not inhibited by the presence of Hg^0 (Table 1, entry 4), suggesting that catalysis is likely not due to the presence of Pd nanoparticles.[17] Similarly, a hot filtration test showed no indication of catalysis by leached homogeneous species. These observations, along with the increased catalytic activity of **1-TFA** versus **1-X**, support the immobilized pincer Pd centers as the active sites for catalysis. Moreover, when 3,5-dimethoxybenzaldehyde (entry 5) and 3,5-dibenzyloxybenzaldehyde (entry 6) were used as substrates with **1-TFA** as the catalyst, 100% and 27% conversion to the corresponding benzylic alcohols was observed. The significant decrease in conversion for the large substrate is consistent with hindered access to active Pd sites within the MOF, indicating that catalysis does not occur exclusively at surface sites.

PXRD analysis of the MOF recovered after catalysis indicated no significant loss of crystallinity (Figure S9). The disappearance of the TFA resonances in the MAS ^{13}C NMR spectrum supports TFA^-/HCO_2^- exchange during catalysis (Figure S7). The MAS ^{31}P NMR spectrum also shows a slight downfield shift of the major resonance corresponding to the immobilized Pd-POCOP complex to 146 ppm (Figure S10). However, an increase in the signal near 30 ppm indicates additional decomposition of the pincer complex during catalysis. Consequently, the catalyst could only be recycled once without a drop in product yield (entries 7 and 8).

Finally, we sought to compare the catalytic activity **1-TFA** with a homogeneous analogue, **^{t}Bu$_4$(L-PdTFA)**. To our surprise, **^{t}Bu$_4$(L-PdTFA)** gave low conversion of benzaldehyde to benzyl alcohol under the optimized conditions (entry 9). Furthermore, a color change of the reaction mixture from pale yellow to dark brown was observed during the course of the reaction. In order to gain insight into the fate of the catalyst, the reaction of **^{t}Bu$_4$(L-PdTFA)** with 4 equiv of HCO_2Na in CD_3OD was monitored by ^{31}P NMR spectroscopy. Similar to the catalytic reaction, the solution darkened over time, and after 12 h, the ^{31}P NMR signal corresponding to **^{t}Bu$_4$(L-PdTFA)** (144 ppm) was completely replaced by a new resonance at 33.8 ppm. ^{1}H NMR and ESI-MS analysis identified the major phosphorus-containing species as $(p\text{-}^t BuO_2CC_6H_4)_2P(O)OCD_3$ (Figures S11 and S12). These results suggest that **^{t}Bu$_4$(L-PdTFA)** decomposes under the catalytic conditions to generate catalytically inactive Pd species. This decomposition pathway seems to be inhibited by rigid immobilization of the complex in **1-TFA**. A possible explanation for this effect is the stabilization of a reactive Pd−H intermediate. In fact, others have noted the inability to isolate or characterize monomeric Pd−H complexes supported by pincer ligands bearing diaryl phosphine donors.[13c,18]

In summary, we have demonstrated the assembly of a porous and robust MOF from linkers based on phosphorus-containing pincer complexes. A novel anion exchange strategy involving oxidation of I^- was used to introduce weakly coordinating $CF_3CO_2^-$ at the Pd sites of the MOF. The resulting material, **1-TFA**, is an active heterogeneous catalyst for transfer hydrogenation of aldehydes using formic acid. However, the homogeneous analogue **^{t}Bu$_4$(L-PdTFA)** is an ineffective catalyst as a result of decomposition under the catalytic conditions. This reveals that rigid immobilization in the MOF inhibits decomposition pathways, allowing for dramatically improved the catalytic activity. Ongoing work is focused on elucidating these effects in other MOF-supported catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12366.

Experimental details and characterization data (PDF)
Crystallographic data (CIF)

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DOI: 10.1021/jacs.5b12366
J. Am. Chem. Soc. 2016, 138, 1780−1783

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund (55281-DNI-3) for support of this research. A.K. is supported by a Schlumberger Faculty for the Future Fellowship. We thank Prof. Marion Emmert and Dr. Kathleen Field for assistance with ICP-OES analysis. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under contract no. DE-AC02-06CH11357

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DOI: 10.1021/jacs.5b12366
J. Am. Chem. Soc. 2016, 138, 1780−1783