CHEMISTRY OF MATERIALS

Three-Dimensional Phosphine Metal–Organic Frameworks Assembled from Cu(I) and Pyridyl Diphosphine

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Supporting Information

ABSTRACT: Metal-organic frameworks (MOFs) with phosphine based ligands are extremely attractive for catalysis. In this paper, phosphine has been successfully incorporated for the first time into three-dimensional (3D) MOFs. The MOFs are based on rigid L_2M_2 dimeric secondary building blocks assembled from Cu(I) and a pyridyl diphosphine ligand, 4-(3,5-bis(diphenylphosphino)phenyl)pyridine, with Br⁻ (CuL-Br), Cl⁻ (CuL-Br), or PF₆⁻ (CuL-PF₆) as counteranions. The structures have a 4.12² net topology, which can be further simplified to $6^4.8^2$ -qtz. The MOFs contain 1D homochiral channels. The PF₆⁻ anions hosted in the 1D channel of CuL-PF₆ can be readily exchanged with Br⁻ or Cl⁻ while keeping the framework intact. The materials show anion-tunable flexible porosity. CuL-Br reveals gradual uptake of MeOH, while



CuL-PF₆ exhibits stepwise sorption for MeOH. The heterogeneous Lewis acid catalytic activity of the MOFs has been shown in ketalization reaction. **CuL-Br** and **CuL-PF**₆ are active in the reactions between ethylene glycol and 2-butanone/cyclohexanone, up to 93% yield with 0.2 mol % catalyst loading. In contrast, no reaction happens between ethylene glycol and bulky benzophenone, suggesting profound size selectivity. The catalysts can be reused with the framework left intact for three runs without loss of activity.

KEYWORDS: metal-organic framework, phosphine, copper, sorption, catalysis

1. INTRODUCTION

The chemistry of metal-organic frameworks (MOFs) has been developing rapidly in last two decades,¹ while phosphine-based networks are less studied, in comparison with the large number of metal carboxylate MOFs.^{1a} Phosphines are a type of ligands in which electronic and steric properties can be tuned over a wide range. Phosphine based ligands are extremely attractive not only in coordination chemistry but also in homogeneous catalysis. Metal complexes with (chiral) phosphorus ligands are among the most efficient and selective catalysts for organic transformations including many industrial processes such as hydrogenation, hydroformylation, coupling reaction, asymmetric synthesis, etc.² Although MOFs are expected to be successful heterogeneous catalysts similar to zeolites,^{3,4} only handful two-dimensional (2D) phosphine materials have been reported so far.⁵ As a good example, James et al. reported that benzene-1,3,5-diphenylphosphine and Ag⁺ yield a 2D MOF with adjacent "chickenwire" layers directly on top of each other, to give 16 Å channels occupied by counteranions and solvent molecules.^{5c} Several tris(4-carboxylphenyl)phosphine oxidebased 3D MOFs were reported by Humphrey and others,⁶ but phosphine-based 3D MOFs still remain unknown partly because the supramolecular coordination behavior of phosphine complexes is less predictable. The pyramidal geometry at phosphorus and relatively free P-C rotation allow a range of accessible orientations of the lone pairs, and steric effects also need to be considered.^{1a} In our efforts for phosphine-based selfassembly, we have developed an approach to synthesize 2D polymeric networks on the basis of rigid L_2M_2 dimeric secondary building blocks (L is a T-shaped pyridyl diphosphine).⁷ In this paper, novel 3D Cu(I) MOFs containing pyridyl diphosphine are generated, which represent the first examples of 3D phosphine-based MOFs, to the best of our knowledge.

