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A New PCP-Pincer for the Rational Synthesis of Coordination Polymers with Versatile Chemical Reactivity: Selective Activation of CO₂ Gas over CO Gas in the Solid-State

Junpeng He,^[a] Nolan W. Waggoner,^[a] Samuel J. Dunning,^[a] Alexander Steiner^[b] Vincent M. Lynch,^[a] and Simon M. Humphrey*^[a]

Abstract: A tetra(carboxylated) PCP-pincer ligand has been synthesized as a versatile new building block for the assembly of porous coordination polymers (PCPs) with programmable chemical reactivity. The pincer ligand is suitable for a range of cyclometallation reactions, to prepare analogues of known molecular catalysts. The air- and moisture-stable PCP metalloligands are rigid tetratopic linkers that are geometrically akin to ligands used in the synthesis of robust metal-organic frameworks (MOFs). Here, the design principle is demonstrated by cyclometallation with Pd(II)Cl and subsequent use of the metalloligand to prepare a crystalline 3D MOF by direct reaction with Co(II) ions and structural resolution by single crystal X-ray diffraction. The Pd-Cl groups inside the pores are accessible to post-synthetic modifications that facilitate chemical reactions previously unobserved in MOFs: a Pd-CH₃ activated material undergoes rapid insertion of CO₂ gas to give Pd-OC(O)CH₃ at 1 atm and 298 K. However, since the material is highly selective for the adsorption of CO₂ over CO, a Pd-N₃ modified version resists CO insertion under the same conditions.

Efforts to prepare PCPs and MOFs with advanced solid-state chemical reactivity are driven by the desire to access materials that can adsorb 'guest' molecules more strongly,^[1] and that could potentially catalytically activate adsorbates inside the pores.^[2] The vast majority of known PCPs and MOFs adsorb small molecules (e.g., N₂, O₂, H₂, CO₂) via simple physisorption (dipolar) interactions, typically with binding energies in the range 5–40 kJ mol⁻¹.^[3] Adsorption and desorption processes in this regime are conveniently reversible, but the adsorption capacity is limited. Recent research by several groups has shown that the zero-coverage binding energy (Q_{st}) of adsorbates can be increased by the inclusion of stronger adsorption sites in the pores. Lewis acid sites tend to induce stronger host-guest binding interactions, as demonstrated for materials with vacant metal coordination sites,^[4] or via the inclusion of polarizable cations.^[5] It has also been shown that pore functionalisation with Lewis bases can induce stronger guest binding, for example in the adsorption of CO₂ by amine-decorated materials.^[6]

The observation of stronger physisorption at vacant metal sites in PCPs and MOFs is perhaps not surprising, since this is a prerequisite of chemical catalysis. In fact, there are an increasing number of examples of organic reactions catalysed

by MOFs that are based on analogues of homogeneous catalysts.^[7] For example, in 2010 Champness and co-workers were able to utilize a Mn(CO)₃Cl-chelated building block to prepare a photoreactive MOF,^[7a] more recently via a similar route, Lin and co-workers used an Ir-functionalized MOF to activate C-H bonds;^[7b] Fujita and co-workers structurally characterized a Pd-containing MOF that could brominate aromatic molecules;^[7c] However, chemisorption and activation of common light gas molecules (for which PCPs and MOFs display very high storage capacities) remains largely elusive.^[8] Arguably, the ability to sequester, activate and convert gas molecules such as CO₂ inside high surface area MOFs would be both economically and environmentally more appealing than targeting organic conversions, for which large-scale homogeneously-catalyzed processes already exist.

The activation of small molecules by organometallic complexes is an important ongoing area of research.^[9] A number of systems have been shown to be proficient in difficult chemical transformations, including the activation of N₂.^[10] The reactivity of such molecular complexes is extremely sensitive to the identity of the metal and its ligand donor set. This chemistry relies primarily on later 4d and 5d metals that engage in increased metal-ligand covalency; the donor sets are correspondingly 'soft' atoms, such as phosphines and carbenes.^[11] This presents a synthetic challenge for the synthesis of PCPs and MOFs containing sites potentially catalytically reactivity, since their assembly is usually conducted in solution via the formation of coordination bonds between 'hard' 3d transition metal ions and carboxylic acid donors.

