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Rational Design of Porous Coordination Polymers Based on Bis(phosphine)MCl$_2$ Complexes That Exhibit High-Temperature H$_2$ Sorption and Chemical Reactivity

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Ⓢ *Supporting Information*

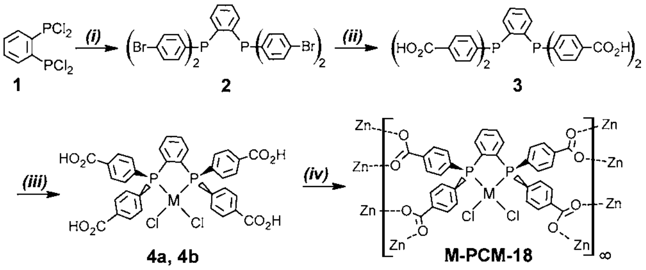
ABSTRACT: MCl$_2$ complexes of a new *p*-carboxylated 1,2-bis(diphenylphosphino)benzene ligand are effectively utilized as tetratopic building blocks to prepare isostructural porous coordination polymers with accessible reactive metal sites (M = Pd, Pt). The crystalline materials exhibit unusual and fully reversible H$_2$ sorption at 150 °C. Post-synthetic reactivity is also possible, in which Pt−Cl bonds can be activated to provide organometallic species in the pores.

Porous coordination polymers (PCPs, i.e., MOFs) that contain unsaturated 4d or 5d transition-metal sites remain somewhat exceptional. Their rarity may be due to difficulties in the preparation of stable networks using heavier transition-metal precursors while concomitantly being able to control the extent of coordination. However, such materials would be useful for specific solid-state applications because guest molecules could access the structurally defined, 'soft' open metal coordination sites inside the micropores.[1] This would allow for adsorbates to engage in moderate or strong bonding interactions with the unsaturated metal sites, potentially resulting in pore-confined chemical reactivity. Some examples of pertinent solid-state applications include: catalysis,[2] enhanced binding of gas molecules via elevated enthalpies of adsorption,[3] molecular sensing,[4] and postsynthetic coordination and/or exchange of organic species.[5]

In some instances it is possible to generate open metal sites in PCPs based on 3d transition metals, *s*-block cations, or lanthanides, via the removal of labile solvate ligands (e.g., OH$_2$ or *N*,*N*-dimethylformaldehyde (DMF)) by heating under vacuum. Examples of this type of activation have shown significantly increased gas adsorption enthalpies and capacities, indicative of direct metal−guest interactions.[6] However, synthetic control over the degree of metal solvation during PCP synthesis is limited. Alternatively, installation of unsaturated metal sites into PCPs has shown recent promise. Notable examples include, incorporation of Cr(CO)$_3$ via η^6-coordination to aromatic structures in the pores,[7a] addition of carbene-bound Pd(II) organometallics,[7b] and uptake of metal cations into pre- or post-synthetically installed chelating groups.[7c−g]

The incorporation of unsaturated metal species into PCPs using pre-formed coordination complexes or organometallic species with known and desirable chemical reactivity—especially those based on heavier and noble transition metals—remains a much more significant synthetic challenge. We have been interested in the construction of PCPs based on organophosphine ligands, where the available soft P: donor sites can be used to coordinate catalytic metals, either pre- or post-synthetically. Phosphine ligands are ubiquitous in homogeneous catalysis and are well suited for coordination of a broad range of heavier transition metals that have not previously been incorporated into PCPs. The coordination of Au(I) to individual P: sites in PCM-10 (PCM = Phosphine Coordination Material) has already been demonstrated.[7e] In a recent extension of this work, we have concentrated on the synthesis of pre-formed metalated building blocks based on bis(phosphines) that would potentially exhibit enhanced chemical stability due to the chelate effect, thus preventing loss or exchange of the metal site upon construction of a PCM in the presence of secondary metal species. Moreover, 1,2-substituted bis(phosphines) are excellent ligands for the activation of soft transition-metal centers toward chemical reactivity and catalysis.[8] The preparation of the previously unreported tetra-*p*-carboxylated bis(phosphine) **3** (Scheme 1) was specifically targeted to provide a versatile building block for the preparation of isostructural coordination polymers, in which numerous different unsaturated metal species

Scheme 1. Synthetic Route to Obtain the M-PCM-18 Materials[a]



[a](i) 4 eq. 4-bromolithiobenzene, THF, 195 K; (ii) 4.5 equiv *n*-BuLi, THF, 195 K, CO$_2$, HCl; (iii) 1 equiv M(COD)Cl$_2$ (M = Pd, Pt), THF, 303 K; (iv) 3.5 equiv Zn(NO$_3$)$_2$·*x*H$_2$O, DMF/EtOH (2.25:1); 10 d, 318 K.