2. RESULTS AND DISCUSSION

Design and Synthesis. 4-(3,5-bis(diphenylphosphino)phenyl)pyridine (L) was chosen as a T-shaped pyridyl diphosphine because L_2M_2 dimerized subunits are apt to adopt a divergent conformation for further construction of polymeric structures.⁷ Such a divergent conformation efficiently restricts the accessible orientations of the phosphorus lone pairs so that the L_2M_2 subunits can be considered as a rigid 4connecting node. Moreover, pyridylphosphines combine phosphorus and pyridyl nitrogen donors, possibly inducing electronic asymmetry on the metal.⁸ By slow diffusion of a solution of CuX (X = Br, Cl, or PF₆) in MeCN into a solution of L in CHCl₃ or toluene, three MOFs, {(LCuBr) $\supset x$ CHCl₃}_∞ (denoted CuL-Br to highlight the structural difference in counteranions), {(LCuCl) $\supset x$ CHCl₃}_∞ (CuL-Cl) and

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{(LCuPF₆) ⊃ xH_2O }_∞ (CuL-PF₆), were successfully synthesized. FT-IR spectra (4000–450 cm⁻¹) were recorded to determine the coordination mode of the ligand, showing the characteristic C==N stretching vibrations of the pyridyl groups at 1601 cm⁻¹ for CuL-Br and CuL-Cl and 1609 cm⁻¹ for CuL-PF₆. In comparison to the vibration band of the free ligand (1592 cm⁻¹), the blue-shifts (9–17 cm⁻¹) are attributed to the coordination of the nitrogen atom from the pyridine ring to the metal center. The IR spectrum of CuL-PF₆ shows the characteristic band of PF₆⁻ at 841 cm⁻¹.

Crystal Structures. The crystal structures of **CuL-Br** and **CuL-Cl** could be unambiguously established by single crystal X-ray crystallography (Figure 1; Figure S1, Supporting



Figure 1. (a) Molecular structure drawing and (b) X-ray structure of the tetrahedral Cu_2L_2 secondary building unit; X-ray structures of (c) a single channel, (d) CHCl₃ molecules located in the channel, and (e) the 3D framework viewed along the *c* axis (hydrogen atoms and solvated CHCl₃ molecules are omitted for clarity); (f) 4.12² topological net; (g) 6⁴.8²-**qtz** topological net of **CuL-Br**.

Information). **CuL-Br** and **CuL-Cl** are isostructural with different counteranions, and only the former is discussed in detail hereinafter. **CuL-Br** crystallizes in the chiral space group $P3_221$. The asymmetric unit consists of one crystallographically independent Cu(I) ion, one L ligand, and a Br⁻ anion. Each L ligand binds three Cu⁺ ions with all three P and N donors, while each Cu⁺ is coordinated with three ligands to form a 3D network. The Cu⁺ ion is tetracoordinate with a distorted

tetrahedral CuP2NBr coordination geometry. Every Cu⁺ ion coordinates one N donor and two P donors from three different ligands (Cu-P = 2.285(4), 2.270(3) Å; Cu-N = 2.065(9) Å). The charge of the network is balanced by one coordinated Br^- ion per copper ion (Cu-Br = 2.422(3) Å). The net topological analysis of CuL-Br reveals a 3D 3connected Archimedean 4.12² topological network if both Cu and the ligand are simplified as 3-connecting nodes. This simple topology represents a novel uniform 3-connected topology. The 4.12^2 net can be simplified to a chiral quartz net (or $6^4.8^2$ -qtz net) if each L_2M_2 subunits is considered as 4connecting tetrahedral node. As predicted by Wells, replacement of the node of the NbO net by 4-gons gives a 4.12^2 net,¹⁰ while the present case reveals an unprecedented way to generate 4.12^2 net by replacing the node of the qtz net with 4-gons. Different from square-planar nodes in NbO-type net and the reported 4.8^2 networks,⁷ the dimeric Cu₂L₂ subunits of CuL-Br are twisted away from planarity and can be regarded as tetrahedral nodes (Figure 2).



Figure 2. Formation of 2D and 3D networks on the basis of M_2L_2 dimeric subunits.