One effective approach to this problem has been demonstrated by Cohen,^[12a,b] and others,^[12c] and involves the post-synthetic modification of MOFs to incorporate secondary coordination sites within the pores, which can be doped with catalytically-active metal species. This type of method offers extensive design flexibility. However, it is relatively common for post-synthetically modified materials tend to lose crystallinity, which impedes absolute structural resolution of the materials.^[13]

An alternative synthetic approach, which is more likely to result in the formation of highly crystalline materials, involves the use of pre-formed catalyst complexes as chemically robust 'metalloligands' for the *direct* assembly of PCPs/MOFs. This can be achieved by strategic positioning of carboxylic acid groups in ancillary positions of a given complex. The resulting metalloligands are closely related to water-soluble versions of homogeneous catalysts, originally designed to facilitate operation under biphasic conditions.^[14] Using this approach, we previously synthesized a tetratopic building block by *para*-carboxylation of the well-known 1,2-*bis*-(diphenylphosphino)benzene ligand, and then formed complexes with PdCl₂ and PtCl₂. The chelating nature of the ligand resulted in geometrically rigid and thermally stable metalloligands, which underwent direct reaction with Zn(NO₃)₂ in a mixed organic/aqueous solvent to provide isostructural porous solids, PCM-18 (PCM = phosphine coordination material).^[15]

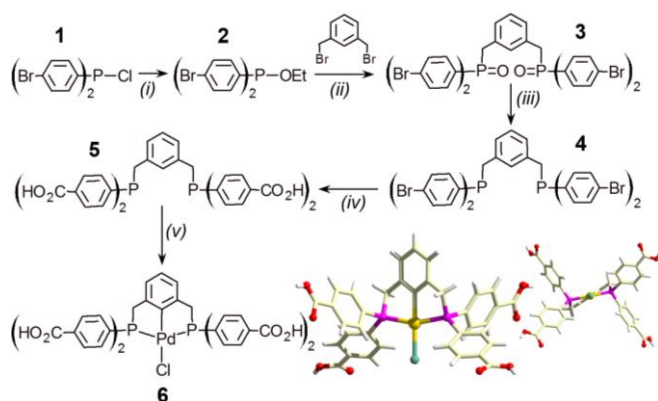
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Notably, the coordinatively-unsaturated square-planar Pd(II) and Pt(II) metal sites showed unusual adsorption behavior towards H₂ at elevated temperatures, the recently elaborated *in silico* by Head-Gordon and co-workers.^[16]

We then looked to apply the same strategy to the preparation of cyclometallated metalloligands in order to further improve the resistance to leaching of the active site during framework assembly, as well as to access more interesting reactivity toward small molecules. PCP-pincer ligands were an obvious choice to achieve both of these aims.^[17] Our approach to the design and synthesis of a suitable PCP-pincer is shown in Scheme 1. Briefly, the *p*-brominated diaryl chlorophosphine (**1**) was prepared by a known literature method^[18] and converted to the diaryl ethylphosphinite (**2**) by slow addition of sodium ethoxide at low temperature. Phosphine **2** was then reacted with 0.5 equivalents of 1,3-bis(bromomethyl) benzene *via* the Arbuzov reaction to yield the bis(phosphine oxide) (**3**), which was subsequently cleanly reduced to the bis(phosphine) (**4**) by excess HSiCl₃. The final ligand **5** was obtained as the free acid by lithiation and direct work-up with solid CO₂, followed by precipitation with HCl.



Scheme 1. Phosphine **1** was obtained *via* a literature route,^[18] (i) 1 eq. NaOEt in EtOH with **1** in Et₂O, -20 °C, 30 min; (ii) **2** and 0.42 eq. 1,3-(CH₂Br)C₆H₄, *p*-xylene reflux, 18 h; (iii) 15 eq. HSiCl₃, toluene reflux, 18 h, NaHCO₃ quench; (iv) 5 eq. *n*-BuLi, THF, -78 °C, 1 h, then added excess CO₂, warmed to r.t., dissolution in degassed H₂O, acidification with 2.0 M HCl to pH 1; (v) 1 eq. PdCl₂(MeCN)₂, THF reflux, 3 d. Bottom left: single crystal structure of metalloligand **6**; inset: view along Cl–Pd–C, showing the C₂-symmetry and rectangular orientation of CO₂H groups.

