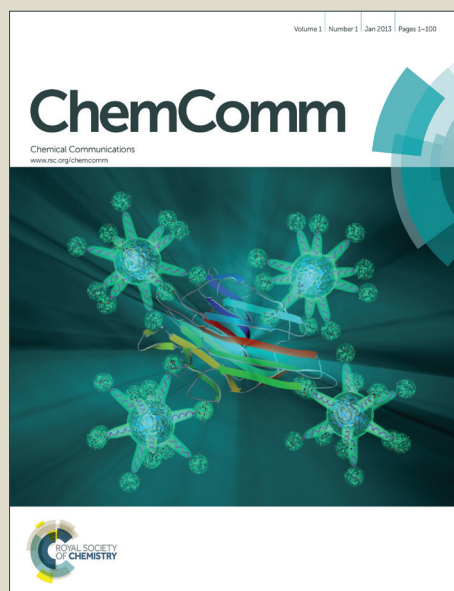


ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A 3-D diamondoid MOF catalyst based on in-situ generated [Cu(L)₂] N-heterocyclic carbene (NHC) linkers: hydroboration of CO₂

Alexandre Burgun,^a Rachel S. Crees,^a Marcus L. Cole,^b Christian J. Doonan^a and Christopher J. Sumbly^{a*}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A new MOF, [Zn₄O{Cu(L)₂}₂] (**1**), with a 4-fold interpenetrated 3D diamondoid structure was synthesised from in-situ generated [Cu(L)₂] NHC linkers. MOF **1** possesses tetrahedral Zn₄O nodes, which are unusually coordinated by four pairs of carboxylates from four [Cu(L)₂] linkers, and 14 Å 1-D pore channels lined with [Cu(L)₂] moieties that catalyse the hydroboration of CO₂.

Metal-organic frameworks (MOFs) are a class of porous materials with potential applications in gas storage,¹ molecular separations² and catalysis.³ MOFs are constructed via a modular approach from metal salts and organic linkers that allows their structures and functionality to be systematically modified.⁴ Such chemical mutability enables the properties of a given material to be tailored for a particular application. This feature, in conjunction with large pore volumes and high surface areas,⁴ has particularly earmarked MOFs as promising materials for heterogeneous catalysis.³ One approach to developing catalytic MOFs relies upon embedding established catalytic moieties into the framework.^{3, 5} In this regard, post-synthetic metalation is a promising strategy that provides a route for encapsulating existing homogenous catalysts within the pore network or anchoring them to the MOF structure.^{5b} Regarding this latter approach, a number of MOFs have been generated that contain sites, such as diols,⁶ cyclometalation sites,⁷ and heterocyclic donors,⁸ with potential for post-synthetic catalytic metal inclusion.

The use of azolium-containing linkers that are precursors to N-heterocyclic carbene (NHC) complexes has also been identified as a route for preparing MOF catalysts.⁹⁻¹¹ Such species are attractive components for MOFs as they are ubiquitous stabilising ligands for catalytic metals. Azolium linkers have been directly employed in MOF synthesis¹² and, in some cases, post-synthetic metalation used to convert these to NHC complexes inside the MOF.⁹ Alternatively, Yaghi and co-workers have shown that pre-formed NHC complexes can be utilized as framework links.¹⁰ Furthermore, NHC complex generation concomitant with MOF synthesis has been reported.¹¹ In these examples the NHC complex is appended to the framework and protrudes into the available pore space. Here, we report the first example of a MOF ([Zn₄O{Cu(L)₂}₂], **1**) that uses a bis(N-heterocyclic) complex ([Cu(L)₂], L = NHC) as a structural element. In addition to limiting the pore volume occupied by the catalytic sites and

ensuring full occupancy of the catalytic metal, the unusual geometric arrangement yields a diamond-like 3-D framework. This 3D network is constructed from Zn₄O nodes that adopt an uncommon coordination environment surrounded by four pairs of ligands. MOF **1** has a 4-fold interpenetrated structure with large 1D channels (limiting pore dimension of ~8.4 Å) and walls comprised of the [Cu(L)₂] links. The [Cu(L)₂] links of **1**, like related homogenous counterparts, were found to be active catalysts for the hydroboration of CO₂.¹³