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may be incorporated. The metalated complexes (e.g., **4**) are structurally rigid. This greatly increases the possibility of readily obtaining porous coordination polymers (e.g., **5**) via the formation of coordination bonds between secondary metal salts and the ancillary *p*-carboxylate moieties.

The ligand was prepared as shown in Scheme 1: low-temperature treatment of 1,2-bis(dichlorophosphino)benzene (**1**) with 1-lithio-4-bromobenzene in tetrahydrofuran (THF) gave the tetra-*p*-brominated intermediate **2** in 64−87% yield. The tetra-lithiated form of **2** was then prepared in cold THF using excess *n*-butyllithium. *In situ* treatment with solid CO_2 afforded the lithium carboxylate salt in near-quantitative yield. The free acid (**3**) was obtained by protonation with HCl in degassed H_2O. The bis(phosphine) **3** is insoluble in most apolar organic solvents but has reasonable solubility in polar solvents, including alcohols. Initial coordination chemistry studies focused on the use of Pd(II) and Pt(II) precursors that incorporate square-planar open metal sites (**4**) and importantly lock the resulting metalloligand building block into a rigid orientation. Metal precursors with basic ligands (e.g., acetates) were unsuitable since these tended to favor deprotonation of the ancillary carboxylic acid groups. Instead, reaction of **3** in THF with $M(COD)Cl_2$ precursors (M = Pd, **4a**; Pt, **4b**; Scheme 1) resulted in the desired P_2-coordination complexes, which were recrystallized from ethanol.

The single crystal structure of the molecular species **4b** confirms that when complexed, each phosphine-P is pseudotetrahedral. The complex has approximate C_2-symmetry in which the four *p*-aryl carboxylic acids project above and below the planar P_2MCl_2 core (Figure 1). As building blocks for the formation of coordination polymers, **4a** and **4b** may be considered planar four-connected nodes (Figure 1; **4b**, inset) that incorporate open metal species at their centers. **4a** and **4b** are structurally similar to the tetratopic organic ligands such as biphenyl-3,5,3′,5′-tetracarboxylate used by Schröder et al. for the NOTT-*x* series[9a] and the larger 4,4′,4″,4‴-benzene-1,2,4,5-tetrayltetrabenzoate employed by Hupp and Farha,[9b] all of which have proven great utility in the construction of highly porous and stable framework materials.

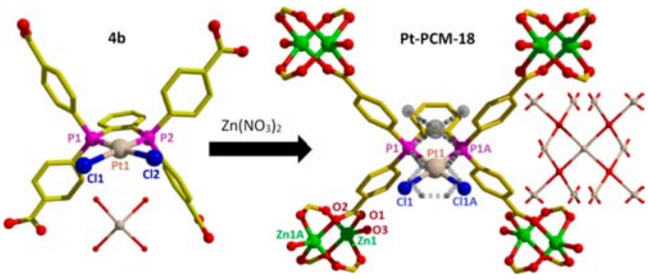

Figure 1. Left: crystal structure of the $PtCl_2$-bis(phosphine) molecular species (**4b**) with simplified node structure (inset). Right: the corresponding Pt-PCM-18 crystal structure with Zn(II) paddlewheel nodes and puckered square grid net (far right); disorder associated with individual monomers is shown in dashed gray bonds.