The ligand **5** is suitable for metallation with a range of transition metal ions. One caveat is that metallation reactions need to be conducted under conditions that disfavor deprotonation of the CO₂H groups. Fortunately, metallation using organometal halides in aprotic organic solvents involves activation of an aromatic C–H bond and the resulting elimination of HX (X = Cl, Br, I) decreases the reaction pH. This negates ligand deprotonation that would otherwise result in the formation of unwanted oligomers. As a simple first example of this strategy, **5** was refluxed directly with PdCl₂(MeCN)₂ in tetrahydrofuran (THF) to yield the cyclometallated complex [PdCl(**5**)] (**6**), which is suitable for purification by column chromatography using acidified silica. Single crystals of **6** were

grown by slow evaporation of a concentrated ethanol solution, allowing for structural determination by single crystal X-ray diffraction (SCXRD; Scheme 1).[†] This study reveals important information regarding the geometry of the metalloligand as a building block for the subsequent formation of polymers. The Cl–Pd–C axis is located on a 2-fold symmetry site, resulting in a symmetric molecule in which the ancillary carboxylates are rigidly locked into a rectangular orientation (Scheme 1; bottom left). The metalloligand **6** is topologically comparable to the 1,2,4,5-tetrasubstituted aromatic carboxylates used widely in MOF synthesis by Hupp & Farha and others.^[19]

Initial attempts to prepare porous polymers based on **6** were conducted using 3*d*-transition metal ions. In addition to the identification of several new materials with 1D (chain) and 2D (layered) structures, large purple crystals of an infinitely porous 3D coordination material were obtained by reaction of **6** with Co(BF₄)₂ in a mixture of *N,N*-dimethylformamide (DMF), ethanol and H₂O (2:3:1) at 50 °C. SCXRD revealed the material (henceforth named PCM-36) to have the formula composition [H₂N(CH₃)₂]₃[Co₈(OH)₃(**6**)₄(OH₂)₁₇].solv.[†] PCM-36 contains two symmetry-unique PCP-PdCl building blocks that are multiply coordinated to Co(II) ions through all available carboxylate groups (Figure 1A). There are two distinct inorganic nodes in this material: a 5-connected [Co₃(μ₃-OH)(OH₂)₅]⁵⁺ node; and a 3-connected [Co₂(μ₂-OH)(OH₂)₆]³⁺ node (Supporting Information). Rotational disorder of two of the *P*-aryl groups results in some of the Co(II) sites having partial occupancies. The formula unit obtained from the SCXRD study is in excellent agreement with results obtained by elemental microanalysis of a bulk crystalline sample that was subjected to treatment under vacuum to remove all residual solvent (observed/calculated): C, 44.22 {44.15}; H, 3.04{3.68}; N, 0.99{1.03}; Cl, 3.24{3.48}%. Crystalline PCM-36 is air- and moisture-stable over months and can be re-submerged in alcohols or aqueous environments *post*-evacuation, resulting in retention of bulk crystallinity (Supporting Information).

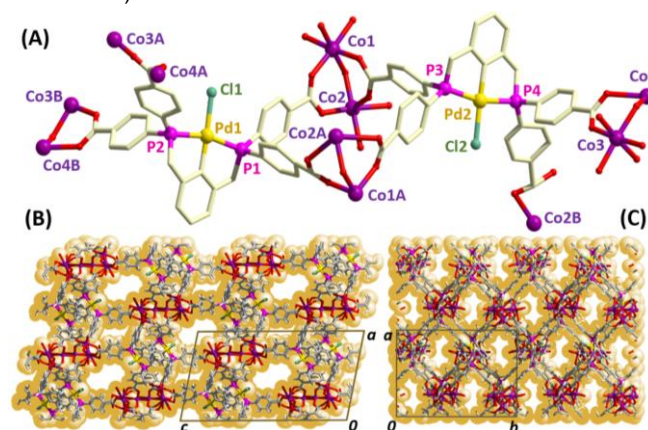


Figure 1. (A) The asymmetric unit of the PCM-36 polymer framework showing Co(II)-carboxylate connectivity (pore constituents are omitted for clarity). (B) Space-filling and superimposed ball-and-stick representation in the crystallographic *ac*-plane showing the largest oval shaped pores. (C) Alternative view in the *ab*-plane.

The extended structure of PCM-36 reveals micropores in all three crystallographic directions (Figure 1B&C); the largest oval-shaped pore openings (seen in the *ac*-plane; Figure 1B) have two accessible Pd–Cl sites, separated by 15.4 Å (Pd...Pd distance).