The Flack parameter with values close to zero implies high enantiopurity of CuL-Br in single crystals, and the network possesses an open structure with 1D homochiral channels along the c axis. All the chiral channels have the same handedness, with 3₂ helical symmetry, and are polygonal, measuring approximately 18.56 Å (a) in diameter. The open channels are lined with Br⁻ ions and one of the PPh₂ phenyl rings. The rest of open channels are filled with CHCl₃ solvent molecules. CHCl₃ resides in the 1D channels with the C-H group pointing to the X⁻ ion via weak C–H···X interaction¹¹ (C···Br 3.38–3.94 Å and ∠C–H…Br 154.5–168.9 for CuL-Br; C…Cl 3.43-3.68 and ∠C-H…Cl 155.8-167.8 for CuL-Cl). Calculations using PLATON¹² show that the solvent accessible volume of CuL-Br is 2385.8 Å³ per unit cell volume and the pore volume ratio is 37.6%. The crystallization of CuL-Br is expected to be racemic with equivalent enantiomeric crystals crystallized in P3₂21 and P3₁21.¹³ However, we failed to determine the other P3₁21 enantiomeric form despite numerous attempts.¹⁴

Single-crystal structural determination of CuL-Br and CuL-Cl and powder X-ray diffraction (PXRD) show that CuL-Br, CuL-Cl, and CuL-PF₆ are isostructural (Figure 3a–d). The bulky purity of all the complexes was confirmed by PXRD analysis, and the results show that the experimental PXRD pattern for each complex is consistent with the simulated ones obtained from the single crystal structures of CuL-Br and CuL-



Figure 3. Powder XRD patterns of (a) CuL-Br simulated from the single crystal data, (b) CuL-Br as-synthesized, (c) CuL-Cl as-synthesized, (d) CuL-PF₆ as-synthesized, and (e) CuL-Br guest-free form obtained by drying in vacuo for 10 h at 50 °C, obtained upon exposing the guest-free form to CHCl₃ vapor (f) and MeOH vapor (g).

Cl. The resulting frameworks do not depend on the nature of the counteranion (strongly coordinating Br^- , Cl^- or weakly coordinating PF_6^-). Br^- or Cl^- coordinates to the copper center, while PF_6^- is expected to reside in the channels, with the tetrahedral geometry of copper(I) probably completed by solvated molecules, considering the structural feature.

CuL-PF₆ contains 1D channels where the weakly coordinated PF_6^- anions are located, and an anion exchange study was performed and monitored using FT-IR and PXRD (Figure 4).



Figure 4. FT-IR spectra and powder XRD patterns of (a) assynthesized CuL-PF₆, (b) CuL-PF₆ after immersing in a toluene-MeCN solution of Bu₄NBr for 2 weeks, (c) as-synthesized CuL-Br, (d) CuL-PF₆ after immersing in a toluene-MeCN solution of Bu₄NCl for 2 weeks, and (e) as-synthesized CuL-Cl.

After immersing **CuL-PF**₆ in a toluene-MeCN (v/v = 1:1) solution of Bu₄NBr or Bu₄NCl, the FT-IR spectrum shows that the strong band of PF₆⁻ anion at 840 cm⁻¹ disappears and the resulting spectrum matches well that of **CuL-Br** or **CuL-Cl**, indicating the PF₆⁻ anions located in the 1D channels were

completely exchanged. The PXRD patterns of the exchanged solid are identical to **CuL-Br** or **CuL-Cl**, revealing that crystalline **CuL-Br** and **CuL-Cl** were obtained, respectively, without framework change.

Thermostability. Thermogravimetric analysis (TGA) shows that **CuL-Br**, **CuL-Cl**, and **CuL-PF**₆ have similar weight loss processes (Figure 5). The guest molecules were released



Figure 5. Thermogravimetric curves of (a) CuL-Br, (b) CuL-Cl, and (c) CuL-PF $_{6}$.

