Heterogeneous Catalysis

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Highly Efficient Cooperative Catalysis by Co^{III}(Porphyrin) Pairs in Interpenetrating Metal–Organic Frameworks

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Abstract: *A series of porous twofold interpenetrated In-Co^{III}(porphyrin) metal–organic frameworks (MOFs) were constructed by in situ metalation of porphyrin bridging ligands and used as efficient cooperative catalysts for the hydration of terminal alkynes. The twofold interpenetrating structure brings adjacent Co^{III}(porphyrins) in the two networks parallel to each other with a distance of about 8.8 Å, an ideal distance for the simultaneous activation of both substrates in alkyne hydration reactions. As a result, the In-Co^{III}(porphyrin) MOFs exhibit much higher (up to 38 times) catalytic activity than either homogeneous catalysts or MOF controls with isolated Co^{III}(porphyrin) centers, thus highlighting the potential application of MOFs in cooperative catalysis.*

Metal–organic frameworks (MOFs) are a class of highly tunable, porous molecular materials with properties suitable for a wide variety of applications, including gas storage[1] separation,[2] catalysis,[3] nonlinear optics,[4] sensing[5] and imaging,[6] drug delivery,[7] and others.[8,9] In particular, MOFs have shown great promise as effective heterogeneous catalysts because of the large channels and cavities that make the catalytic sites readily accessible to substrates. Although MOFs with isolated catalytic sites have been used to effect a variety of organic transformations,[10,11] MOF catalysts with multiple active sites are far less explored. We surmized that MOFs with active sites in close proximity can be used for cooperative catalysis by synergistic substrate activations or for tandem/cascade catalysis.[12]

Cooperative catalysis, in which multiple catalytic sites work synergistically to effect an organic transformation, is prevalent in nature[13] and has emerged as a powerful strategy in synthetic chemistry.[14] Cooperative catalysis can afford improved efficiency and specificity over monocatalytic systems but is not operative at the low catalyst loading typical of traditional homogeneous catalysis. Because MOFs can be designed with multiple, precisely spaced catalytic sites at very high local concentrations, they are an ideal platform to engineer recyclable and reusable solid catalysts for cooperative catalysis. Herein we report the design of porous and interpenetrating MOFs with strategically placed Co^{III}(porphyrin) active sites for efficient cooperative hydration of terminal alkynes by dual substrate activation.

The new In-TBP MOF with the framework formula In(TBP)$_x$[In(TBP)(H$_2$O)]$_{(1-x)}$[DMA]$_x$, (DMA = dimethylammonium; $x > 0.9$), was synthesized by heating indium nitrate and tetrakis(4-benzoic acid)porphyrine (H$_4$TBP) in a mixture of DEF, DMF, and H$_2$O, to result in purple crystals in 40% yield. The TBP ligand was partially metallated with indium during the reaction. The porphyrin in the In-TBP MOF could be metallated with Co^{III} ions in situ by adding Co^{2+} salts to the reaction mixtures to afford In-Co(TBP) in a similar yield. The extent of TBP metallation can be tuned by varying the amounts of metal salts. For example, the presence of 0 to 38.8 equivalents of Co^{2+} ions, with respect to H$_4$TBP, led to the formation of 0 to 93.8% Co(TBP) in the resulting MOF, as quantified by inductively coupled plasma-mass spectrometry (ICP-MS; see Table S1 in the Supporting Information) and UV/Vis spectra analysis (see Table S5). The addition of HfOCl$_2$·8H$_2$O improved the crystallinity of the MOFs, although no Hf was detected in the MOFs by ICP-MS. The In-Co(TBP)-MOF could also be synthesized by using the premetallated ligand Co^{III}-TBP (see the Supporting Information).