[Zn₄O{Cu(L)₂}₂] (**1**) was synthesised in 59% yield by solvothermal treatment of H₃LCl with one equivalent of Zn(NO₃)₂·6H₂O and half an equivalent of [Cu(CH₃CN)₄]PF₆ in DMF at 120°C over 14 days (Figure 1a). This provided X-ray quality, pale yellow crystals of **1**. Cu₂O can also be employed as a Cu(I) source for MOF **1** synthesis¹¹ but in our hands gave mixtures containing residual Cu₂O that were challenging to separate. Crystalline samples synthesised using both routes readily matched the powder X-ray diffraction (PXRD) pattern simulated from the single crystal data (Figure 2) and dried samples gave satisfactory EDX and elemental analyses.[†]

Single crystal X-ray crystallography revealed that **1** has a diamondoid 3D framework (Figure 1a). This is formed from a Zn₄O structural node possessing a novel coordination mode and the first example of an *in-situ* generated [Cu(L)₂] (Cu(I) bis-NHC) linker. Due to the presence of four pairs of ligands around the Zn₄O node (i.e. four [Cu(L)₂] linkers), the cluster acts as a tetrahedral rather than octahedral structural unit (Figure 2c). Four carboxylate groups adopt the coordinating mode seen in the IRMOF series¹⁴ but an additional carboxylate that is held in close proximity to the first in each [Cu(L)₂] entity also coordinates in a monodentate fashion to each node. The bond lengths and angles about the Zn(II) centres are typical but with the coordination requirements of eight carboxylate groups leading to the presence of four chelating carboxylates and four monodentate donors. The Zn₄O node is not strictly tetrahedral but flattened slightly with Cu-Zn-Cu angles of 93.5, 95.0, 120.4 and 114.9°.

During MOF synthesis the imidazolium link H₃L undergoes deprotonation and conversion to its NHC form. Such reactions can require the addition of a strong base but it has previously been shown that Cu(I) NHC entities are formed concomitantly with MOF synthesis,¹¹ although this is the first report of the formation of a bis-NHC ligand. NHC complex formation during MOF synthesis is facile because basic species such as