from room temperature (RT) to ca. 190 °C for CuL-Br and CuL-Cl, and from RT to ca. 230 °C for CuL-PF₆. All the frameworks began to collapse from ca. 330 °C upon further heating. Removal of the guest molecules by treating $CuL-PF_{6}$ CuL-Br, or CuL-Cl under vacuum at 50 °C causes a change on the framework, revealed by the PXRD patterns of the materials showing significant peak broadening (Figure 3e; Figures S2-S4, Supporting Information). However, the desolvated materials still possessed some degree of crystallinity, especially for CuL-PF₆, suggesting only partial loss of long-range order. The crystalline solids can be fully regenerated upon exposure to CHCl₃ or MeOH vapor/liquid, as indicated by the PXRD measurements (Figure 3f, g). The PXRD patterns are in good agreement with those of as-synthesized and simulated from single-crystal data. Therefore, the original crystal structure came back completely. No dissolution occurred in this process to rule out the possibility of recrystallization. Although the structures of guest-free solids were inaccessible, such guest-induced recovery may imply that the overall frameworks were kept intact. The partial loss of long-range order may result from unrestricted P-C rotation and framework distortion in the absence of guest. The recovery of CuL-Br and CuL-Cl may be partly driven by $C-H\cdots X$ (X = Br, C) weak host-guest interactions between guest and host framework, as revealed by structural analysis.

Sorption Studies. To study the porosity of the materials, sorption isotherms have been measured (Figure 6; Figure S6, Supporting Information). Both MeOH and CHCl₃ sorption studies of **CuL-Br** reveal gradual uptake with increasing pressure and final uptakes of 92 and 76 mL g⁻¹ without saturation, corresponding to 2.7 and 2.2 molecules of MeOH and CHCl₃ per copper, respectively. The amount of CHCl₃ is consistent with the single-crystal X-ray diffraction analysis (two CHCl₃ molecules per copper). The desorption curves do not trace the adsorption branches and form hysteresis loops. In contrast, the MeOH profile of **CuL-PF₆** displays prominent stepwise adsorption and repeated hysteresis. It reveals a gradual uptake at the low P/P_0 region and a steep uptake as the



Figure 6. MeOH adsorption isotherms of CuL-Br and CuL-PF₆ at 298 K. Closed symbols, adsorption; open symbols, desorption.

pressure increases to 0.20 P/P_0 . The isotherm reaches saturation at 111 mL g⁻¹, corresponding to 3.6 molecules of MeOH per copper and 15.9 wt % uptake by the framework. The sudden adsorption jump of CuL-PF₆ in the isotherm may originate from the breathing effect of the framework with bigger PF_6^- anions, disclosing anion-responsive dynamic behavior upon removal and readsorption of guests.^{15} Similar sorption properties have also been revealed by the CO₂ profiles of CuL-Br and CuL-PF₆ at 195 K. The CO₂ isotherms of CuL-Br reveal a gradual uptake (final uptake 47 mL g^{-1}) without apparent hysteresis, while those of CuL-PF₆ show stepwise sorption (final uptake >103 mL g⁻¹) with large hysteresis. In addition, both the MOFs favor CO_2 over Ar in porous adsorption. The reasons may be that CO₂ with a quadrupole moment of -1.4×10^{-39} C m² interacts with the framework more effectively.¹⁶ Thus, the present MOFs have flexible porous behavior at low pressure, and the guest uptake is triggered by synergistic interactions of guest molecules and counteranions (PF_6^{-}) . As shown above, weak host-guest interactions between probe molecules and the host framework and relatively free P-C rotation may play key roles in the structural flexibility.

Catalytic Properties. The framework materials are stable in usual solvents such as CHCl₃, CH₂Cl₂, MeCN, toluene, water, and alcohols, as revealed by PXRD analyses (Figure S7, Supporting Information). The materials also have good stability in weak acidic/basic media. Thus, further evaluation of their catalytic performance as well as their adsorption for small molecules is possible. The catalytic activity of the phosphinebased MOFs in heterogeneous Lewis acid catalysis was measured by using a ketalization reaction as a model reaction.¹⁷ Guest-free CuL-Br and CuL-PF₆ (dried in vacuum at 50 °C for 10 h) were used for catalysis. The crystallinity was examined after immersing the guest-free CuL-Br in the substrates (ethylene glycol and ketones) or the solvent (toluene) used, showing that the crystalline solids can be regenerated in toluene, 2-butanone, cyclohexanone, and a solution of benzophenone in toluene, and partly regenerated in acetophenone (Figure 7).