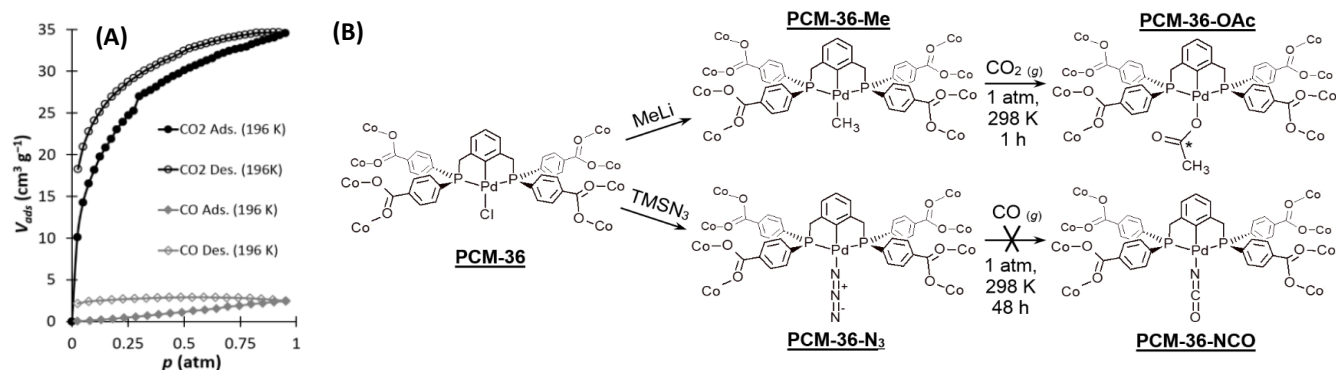
Thermogravimetric analysis (TGA) of as-synthesized PCM-36 indicated that free solvent was removed below 120 °C after which no further mass loss occurred until the onset of framework decomposition at approximately 370 °C (Supporting Information). The bulk surface area of evacuated PCM-36 was relatively low (112 m² g⁻¹; BET method using CO₂ as the probe gas), but the type-I form of the adsorption-desorption isotherm is indicative of bulk microporosity (Figure 2A). The crystallinity of samples of PCM-36 was also assessed by powder X-ray diffraction (PXRD; Supporting Information), which confirmed phase purity with the SCXRD result (Supporting Information).

Next, reactions were conducted to explore the potential activation of Pd(II) sites inside the pores, by substitution of Cl⁻ ligands with more weakly coordinating anions. There are many such precedents in the literature for analogous molecular Pd-based pincer complexes, whereby replacement of Cl anions has been shown to facilitate chemical reactivity towards various small molecule adsorbates.^[20,21,23,24b] In all studies, fresh crystalline samples of PCM-36 were desolvated by heating at 80 °C overnight *in vacuo*. The crystals were subsequently immersed in dry organic solvents and reagents were slowly added drop-wise and allowed to stand for 2–24 h under N₂ and without stirring. The treated crystals were then subjected to cycles of solvent exchange using the same solvent, before drying under vacuum prior to characterization (see PXRD; Supporting Information).

First, we attempted to generate Pd–H groups *via* reaction with NaBH₄ in methanol by the method of Goldberg and co-workers,^[20] but the PCM-36 framework underwent decomposition and elemental Co was observed. In contrast, slow addition of a dilute solution of methylolithium (MeLi) in THF (approx. 10 equiv. *per* Pd; Milstein and co-workers^[21]) did not cause decomposition and appeared to result in the generation of Pd–Me groups *via* elimination of LiCl. Quantitative analysis of

band ca. 279 cm⁻¹ that is attributed to the methyl Pd–C stretch, based on literature values for a series of square-planar PdCl₂X₂ complexes (Supporting Information).^[22] In addition, the Pd–C(*sp*²) stretching band (ca. 410 cm⁻¹) becomes broadened toward lower wavenumbers in the Me-modified material, which is expected due to the stronger *trans*-influence of CH₃⁻ *versus* Cl⁻. In addition, the elemental microanalysis of the product showed a reduction in the total amount of Cl (to <1%, *vide supra*). Collectively, these data suggest that a fraction of the Pd–Cl sites in PCM-36 were successfully modified.