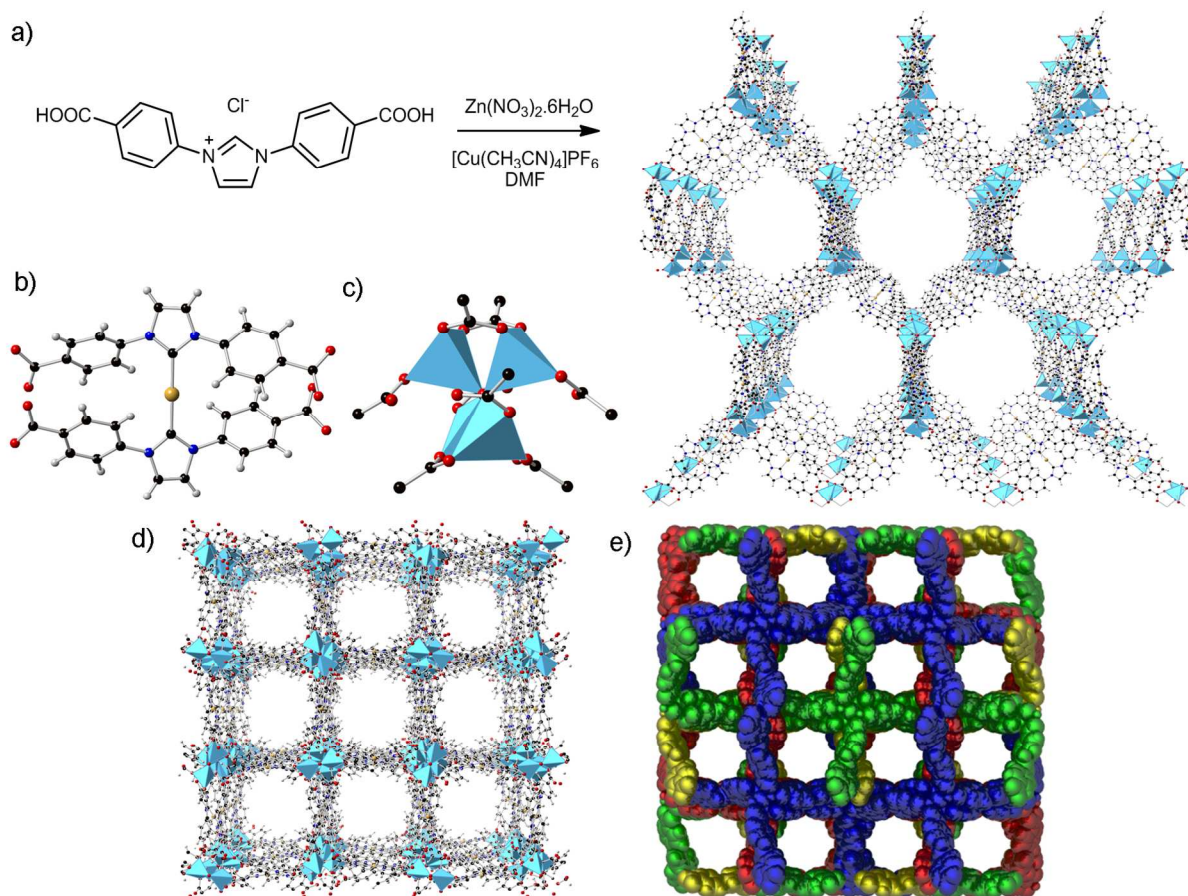


Figure 1. a) Synthesis of $[\text{Zn}_4\text{O}\{\text{Cu}(\text{L})_2\}_2]$ (**1**) and a perspective view of one diamond-like net of the structure down the a -axis. b) The $[\text{Cu}(\text{L})_2]$ bis-NHC link, c) the unusual coordination of the Zn_4O node in **1**, and views of the four-fold interpenetrated structure down the b -axis in d) ball and stick or e) space-filling representations. For a)-d): zinc - cyan, copper(I) - gold, carbon - black, nitrogen - blue, oxygen - red, hydrogen - white; for e): each framework is shown a single colour (red, green, yellow and blue).

dimethylamine are formed in situ via DMF decomposition.¹⁵ One of the $[\text{Cu}(\text{L})_2]$ moieties (Figure 1b) adopts an essentially planar conformation that is not normally seen for free $[\text{Cu}(\text{NHC})_2]$ species¹⁶ with N-C-Cu-C torsion angles around Cu4 being 15.7 and 16.1° (the other linker shows a greater twist with a torsion angles of 76.7 and 81.0° but still a relatively flat conformation). This brings the carboxylate donors of the pairs of NHCs into close proximity and favours the unusual coordination of the Zn_4O node. The unusual geometry observed for $[\text{Cu}(\text{L})_2]$ can be attributed to its confinement within the MOF architecture.

The combination of a tetrahedral node and the topologically trivial $[\text{Cu}(\text{L})_2]$ links generates a diamondoid framework (Figure 1a). The MOF is four-fold interpenetrated (Figures 1d and 1e) which produces a material with *ca.* 14 Å channels parallel to the b -axis with an octagonal cross-section. These channels are lined with exposed $[\text{Cu}(\text{L})_2]$ moieties that act as the channel walls. The Cu-Cu distances across the channel and to a Cu centre perpendicular to the first are *ca.* 14 and 9.6 Å respectively.

Thermogravimetric analysis of a sample of **1** indicated that after solvent loss the material is thermally stable up until 400°C (Figure S3). Furthermore, PXRD experiments on solvent exchanged samples indicated that the material is stable to a range of solvents (DMF, dichloromethane, and THF). Despite its thermal stability, drying a sample of **1** at room temperature under

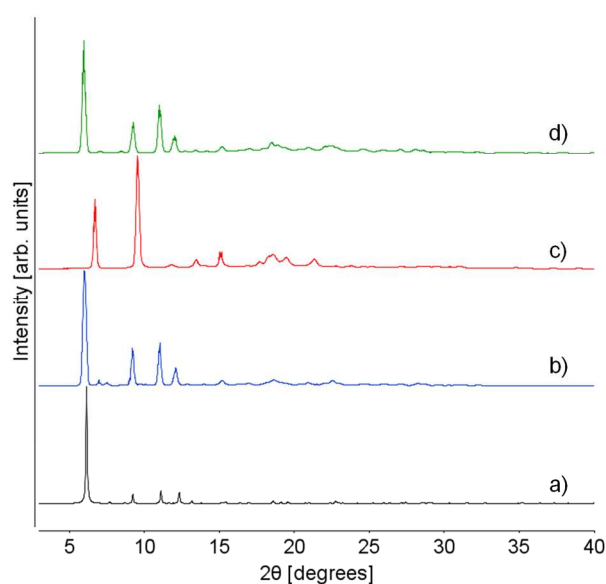


Figure 2. PXRD patterns of $[\text{Zn}_4\text{O}\{\text{Cu}(\text{L})_2\}_2]$ (**1**): a) simulated from the single crystal data, b) as-synthesised, c) dried, and d) after one catalytic cycle.