Both materials display heterogeneous catalytic activity in ketal formation with 0.2 mol % catalyst loading (Table 1; Figure S8, Supporting Information). CuL-PF₆ shows significantly higher activity than CuL-Br, such as in transforming 2-butanone to 2-ethyl-2-methyl-1,3-dioxolane (93% vs 67%), indicating that the activity is anion responsive. Such a responsive behavior is probably because PF_6^- is a weakly coordinating anion, so that the Cu(I) coordination sphere is easily accessible for the substrate.



Figure 7. Powder XRD patterns of CuL-Br (a) as-synthesized and obtained upon immersing the guest-free form in (b) toluene, (c) 2-butanone, (d) cyclohexanone, (e) acetophenone, (f) a solution of benzophenone (solid) in toluene, and (g) ethylene glycol for 5 days at RT.

Table 1. Ketalization Reaction between Ethylene Glycol and Ketones Catalyzed by CuL-Br and $CuL-PF_6$

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R' R ⁴		Phile, reflux R ¹	R ²
ketone substrate ^a	yield (CuL-Br)	yield (CuL-PF ₆)	yield (2D-Ag)
2-butanone	67%	93%	63%
cyclohexanone	36%	93%	99%
acetophenone	17%	30%	47%
benzophenone	0	0	16%

^{*a*}All reactions were carried out under Dean–Stark conditions: 7.5 mmol of ketone, 7.5 mmol of ethylene glycol, 9 mmol of toluene, 0.015 mmol of catalyst, reaction time 12 h. The quantitative analysis of the products was determined by 1 H NMR.

2-Butanone, cyclohexanone, acetophenone, and benzophenone were chosen as substrates with varied sizes and shapes to test the size selectivity of the MOFs. Compared with the activity in 2-butanone transformation, the conversions drop to 36 and 17% for the size enlarged substrates cyclohexanone and acetophenone, respectively, catalyzed by CuL-Br. A similar trend was also observed when catalyzed by CuL-PF₆. When using bulky benzophenone as substrate, no conversion was detected when catalyzed by CuL-Br or CuL-PF₆. Therefore, both materials reveal remarkable size dependence on the substrate. However, the reactivity may be affected by electronic effects as well, because the weak Cu(I) Lewis acidicity^{3a} of the present MOFs is expected to boost the catalysis of electron-rich substrates (2-butanone and cyclohexanone) rather than more electron-deficient substrates (acetophenone and benzophenone). Further control experiments were performed for a related 2D coordination network, 2D-Ag, based on AgOTf and 3-(3,5-bis(diphenylphosphino)phenyl)pyridine.^{7b} The Ag(I) Lewis acidic center of 2D-Ag has a similar MP₂N coordination environment. The activity of 2D-Ag is mainly affected by electronic effects, and the reactions of 2-butanone, cyclohexanone, acetophenone, and benzophenone yielded the corresponding products in 63%, 99%, 47%, and 16% yield, respectively (Table 1). Compared with 2D-Ag, the different reactivity pattern observed for CuL-Br and CuL-PF₆ further confirms the size selective effect.

The MOFs were readily isolated from the reaction mixture by simple filtration. ³¹P NMR spectroscopy shows that the supernatant was free from ligand contamination.^{3c} The reaction was apparently catalyzed heterogeneously, as evidenced by the conventional filtration test that no reaction took place after removal of the catalyst (Figure S9, Supporting Information). PXRD experiments were conducted to study the stability of the materials before and after ketalization (Figures S10 and S11, Supporting Information). The recovered catalysts had a powder XRD pattern similar to that of the guest free materials, while an identical diffraction pattern to the as-synthesized material was obtained after the recovered catalysts were immersed in toluene-MeCN for **CuL-Br** or **CuL-PF**₆. The results suggest that the framework structure survived the reactions. The cycling results reveal that there was no obvious loss of catalytic activity for three successive runs.¹⁸