Wendt and co-workers have shown that CO₂ can undergo insertion into Pd–C bonds of pincer complexes in benzene solution; insertion is commonly rapid at room temperature for allyl substituents and occurs at 80 °C for CH₃.^[23] When evacuated PCM-36-Me was exposed to dry CO₂ for 6 h at 298 K, an intense new band was observed in the FT-IR spectrum ca. 1645 cm⁻¹ that was not observed when the parent PCM-36 was exposed to CO₂ gas (Figure 3A). We suspected this might be due to the carbonyl asymmetric stretch (*ν*'_{CO}) of a Pd–OC(O)Me moiety obtained by CO₂ insertion into Pd–Me bonds (Figure 2B). By comparison, μ₂-bridging acetates in Pd(OAc)₂ have *ν*'_{CO} = 1593 cm⁻¹ while free methylacetate has *ν*'_{CO} = 1740 cm⁻¹. The intermediate *ν*'_{CO} value observed here is indicative of a *pseudo*-monodentate acetate binding mode, in which one Pd–O bond is much shorter than the other; this is expected based on known crystal structures of PCP-M-OAc complexes (M = Ni, Pd).^[23b,24] It should also be noted that the carbonyl stretch for lithium acetate occurs in the solid state at 1588 cm⁻¹. Therefore, it is highly unlikely that reaction of any residual MeLi with CO₂ in the pores of PCM-36 is responsible for the new feature at 1645 cm⁻¹ (Figure 3A). To support this premise, a sample of PCM-36-Me was then exposed to 99.5% ¹³C CO₂ for 4 h and analyzed by direct excitation ¹³C-MAS-NMR: a single broad peak was observed at 167 ppm accompanied by intense side bands, which is directly in the range of other known PCP-Pd-OAc complexes (152–175 ppm; Supporting Information).^[25] Furthermore, the corresponding carbonyl-C peak for LiOAc occurs significantly more up-field, at 181 ppm.



this transformation is not straightforward to perform because, unlike in the molecular regime, NMR is not a generally applicable tool in the solid-state, especially when there are multiple paramagnetic centers present (e.g., high-spin Co(II), *S* = 3/2). However, solid-state FT-IR provides some important insights: a comparison of the far-IR spectra for the parent PCM-36 and MeLi-treated samples shows the appearance of a new

Figure 2. (A) Adsorption-desorption isotherms for CO₂ and CO gas in PCM-36. (B) Post-synthetic modifications applied to PCM-36 and reaction outcomes upon exposure of dry crystalline samples of modified PCM-36 to CO₂ and CO gas.

In an alternative experiment, treatment of PCM-36 with trimethylsilyl azide (TMS-N₃; 15 eq.) in THF gave a partially Pd-N₃-substituted material *via* elimination of TMS-Cl. The FT-IR spectrum of this material shows an intense new band due to the characteristic N₃ symmetric stretching mode ($\nu_{N_3} = 2075 \text{ cm}^{-1}$), which is significantly shifted compared to the corresponding band for free TMS-N₃ ($\nu_{N_3} = 2130 \text{ cm}^{-1}$) and is in good agreement with the observation of Lee *et. al* (Figure 3B).^[26] Elemental microanalysis of the PCM-36-N₃ material showed a significant increase in the total amount of N (to 3.06%, *vide supra*). We were interested in generating the azide-functionalized material because molecular analogues are able to directly react with CO gas to form NCO ligands by an *intra*-molecular rearrangement, accompanied by the release of N₂ gas (Figure 2B). When PCM-36-N₃ was exposed to 1 atm of CO, no reaction was observed even after 48 h at 298 K. Increasing the pressure to 4 atm for 72 h resulted in conversion of a minority of N₃ groups to NCO ligands, as evidenced by the appearance of a new peak at *ca.* 2188 cm⁻¹ (Figure 3C).^[26] One explanation for the lack of reactivity observed in this case may be that the Pd-N₃ groups are inert due to the electronic nature of the metal centre when incorporated into the MOF. However, this explanation is directly contradicted by the apparent reactivity of the Pd-Me material towards CO₂, which appears to proceed at lower temperature than in the molecular regime. An alternative explanation is that CO gas is not permitted access to the pores and therefore only a minority of Pd-N₃ groups at (or near) the surface of the PCM-36 crystallites may undergo reaction. In accordance with this hypothesis, it was found that CO gas was not adsorbed inside an evacuated sample of PCM-36 that was subsequently able to adsorb CO₂ without impediment (Figure 2A).