vacuum led to a significant change in the PXRD pattern (Figure 1c). Zn₄O clusters can be hydrolytically unstable and prone to structure collapse upon desolvation.¹⁷ In **1** the unusual monodentate coordination mode for four of the carboxylates may predispose the material toward a structural rearrangement. A 77 K N₂ isotherm confirmed that the structure of the desolvated material is not accessible to this probe molecule (despite a calculated surface area of ~1300 m²/g). Nonetheless, the material can be resolvated by heating **1** at 85°C in DMF for 24 h and PXRD reveals the as-synthesised structure to be partially regained (Figure S2). Structural recovery upon desolvation/resolvation cycles is not uncommon in MOF chemistry.¹⁸

A survey of the literature indicates that Zn forms a number of common SBUs with carboxylate ligands, including three- and four-bladed dinuclear paddlewheels,¹⁹ Zn₄O tetrahedra,¹⁴ and infinite 1-D Zn chains.²⁰ More recently, examples of higher nuclearity SBUs have been observed with Zn, including Zn₆O₂²¹ and Zn₈O clusters,^{12g} the latter of which forms from the same imidazolium link (H₃LCl) under different conditions. In the present example charge balance of the resulting framework appears to be an important driving force for the formation of the MOF. For example, attempts to prepare a palladium(II) chloride containing analogue of **1** were not successful, consistent with a different charge on the in situ generated link (i.e. [Cu(L)₂] has an overall -3 charge whereas [PdCl₂(L)₂] would have a -4 charge).

Relatively few MOFs comprised of NHC ligands have been assessed for their catalytic performance.⁹ Accordingly, we sought to investigate the potential of **1** to activate CO₂ via hydroboration.¹³ In addition to hydroboration of CO₂, copper(I) NHC complexes are also known to catalyse reactions such as the azide-alkyne “click chemistry”²² and the hydrosilylation of ketones.^{16a, 23} Of interest is that the cationic bis(NHC) complexes generally have improved catalytic activity by comparison with their neutral mono(NHC) parent.^{16a, 22b} The CO₂ hydroboration reactions (Scheme 1) were conducted in THF at 35°C under CO₂ atmosphere (1 atm) in the presence of pinacolborane and different amounts of MOF **1** (Table 1) as the catalyst. The product HCO₂B(pin) was not isolated, but instead immediately used as a formylating reagent for benzylamine¹³ after the MOF catalyst was removed by filtration. Almost quantitative conversion was obtained when 10 or 5 mol% of **1** was used (entries 2 and 3, respectively) whereas 66% of conversion was observed when only 1 mol% was employed (entry 4). These results are similar to data previously obtained involving a related homogeneous catalyst Cu(O*t*-Bu)(IPr) (entry 5).¹³

Crystals of **1** can be readily recovered after the reaction and no significant structural changes were observed in the PXRD pattern (Figure S6). An important aspect of using a MOF based NHC as a heterogeneous catalyst is that the MOF can be recovered from the reaction medium. We also assessed recyclability of the catalyst by using a 5 mol% loading of **1** over five cycles (Table S3). These experiments revealed that the catalytic activity of **1** decreased over the first two cycles and then stabilised at about 50% conversion thereafter. PXRD analysis of **1** after the fifth cycle clearly showed that the structure is retained (Figure S6), but the broadness and reduced intensity of the PXRD peaks indicate diminished crystallinity. Inductively-coupled plasma mass

spectrometry (ICP-MS) measurements (Table S4) of the reaction mixture after the first catalytic cycle indicated that a very small amount of copper (0.023%, 50±2 ppb) leaches from **1** during the course of the catalytic reaction. The copper leakage from MOF **1** can be rationalised on the basis of proposed mechanisms for catalytic reactions involving Cu(I) bis-NHC complexes, which involve de-coordination of at least one NHC ligand during the catalytic cycle.^{13, 22, 23} The regeneration of the starting Cu(I) bis-NHC moieties within MOF **1** requires re-coordination of one NHC ligand. Based on the minor loss of copper during the catalytic cycle, as measured by ICP-MS, regeneration is not quantitative and, most likely, disfavoured at the crystal surface where the NHC link is less spatially constrained than within the centre of the framework. This may be the origin of the slightly depressed catalytic activity shown in subsequent reactions.