Milligram quantities of **4** were subsequently reacted with Zn(II) salts in solvent mixtures that have been previously established as ideal for the formation of other PCM materials.[7e,10] Direct treatment of $Zn(NO_3)_2$ with **4a** or **4b** in ethanol/DMF mixtures resulted in deprotonation of the carboxylic acids and Zn−O coordination to give crystalline products. Single crystal XRD analysis revealed two isostructural porous PCMs with the formula unit, $[Zn_2(\mathbf{4a/b})(OH_2)_2]\cdot$solv, hereafter referred to as M-PCM-18 (M = Pd, Pt). The most immediately striking feature of the polymer structures was their significantly high symmetry compared to the monomeric precursors. M-PCM-18 crystallizes into the body-centered orthorhombic space group *Imma*, whereas the monomer **4b** was solved in the much lower-symmetry monoclinic space group, $P2_1/c$. A direct comparison of the structures shows that configurational freedom in the molecular species (originating from rotation of P-aryl groups around P−C bonds) has been removed upon insertion into the polymer. In fact, the high symmetry of the polymeric metalated bis(phosphine) complex imposes a site symmetry of $2/m$ at the center of the chelate ring, which is higher than the inherent symmetry of the ligand itself. As a result, each monomer can be inverted and superimposed upon itself while maintaining the geometry of the P-aryl groups (Figure 1; gray dashed bonds). This induces disorder in the lattice of PCM-18 such that monomers are randomly arranged in one of the two possible orientations. PCM-18 has infinite 3D connectivity, in which each carboxylate group is coordinated to Zn(II) paddlewheel dimers with axial OH_2 ligands. The result is an unusual puckered square grid topology based on two different four-connected square-planar nodes (Figure 1; Pt-PCM-18, inset). There are large pore openings in all three crystallographic planes (Figure 2); the largest pore windows in the *ac*-plane have maximum accessible dimensions of 1.7 × 2.0 nm.

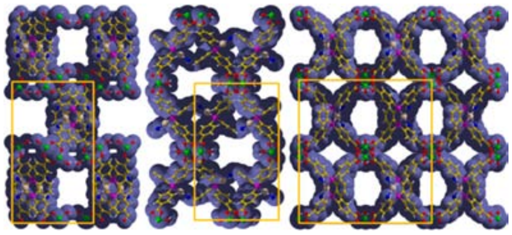

Figure 2. Space-filling representation of Pt-PCM-18 viewed normal to the *bc*- (left), *ac*- (center), and *ab*-planes (right).

The ability to construct isostructural and noninterpenetrated frameworks using the building blocks **4a** and **4b** offers a range of interesting opportunities to compare and contrast their resulting solid-state properties and reactivity. According to TGA, the as-synthesized M-PCM-18 materials are thermally stable >300 °C after removal of uncoordinated DMF and H_2O solvent molecules from the pores (Figures S1 and S2). PXRD confirmed that the crystalline products are stable in air for weeks or upon solvent exchange with $CHCl_3$ and subsequent suspension in fresh DMF/EtOH mixtures (Figure S3). To probe the bulk surface areas of the M-PCM-18 materials, samples were subjected to repeated cycles of solvent exchange by suspension in $CHCl_3$ over 3 days followed by evacuation at 423 K for 12 h. N_2 was not significantly adsorbed inside the pores of either Pd- or Pt-PCM-18. However, CO_2 was found to be an appropriate probe gas, revealing BET surface areas of 211 and 244 $m^2\ g^{-1}$ at 196 K (for Pd and Pt, respectively); at this temperature, CO_2 was reversibly adsorbed inside M-PCM-18 (Figure S4).

Next, the H_2 sorption properties of the M-PCM-18 materials were assessed. At 77 K, both Pd- and Pt-containing materials showed modest H_2 uptakes of 36 and 53 $cm^3\ g^{-1}$ with reversible type I isotherms (Figure S5). The isosteric heats of H_2 adsorption (Q_{st}) were obtained using the accepted virial expansion method,[11] yielding values of 2.75 and 4.82 kJ mol^{-1}