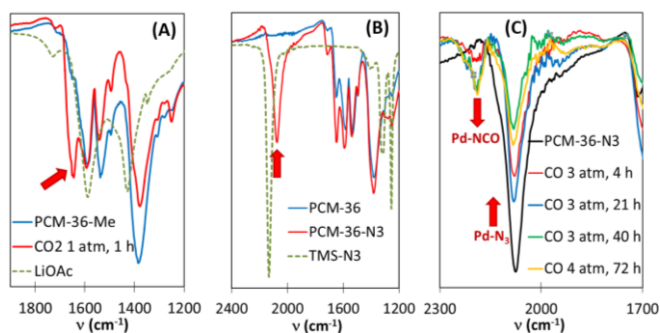


Figure 3. (A) Comparison of solid-state FT-IR spectra in the carbonyl stretching region as a function of PCM-36-Me exposure to CO₂. (B) The N₃ symmetric stretching band region. (C) Appearance of NCO stretching band upon high pressure treatment of PCM-36-N₃ to CO.

Selective adsorption of small molecule adsorbates by MOFs and PCPs has been widely documented and studied.^[27] Most commonly, CO₂ is preferentially adsorbed over other gases such as N₂, O₂ and CO.^[27] This unique property of microporous materials could be exploited in selective catalysis using crude mixtures of unrefined reagents, in which the MOF-catalyst acts as its own ‘filter’, to prevent unwanted side-reactions and/or catalyst poisoning. The intriguing preliminary results discussed

here for this new class of PCP-pincer-based MOFs lends some support to this premise. We are presently investigating the preparation of other PCMs based on Ru-, Rh- and Ir-PCP pincer building blocks for fundamental studies of other important small molecule activations, including C–H bond activation.

Acknowledgements

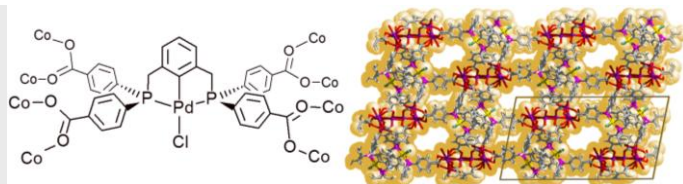
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Keywords: PCP-pincer • coordination polymer • Metal-Organic Framework • CO₂ activation • selective adsorption

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- [1] a) S. Horike, D. Umeyama, S. Kitagawa, *Acc. Chem. Res.* **2013**, *46*, 2376-2384; b) J. L. C. Rowsell, J. Eckert, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 14904-14910; c) N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda, S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 4501-4504; d) R. Krishna, J. M. van Baten, *J. Phys. Chem. C* **2012**, *116*, 23556-23568.
- [2] a) D. Jiang, T. Mallat, F. Krumeich, A. Baiker, *J. Catal.* **2008**, *257*, 390-395; b) L. Chen, S. Rangan, J. Li, H. Jiang, Y. Li, *Green Chem.* **2014**, *16*, 3978-3985; c) Z. Wang, J. Liu, H. K. Arslan, S. Grosjean, T. Hagendorn, H. Gliemann, S. Bräse, C. Wöll, *Langmuir* **2013**, *29*, 15958-15964.
- [3] a) M. Sabo, A. Henschel, H. Fröde, E. Klemm, S. Kaskel, *J. Mater. Chem.* **2007**, *17*, 3827-3832; b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724-781; c) S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 14176-14177; d) Q. Yang, C. Zong, *J. Phys. Chem. B* **2006**, *110*, 655-658.
- [4] a) L. J. McCormick, S. G. Duyker, A. W. Thornton, C. S. Hawes, M. R. Hill, V. K. Peterson, S. R. Batten, D. R. Turner, *Chem. Mater.* **2014**, *26*, 4640-4646; b) S. Yang, G. S. B. Martin, J. J. Titman, A. J. Blake, D. R. Allan, N. R. Champness, M. Schröder, *Inorg. Chem.* **2011**, *50*, 9374-9384; c) B. Chen, X. Zhao, A. Putkham, K. Hong, E. B. Lobkovsky, E. J. Hurtado, A. J. Fletcher, K. M. Thomas, *J. Am. Chem. Soc.* **2008**, *130*, 6411-6423; d) T. K. Prasad, D. H. Hong, M. P. Suh, *Chem. Eur. J.* **2010**, *16*, 14043 – 14050.
- [5] a) A. Karmakar, A. V. Desai, S. K. Ghosh, *Coord. Chem. Rev.* **2016**, *307*, 313-341; b) M. Owczarek, P. Szklarz, R. Jakubas, A. Miniewicz, *Dalton Trans.* **2012**, *41*, 7285–7294; c) D. D. Sante, A. Stroppa, P. Jain, S. Picozzi, *J. Am. Chem. Soc.* **2013**, *135*, 18126–18130; d) R. Shang, G. Xu, Z. Wang, S. Gao, *Chem. Eur. J.* **2014**, *20*, 1146 – 1158.
- [6] a) T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong, J. R. Long, *J. Am. Chem. Soc.* **2012**, *134*, 7056–7065; b) A. M. Fracaroli, H. Furukawa, M. Suzuki, M. Dodd, S. Okajima, F. Gándara, J. A. Reimer, O. M. Yaghi, *J. Am. Chem. Soc.* **2014**, *136*, 8863–8866; c) J. A. Mason, T. M. McDonald, T. Bae, J. E. Bachman, K. Sumida, J. J. Dutton, S. S. Kaye, J. R. Long, *J. Am. Chem. Soc.* **2015**, *137*, 4787–4803; d) S. Choi, T. Watanabe, T. Bae, D. S. Sholl, C. W. Jones, *J. Phys. Chem. Lett.* **2012**, *3*, 1136–1141.
- [7] a) A. J. Blake, N. R. Champness, T. L. Easun, D. R. Allan, H. Nowell, M. W. George, J. Jia, X.-Z. Sun, *Nature Chem.* **2010**, *2*, 688; b) K. Manna, T. Zhang, F. X. Greene, W. Lin, *J. Am. Chem. Soc.* **2015**, *137*, 2665–2673; c) K. Ikemoto, Y. Inokuma, K. Rissanen, M. Fujita, *J. Am. Chem. Soc.* **2014**, *136*, 6892–6895; d) J. Lee, O. K. Farha, J. Roberts, K. A. Schidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*,