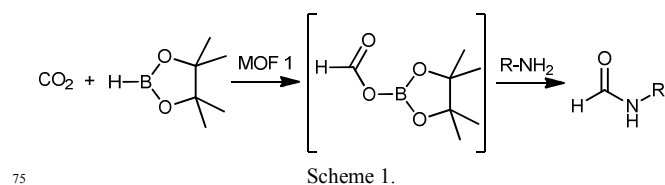


Table 1. N-Formylation of benzylamine using HCO₂B(pin) prepared by a [Zn₄O{Cu(L)₂}₂]-catalysed hydroboration of CO₂.

entry	Cu catalyst	mol % Cu	conv. (%) ^a
1	none	0	6
2	[Zn ₄ O{Cu(L) ₂ } ₂]	10 ^b	92
3	[Zn ₄ O{Cu(L) ₂ } ₂]	5 ^b	92
4	[Zn ₄ O{Cu(L) ₂ } ₂]	1 ^b	66
5 (ref. 13)	Cu(O <i>t</i> -Bu)(IPr)	10	98

^a Determined by ¹H NMR spectroscopy.

^b 1 mol % Cu = 0.5 mol % MOF

Our preliminary catalytic studies indicate that MOF **1** acts to heterogeneously catalyse the hydroboration of CO₂. Examination of the catalysis reaction solution shows no evidence of a homogenous NHC species[‡] being present in solution (excepting a very small amount of copper). On this basis, and due to the data obtained from recycling experiments, we can be confident the material is not a supplier of a homogenous catalyst species for the reaction. Additional evidence for this conclusion comes from additional catalytic experiments we have briefly investigated, namely “click chemistry” and hydrosilylation reactions, where we observed that the MOF does not catalyse these reactions. This observation we attribute to increased molecular size of the reactants involved and heterogeneous nature of this MOF catalyst.

In conclusion, we have reported the first example of a MOF comprising a Cu(I) bis-NHC ligand catalytic site. This entity is formed in-situ from an azolium ligand and a Cu(I) source. The ‘pairing’ of ligands in the MOF generates an unusual Zn₄O SBU and a structurally flexible diamonded 3D network. As the Cu(I) bis-NHC site is a structural building block the catalytic sites are well defined and the MOF shows similar catalytic behaviour to related homogenous Cu(I) NHC species yet has the advantage of being a heterogeneous system that can be recovered following a reaction. Our results show for the first time that catalysis by bis-NHC species within a MOF is possible however, a more robust

framework will be required to realise the full potential of these moieties.

Notes and references

This research is supported by the Science and Industry Endowment Fund (SIEF). CJD and CJS would like to acknowledge the Australian Research Council for funding FT100100400 and FT0991910, respectively.

^a School of Chemistry & Physics, The University of Adelaide, Adelaide, Australia. CJS: Phone +61 8 8313 7406. Fax: +61 8 8313 4358. Email: christopher.summy@adelaide.edu.au

^b School of Chemistry, University of New South Wales, Sydney, Australia.

† Electronic Supplementary Information (ESI) available: synthesis and characterisation of MOF 1, further details of X-ray crystallography and catalysis results. See DOI: 10.1039/b000000x/

‡ In some instances MOFs are known to catalyse reactions via dissolution to produce homogenous chemical species.³ In this case we believe that the evidence presented for MOF 1 indicates that the material remains intact and acts as a heterogenous catalyst although, like many systems, we cannot entirely rule out the presence of a highly active homogenous entity.