for Pd- and Pt-PCM-18, respectively (Figures S6−S10). The relatively low magnitude of these values did not suggest any significant interaction of H_2 with the metals at 78 K. However, it is known that open Pd(II) or Pt(II) sites can interact with the filled 1σ and empty $1\sigma^*$ orbitals of H_2 via their d_{z^2} and d_{xz} orbitals, perpendicular to the P_2MCl_2 plane,[8,12] or can induce H_2 clevage.[13] A number of reports that show Kubas-type[12a,b] η^2−H_2 interactions are commonly observed at ambient or elevated temperatures for transition-metal centers that contain bis(phosphine) ligands. For example, the isolable complex *trans*-$[Ru(L)_2H(\eta^2\text{-}H_2)]$ (L = η^2-bis(phosphinoethane)) is formed at 358 K under 24.1 bar of H_2.[12c] Recent theoretical studies have also predicted moderately strong $PdCl_2$−H_2 interactions in modified COF-301[12f] and axial η^2-H_2 bonding at vacant Ni^{2+} sites in other PCPs.[12g] So, it was decided to study H_2 adsorption in M-PCM-18 over a wider temperature range. Interestingly, at temperatures above 300 K both Pd- and Pt-PCM-18 showed marked increases in H_2 adsorption between 0−1 bar. Adsorption−desorption isotherms were collected on freshly activated samples at 25 K increments, which revealed maximum H_2 sorption occurred at ~425 K and 1.0 bar H_2 for both materials (Figure 3a,b; black lines). Between 425−500 K the total amount of adsorbed H_2 was diminished but remained higher than at ambient temperature; the high-temperature H_2 adsorption isotherms were always linear, suggesting that saturation was not reached at 1.0 bar (Figure S11; closed circles). In addition, desorption phases showed marked hysteresis, indicative of relatively strong H_2 binding inside the materials, even at 425 K (Figure S11; open circles). When these samples were immediately subjected to readsorption−desorption, no further H_2 was adsorbed, presumably because the available H_2 sorption sites in the pores were still occupied (Figure S11; triangles). If the same samples were reactivated *in situ* by prolonged evacuation (4 h; also at 425 K), it was possible to obtain the original hysteretic adsorption−desorption profiles over repeated cycles, without any decrease in H_2 capacity (Figure S12).

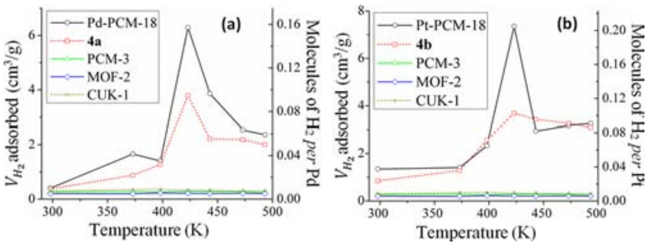

Figure 3. (a) Temperature-dependence of H_2 adsorption in Pd-PCM-18 (**4a**), the ligand (**2**), complex (**3**), and other PCP materials at elevated temperature. (b) Corresponding data for Pt-PCM-18.

To further investigate the nature of the high-temperature H_2 adsorption observed in the M-PCM-18 solids, a number of control adsorption measurements were performed under otherwise identical conditions. First, three other previously reported PCP materials were studied in an attempt to confirm the role of the accessible bis(phosphine)MCl_2 sites in the H_2 adsorption. These materials were specifically chosen because they each contain structural subunits that are also present in M-PCM-18: PCM-3[10] contains free R_3P: sites and Zn(II) metal nodes; MOF-2[14] is constructed entirely of 1,4-terephthalate and Zn_2 paddlewheels with apical OH_2 groups, structurally identical to the nodes in M-PCM-18; CUK-1[15] is a highly robust 3D PCP based on Co(II) and pyridine-2,4-dicarboxylate that adsorbs 1.6 wt % H_2 at 77 K with characteristic reversible type-I behavior. None of these materials showed any measurable H_2 adsorption across the entire temperature range 300−500 K when activated and measured using the same methods and apparatus as for M-PCM-18 (Figure 3a,b). Thus, it can be reasonably assumed that neither the phosphine moieties nor the Zn paddlewheel nodes are responsible for the observed H_2 sorption behavior of M-PCM-18. In stark comparison, when the amorphous metalated ligands **4a** and **4b** were studied under identical conditions, significant H_2 adsorption was observed above 300 K, also with a peak around 425 K. The overall w/w H_2 uptakes were slightly lower compared with the crystalline PCMs, which is reasonable because the ligands do not contain open pore networks to permit easy movement of H_2 throughout the samples. Moreover, the metal-free ligand (**3**) showed no H_2 uptake at elevated temperatures (Figure 3). Thus, the analogous behavior of the complexes and M-PCM-18 materials strongly indicates the role of the Pd^{2+} or Pt^{2+} bis(phosphine) sites in the high-temperature H_2 binding behavior.