- 1450–1459; e) K. K. Tanable, S. M. Cohen, *Chem. Soc. Rev.* **2011**, *40*, 498–519; f) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*, 1196–1231; g) C. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940–8941; h) S. A. Burgess, A. Kassie, S. A. Baranowski, K. J. Fritzsche, K. Schmidt-Rohr, C. M. Brown, C. R. Wade, *J. Am. Chem. Soc.* **2016**, *138*, 1780–1783.
- [8] a) W. Gao, L. Wojtas, S. Ma, *Chem. Commun.* **2014**, *50*, 5316–5318; b) C. Wang, Z. Xie, K. E. deKrafft, W. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 13445–13454; c) H. Jiang, B. Liu, T. Akita, M. Haruta, H. Sakurai, Q. Xu, *J. Am. Chem. Soc.* **2009**, *131*, 11302–11303; d) J. Liu, Y. Wang, A. I. Benin, P. Jakubczak, R. R. Willis, M. D. LeVan, *Langmuir* **2010**, *26*, 14301–14307.
- [9] a) L. Zhou, X. Lin, T. Huang, A. Yu, *Electrochim. Acta* **2014**, *116*, 210–216; b) J. Graciani, K. Mudiyansele, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz, J. A. Rodriguez, *Science* **2014**, *345*, 546–550; c) N. P. Wickramaratne, J. Xu, M. Wang, L. Zhu, L. Dai, M. Jaroniec, *Chem. Mater.* **2014**, *26*, 2820–2828; d) K. T. Cho, S. B. Lee, J. W. Lee, *J. Phys. Chem. C* **2014**, *118*, 9357–9367.
- [10] a) B. M. Hoffman, D. Lukoyanov, Z. Yang, D. R. Dean, L. C. Seefeldt, *Chem. Rev.* **2014**, *114*, 4041–4062; b) T. M. Figg, P. L. Holland, T. R. Cundari, *Inorg. Chem.* **2012**, *51*, 7546–7550; c) Q. Cui, D. G. Musaev, M. Svensson, S. Sieber, K. Morokuma, *J. Am. Chem. Soc.* **1995**, *117*, 12366–12367.
- [11] a) S. Park, Y. Chun, S. J. Cho, S. Lee, K. S. Kim, *J. Chem. Theory Comput.* **2012**, *8*, 1983–1988; b) A. M. Chapman, M. F. Haddow, D. F. Wass, *J. Am. Chem. Soc.* **2011**, *133*, 18463–18478; c) S. N. Riduan, Y. Zhang, J. Y. Ying, *Angew. Chem. Int. Ed.* **2009**, *48*, 3322–3325.
- [12] a) X. Yu, S. M. Cohen, *Chem. Commun.* **2015**, *51*, 9880–9883; b) P. V. Dau, M. Kim, S. M. Cohen, *Chem. Sci.* **2013**, *4*, 601–605; c) W. M. Bloch, A. Burgun, C. J. Coghlan, R. Lee, M. L. Coote, C. J. Doonan, C. J. Sumbly, *Nature Chem.* **2014**, *6*, 906–912.
- [13] a) W. M. Block, N. R. Champness, C. J. Doonan, *Angew. Chem. Int. Ed.* **2015**, *54*, 12860; *Angew. Chem.* **2015**, *127*, 13052–12867; b) F. Wang, Y. Tan, H. Yang, Y. Kang, J. Zhang, *Chem. Commun.* **2012**, *48*, 4842–4844; c) L. Zhang, Y. Qin, Z. Li, Q. Lin, J. Cheng, J. Zhang, Y. Yao, *Inorg. Chem.* **2008**, *47*, 8286–8293.