3. CONCLUSIONS

In summary, three isostructural 3D phosphine-based MOFs have been successfully synthesized with Br⁻, Cl⁻, or PF₆⁻ as counteranions on the basis of Cu_2L_2 dimeric subunits. These complexes have 3-connected networks with an unprecedented chiral 4.12² topology and can be further simplified as a 6⁴.8²-**qtz** net arising from the rigid Cu_2L_2 tetrahedral node. The complexes possess 1D chiral channels to show anion-tunable flexible sorption properties. Preliminary study indicates that the materials have size-selectivity for ketalization reaction. Future work will focus on synthesis of enantiopure 3D phosphine materials with larger porosity, on the basis of tailored achiral subunits and chiral reticular synthesis, ^{1d,19} which may find potential application in asymmetric catalysis and separation.

4. EXPERIMENTAL SECTION

All starting materials and solvents were obtained from commercial sources and used without further purification unless otherwise stated. 4-(3,5-bis(diphenylphosphino)phenyl)-pyridine (L) was prepared according to published procedures.^{7a} The sorption isotherms were measured with a BELSORP-max automatic volumetric sorption apparatus. Before sorption measurement, the as-synthesized samples were dried at 50 °C under high vacuum for 10 h to remove the solvated molecules. Powder X-ray diffraction patterns were measured on a Bruker D8 Advance diffractometer at 40 kV and 40 mA with a Cu target tube and a graphite monochromator. Thermogravimetric analyses were performed in nitrogen and under 1 atm at a heating rate of 10 °C min⁻¹ on a NETZSCH Thermo Microbalance TG 209 F3 Tarsus.

Synthesis of CuL-Br. A mixture of CHCl₃-MeCN (v/v = 1:1, 4 mL) was carefully layered over a solution of L (5.2 mg, 0.01 mmol) in CHCl₃ (1 mL). Then, a solution of CuBr (1.4 mg, 0.01 mmol) in MeCN (2 mL) was layered over the mixture layer. The solution was left to stand at ~40 °C, and pale yellow block crystals appeared after about 4 days (5.0 mg, 73%). Elemental analysis (after drying in vacuo): found (calcd.) for $C_{35}H_{27}BrCuNP_2$ ·0.2(CHCl₃): C, 61.44 (61.34); H, 4.43 (3.99); N, 2.15 (2.03)%. IR (cm⁻¹, KBr): 3431(s), 3048(w), 2916(w), 1799(w), 1601(m), 1538(w), 1478(w), 1434(m), 1399(w), 1314(w), 1269(w), 1094(s), 878(w), 823(w), 742(m), 694(s), 598(w), 552(w), 496(w) cm⁻¹.

Synthesis of CuL-Cl. CuL-Cl was synthesized using a procedure analogous to that described for **CuL-Br**, except that CuBr was replaced by CuCl. After about 4 days, yellow block crystals were obtained (27%). Elemental analysis (after drying in vacuo): found (calc.) for $C_{35}H_{27}ClCuNP_2$ ·CHCl₃: *C*, 58.23 (58.46); H, 4.24 (3.83); N, 1.94 (1.90)%. IR (cm⁻¹, KBr):

3432(s), 3049(w), 2919(w), 1790(w), 1600(m), 1542(w), 1480(w), 1430(m), 1394(w), 1318(w), 1264(w), 1090(s), 877(w), 825(w), 744(m), 694(s), 598(w), 550(w), 496(w) cm⁻¹.

Synthesis of CuL-PF₆. CuL-PF₆ was synthesized using a procedure analogous to that described for **CuL-Br**, except that CuBr and CHCl₃ were replaced by CuPF₆·4MeCN and toluene, respectively. Colorless block crystals appeared after about 4 days (71%). Elemental analysis (after drying in vacuo): found (calc.) for $C_{35}H_{27}CuF_6NP_3\cdot0.5H_2O$: C, 57.03 (56.73); H, 4.43 (3.81); N, 2.09 (1.89)%. IR (cm⁻¹, KBr): 3410(m), 3050(w), 2920(w), 1800(w), 1610(m), 1543(w), 1480(w), 1430(m), 1400(w), 1310(w), 1263(w), 1096(m), 1026w), 999(w), 841(vs), 742(m), 695(s), 598(w), 557(m), 507(w) cm⁻¹.