- 1 L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; J. Sculley, D. Yuan and H.-C. Zhou, *Energy Environ. Sci.*, 2011, **4**, 2721; J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, **41**, 2308; K. Konstas, T. Osl, Y. Yang, M. Batten, N. Burke, A. J. Hill and M. R. Hill, *J. Mater. Chem.*, 2012, **22**, 16698.
- 2 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869; B. Van de Voorde, B. Bueken, J. Denayer and D. De Vos, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00006D.
- 3 L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; A. Corma, H. Garcia and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606; M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196.
- 4 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 974; M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343–1370; W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00003J; J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS000094C.
- 5 (a) P. Deria, J. E. Mondloch, O. Karagiari, W. Bury, J. T. Hupp and O. K. Farha, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00067F; (b) J. D. Evans, C. J. Sumby and C. J. Doonan, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00076E; (c) Y. Han, J.-R. Li, Y. Xie and G. Guo, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00033A; (d) C. K. Brozek and M. Dincă, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00002A.
- 6 For example, see: (a) C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940; (b) K. K. Tanabe, C. A. Allen and S. M. Cohen, *Angew. Chem. Int. Ed.*, 2010, **49**, 9730; (c) D. Rankine, A. Avellaneda, M. R. Hill, C. J. Doonan and C. J. Sumby, *Chem. Commun.*, 2012, **48**, 10328.
- 7 For example, see: (a) P. V. Dau, M. Kim and S. M. Cohen, *Chem. Sci.*, 2013, **4**, 601; (b) P. V. Dau and S. M. Cohen, *Chem. Commun.*, 2013, **49**, 6128; (c) C. Wang, J.-L. Wang and W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 19895; (d) K. Manna, T. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 6566.
- 8 For example, see: (a) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382; (b) T. Jacobs, R. Clowes, A. I. Cooper and M. J. Hardie, *Angew. Chem. Int. Ed.*, 2012, **51**, 5192.
- 9 (a) G.-Q. Kong, X. Xu, C. Zou and C.-D. Wu, *Chem. Commun.*, 2011, **47**, 11005; (b) G.-Q. Kong, S. Ou, C. Zou and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 19851; (c) M. B. Lalonde, O. K. Farha, K. A. Scheidt and J. T. Hupp, *ACS Catal.*, 2012, **2**, 1550.
- 10 K. Oisaki, Q. Li, H. Furukawa, A. U. Czaja and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 9262.
- 11 (a) J. Chun, I. G. Jung, H. J. Kim, M. Park, M. S. Lah and S. U. Son, *Inorg. Chem.*, 2009, **48**, 6353; (b) J. Chun, H. S. Lee, I. G. Jung, S. W. Lee, H. J. Kim and S. U. Son, *Organometallics*, 2010, **29**, 1518.
- 12 (a) Z. Fei, T. D. Geldbach, D. Zhao, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2005, **44**, 5200; (b) Z. Fei, T. D. Geldbach, D. Zhao, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 6331; (c) L. Han, S. Zhang, Y. Wang, X. Yan and X. Lu, *Inorg. Chem.*, 2009, **48**, 786; (d) R. S. Crees, M. L. Cole, L. R. Hanton and C. J. Sumby, *Inorg. Chem.*, 2010, **49**, 1712; (e) J. Y. Lee, J. Roberts, O. K. Farha, J. T. Hupp and K. A. Scheidt, *Inorg. Chem.*, 2009, **48**, 9971; (f) J. M. Roberts, O. K. Farha, A. A. Sarjeant, J. T. Hupp and K. A. Scheidt, *Cryst. Growth Des.*, 2011, **11**, 4747; (g) S. Sen, N. N. Nair, T. Yamada, H. Kitagawa and P. K. Bharadwaj, *J. Am. Chem. Soc.*, 2012, **134**, 19432; (h) A. Burgun, C. J. Doonan and C. J. Sumby, *Aust. J. Chem.*, 2013, **66**, 409.
- 13 R. Shintani and K. Nozaki, *Organometallics*, 2013, **32**, 2459.
- 14 (a) H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.
- 15 D. J. Tranchemontagne, J. R. Hunt and O. M. Yaghi, *Tetrahedron*, 2008, **64**, 8553; N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933.
- 16 (a) S. Díez-González, E. D. Stevens, N. M. Scott, J. L. Petersen, S. P. Nolan, *Chem. Eur. J.*, 2008, **14**, 158; (b) S. Díez-González and S. P. Nolan, *Acc. Chem. Res.*, 2008, **41**, 349; (c) M. Poyatos, J. A. Mata and Eduardo Peris, *Chem. Rev.*, 2009, **109**, 3677.
- 17 (a) S. S. Kaye, A. Dailly, O. M. Yaghi, and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176; (b) J. A. Greathouse and M. D. Allendorf, *J. Am. Chem. Soc.*, 2006, **128**, 10678.
- 18 A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00101J.
- 19 S. I. Vagin, A. K. Ott and B. Rieger, *Chem-Ing-Tech.*, 2007, **79**, 767.
- 20 N. L. Rosil, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 2002, **41**, 284.
- 21 J. Cui, Y. Li, Z. Guo and H. Zheng, *Chem. Commun.*, 2013, **49**, 555.
- 22 (a) S. Díez-González, A. Correa, L. Cavallo and S. P. Nolan, *Chem. Eur. J.*, 2006, **12**, 7558; (b) S. Díez-González and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2008, **47**, 8881.
- 23 S. Díez-González, N. M. Scott and S. P. Nolan, *Organometallics*, 2006, **25**, 2355