- [14] a) K. W. Anderson, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2005**, *44*, 6173–6177; b) D. E. Bergbreiter, P. L. Osburn, A. Wilson, E. M. Sink, *J. Am. Chem. Soc.* **2000**, *122*, 9058–9064.
- [15] A. M. Bohnsack, I. A. Ibarra, V. I. Bakhmutov, V. M. Lynch, S. M. Humphrey, *J. Am. Chem. Soc.* **2013**, *135*, 16038–16041.
- [16] E. Tsivion, J. R. Long, M. Head-Gordon, *J. Am. Chem. Soc.* **2014**, *136*, 17827–17835.
- [17] a) W. Leis, H. A. Mayer, W. C. Kaska, *Coord. Chem. Rev.* **2008**, *252*, 1787–1797; b) C. M. Jensen, *Chem. Commun.* **1999**, 2443–2449; c) D. Benito-Garagorri, K. Kirchner, *Acc. Chem. Res.* **2008**, *41*, 201–213.
- [18] J. J. M. de Pater, C. E. P. Maljaars, E. de Wolf, M. Lutz, A. L. Spek, B. Deelman, C. J. Elsevier, G van Koten, *Organometallics* **2005**, *24*, 5299–5310.
- [19] See for example: a) O. K. Farha, C. D. Malliakas, M. Kanatzidis, J. T. Hupp, *J. Am. Chem. Soc.* **2010**, *132*, 950–952; b) Y. Yan, M. Juriček, F.-X. Coudert, N. A. Vermeulen, S. Grunder, A. Dailly, W. Lewis, A. J. Blake, J. F. Stoddart, M. Schroder, *J. Am. Chem. Soc.* **2016**, *138*, 3371–3381.
- [20] M. C. Denney, N. A. Smythe, K. L. Cetto, R. A. Kemp, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 2508–2509.
- [21] H.-B. Kraatz, M. E. van der Boom, Y. Ben-David, D. Milstein, *Israel J. Chem.* **2001**, *41*, 163–171.
- [22] J. R. Durig, R. Layton, D. W. Sink, B. R. Mitchell, *Spectrochim. Acta* **1965**, *21*, 1367–1378.
- [23] a) R. Johansson, O. F. Wendt, *Dalton Trans.* **2007**, 488–492; b) M. T. Johnson, R. Johansson, M. V. Kondrashov, G. Steyl, M. S. G. Ahlquist, A. Roodt, O. F. Wendt, *Organometallics*, **2010**, *29*, 3521–3529.
- [24] T. J. Schmeier, N. Hazari, C. D. Incarvito, J. A. Raskatov, *Chem. Commun.* **2011**, *47*, 1824–1826; b) R. Johanssen, M. Jarenmark, O. F. Wendt, *Organometallics* **2005**, *24*, 4500–4502.
- [25] a) B. Ding, Z. Zhang, Y. Liu, M. Sugiyama, T. Imamoto, W. Zhang, *Org. Lett.* **2013**, *15*, 3690–3693; b) X.-Y. Yang, J. H. Gan, Y. Li, S. A. Pullarkat, P.-H. Leung, *Dalton Trans.* **2015**, *44*, 1258–1263.
- [26] H. J. Lee, S. H. Lee, H. C. Kim, Y.-E. Lee, S. Park, *J. Organomet. Chem.* **2012**, *717*, 164–171.
- [27] J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869–932.

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