In absolute terms, the maximum H_2 adsorption observed at 425 K was equivalent to 0.16 or 0.22 H_2 molecules per Pd or Pt site, respectively. This is similar in magnitude to what has been recently observed for Kubas-type H_2 adsorption at 298 K in coordinatively unsaturated V(III)-based PCPs (albeit under 85 bar H_2), in which 0.25−0.88 H_2/V were reported.[12h] Further analysis of the M-PCM-18 materials post-H_2 adsorption at high temperature was performed to check for stability and reversibility. The 77 K H_2 sorption characteristics were recollected for each sample after consecutive high-temperature sorption runs, which also gave sorption behavior that was unchanged from the as-synthesized materials (Figure S13). The ^1H and ^{31}P CP-MAS NMR spectra of Pt-PCM-18 were collected for the as-synthesized material and post-H_2 addition at 425 K. The spectra were unchanged in both cases, and no hydride signals were observed in the latter at room temperature (Figure S14). The %Cl elemental microanalysis was also unchanged after repeated cycles of 425 K H_2 adsorption−desorption, and there was no visible change in the far-IR spectra of the materials. Hence, it appears that Pt−Cl bonds were not activated (which would be the case for chemisorption of H_2 followed by reductive elimination of HCl). Furthermore, TGA studies in which samples were heated in a 5% H_2 atmosphere did not reveal unusual decomposition versus the same measurement when carried out under He (Figure S2).

To explore the potential of the M-PCM-18 materials for catalytic applications, reactions to postsynthetically activate the Group 10 metal sites via substitution of the chloride ligands were also attempted. Initial studies in this regard focused on reactions that can be conducted at low temperature using reagents that are selective for M−Cl bonds. Pringle et al. demonstrated that similar bis(phosphine)$PtCl_2$ complexes could be employed to prepare organometallic metal−alkyl species by direct treatment of the Pt−Cl bond with diazoalkanes, resulting in α-migration of the chloride at ambient temperature (e.g., Scheme 2).[16] The platinum(II)-alkyls thus obtained could be employed in catalytic reductive elimination reactions with alkynes.[17] In a control study, the molecular complex **4b** was easily converted into the racemic organometallic complex $[PtCl(CHClCO_2Et)(\eta^2\text{-}\mathbf{3})]$ by reaction of excess ethyldiazoacetate in ethanol/CH_2Cl_2 at 303 K over 48 h (see SI). Similar treatment of Pt-PCM-18 was then attempted by covering single crystals with a solution of the diazo compound in CH_2Cl_2 and standing for 3 days at ambient temperature (Scheme

Scheme 2. Post-Synthetic Reaction of Pt-PCM-18 with Ethyldiazoacetate to Generate Activated Pt(II)-Organometallic Species

2). The crystals were washed several times with fresh CH_2Cl_2 and air-dried.

Detailed solid-state NMR studies on the product confirmed near-quantitative conversion of $PtCl_2$ sites inside the crystallites (Scheme 2). In comparison to the parent Pt-PCM-18, the ^{1}H-MAS NMR revealed a new resonance at 1.1 ppm corresponding to aliphatic protons in the structure (Figure S15A). The ^{13}C-{^{1}H}-CP/MAS NMR spectrum showed two clear resonances at 12.8 and 60.1 ppm corresponding to the CH_3CH_2 group, while resonances were also observed at 183 and 166 ppm due to the ester C═O groups. In addition, a broad resonance at 73.9 ppm corresponds to the chiral Pt−C fragment (Figure S15B). The ^{31}P{^{1}H}CP/MAS spectrum obtained at a regular contact time of 5000 μs revealed a broad and nonsymmetrical resonance due to overlapping of at least two resonances, as expected due to lowering of symmetry at the Pt center (Figure S15C). The peaks were more resolved at a contact time of 100 μs, yielding chemical shift values of 46.1 and 40.6 ppm, which correspond closely to what was observed for the monomer **4b** (45.3 and 40.9 ppm), and in the original work.[16,17] In contrast, the precursor Pt-PCM-18 spectrum only showed a single, symmetrical peak ∼42 ppm (Figure S14B). Additional peaks were also observed in the FT-IR spectrum ∼1689 and 355 cm^{-1}, corresponding to the ester and Pt−C moieties, respectively (Figure S16).

In summary, we have developed a versatile bis(phosphine) ligand that can be used to construct coordination polymers containing a variety of open metal sites, as a means to impart unusual chemical reactivity by rational design. We are presently investigating further the catalytic properties of the M-PCM-18 materials, in addition to the incorporation of earlier 4d and 5d transition metals, such as Rh(CO)Cl into similar polymers, to access fundamental catalytic reactions, such as hydroformylation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterizing data. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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