Single-Crystal Structure Analyses. Determination of the unit cell and X-ray crystallographic data collection were performed on an Oxford Gemini S Ultra diffractometer equipped with graphite monochromated Enhance (Cu) X-ray source ($\lambda = 1.54178$ Å) at 150(2) K. The structures were solved by direct (CuL-Br) or Patterson (CuL-Cl) methods, following different Fourier syntheses, and refined by the fullmatrix least-squares method against F_0^2 , using SHELXTL software.²⁰ Anisotropic thermal factors were assigned to the non-hydrogen atoms, except those showing severe disorder. Hydrogen atoms were introduced in calculated positions. For CuL-Br, two CHCl₃ guests and one PPh group show crystallographically imposed disorder over two positions, and fractional occupancies, 0.45/0.25, 0.35/0.45, and 0.51/0.49, were assigned to the two positions, respectively, and restrained refinement was carried out. For CuL-Cl, restraints on anisotropic displacement parameters were applied to the disordered phenyl rings.

Crystallographic data for **CuL-Br**: $C_{73}H_{57}Br_2Cl_9Cu_2N_2P_4$, FW = 1692.04, trigonal, P3₂21, a = b = 18.5561(4) Å, c = 21.2628(5) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120.00^{\circ}$, V = 6340.5(2) Å³, Z = 3, $\rho_{calcd} = 1.329$ g cm⁻³, $\mu = 5.354$ mm⁻¹, 13013 reflections were collected (6509 were unique) for $3.45 < \theta < 62.38$, R(int) = 0.0300, $R_1 = 0.1041$, $wR_2 = 0.2175$ [$I > 2\sigma(I)$], $R_1 = 0.1139$, $wR_2 = 0.2221$ (all data) for 536 parameters, Flack absolute structure parameter = -0.04(6), GOF = 1.091. CCDC-821756.

Crystallographic data for **CuL-Cl**: $C_{37}H_{29}Cl_7CuNP_2$, FW = 861.24, trigonal, $P3_221$, a = b = 18.410(4) Å, c = 21.321(2) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120.00^{\circ}$, V = 6258(2) Å³, Z = 6, $\rho_{calcd} = 1.371$ g cm⁻³, $\mu = 5.794$ mm⁻¹, 10618 reflections were collected (5802 were unique) for 2.77 < θ < 59.98, R(int) = 0.1392, $R_1 = 0.1237$, $wR_2 = 0.2375$ [$I > 2\sigma(I)$], $R_1 = 0.2134$, $wR_2 = 0.2615$ (all data) for 409 parameters, Flack absolute structure parameter = 0.16(8), GOF = 1.118. CCDC-824217.

Catalytic Acetalization. Prior to catalysis, as-synthesized **CuL-Br** or **CuL-PF**₆ was dried at 50 °C in vacuo for 10 h to remove the guest molecules. 7.5 mmol of ketone (2-butanone, cyclohexanone, acetophenone, or benzophenone), 7.5 mmol of ethylene glycol, and 0.015 mmol of catalyst were introduced into 9 mmol of toluene. The reaction mixture was refluxed under Dean–Stark conditions for 12 h. CDCl₃ (2 mL) was added to the reaction mixture and the resulting suspension was centrifuged for ¹H NMR study. The quantitative analysis of the products was determined by ¹H NMR. For subsequent run, the catalyst was recovered by filtration, washed fully with toluene and Et₂O in turn, immersed in toluene-MeCN for ca. 6 days, and degassed in vacuo at 50 °C for 10 h.

Chemistry of Materials

ASSOCIATED CONTENT

S Supporting Information

Crystallographic data in CIF format, additional structural data and figures, XRPD, adsorption, CD and NMR analyses. This material is available free of charge via the Internet at http:// pubs.acs.org.

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