Single-crystal X-ray crystallographic[15] study of the In-Co(TBP)-MOF revealed that each four-connected Co(TBP) ligand links four four-connected [In(COO$^-$)$_4$] secondary building units (SBUs), thus forming a twofold interpenetrated three-dimensional (3D) framework of **pts** (PtS) topology (the [In(COO$^-$)$_4$] tetrahedral node has a vertex symbol of $4\bullet4\bullet8_2\bullet8_2\bullet8_8\bullet8_8$ and the CoTBP square planar node has a vertex symbol of $4\bullet4\bullet8_7\bullet8_7\bullet8_7\bullet8_7$). The void space was 54.8%, as calculated by PLATON. However, a low surface area of (186.0 ± 10.2) m^2 g^{-1} was obtained by nitrogen adsorption studies, which is likely due to the severe distortion of the MOF framework during the drying process (see Figure S9). This drying process was not needed for the MOF catalysts used in liquid-phase catalytic reactions. Within each Co(TBP) unit, the cobalt cation has a pentacoordinated environment completed by the four N atoms of the TBP and an axial aqua group to form a [Co(TBP)(OH$_2$)] unit. The Co–N bond lengths ranged from 1.94 to 1.97 Å, and the Co–O bond length was 2.05 Å. In one 3D unit of the twofold interpenetrated framework, the Co(TBP) functional units were parallel to each other, with distances of 1.72 and 1.44 nm,

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respectively, and each 3D porous framework possessed different pores, 1.52 nm × 1.52 nm and 2.23 nm × 1.25 nm in size, which were large enough to accommodate a second 3D framework, thus resulting in a twofold interpenetrated structure (see Figure S5). Interpenetration of the 3D frameworks brings a pair of CoTBP units into close proximity with each other, with a Co–Co distance of about 8.8 Å (Figure 1), thus affording an excellent platform for cooperative catalysis.

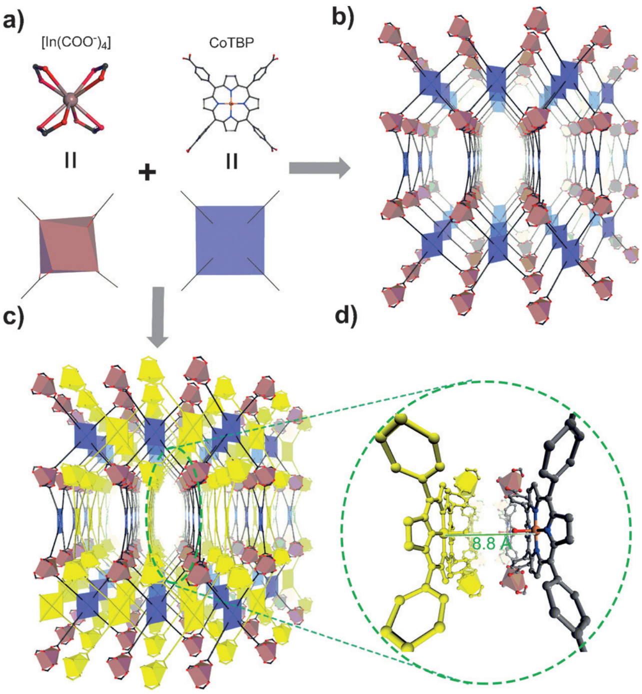


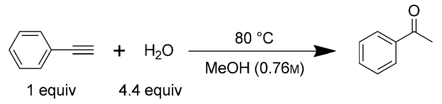
Figure 1. a) Chemical structure of [In(COO$^-$)$_4$] SBUs and Co(TBP) linkers. A graphic representation of the structure and connectivity of b) one 3D unit of a MOF and c) twofold interpenetrated In-Co(TBP)-MOF. d) Close-up view of two Co^{III}(TBP) units brought into proximity to each other by twofold interpenetration. Yellow color indicates the interpenetrated 3D framework.

X-ray absorption fine structure (XAFS) spectroscopy at the Co K-edge was used to investigate the oxidation states and local coordination environment of Co within the In-Co(TBP)-MOF. These data were processed and analyzed using the Athena and Artemis programs of the IFEFFIT package based on FEFF 6. The X-ray absorption near edge structure (XANES) analysis indicated the 3+ oxidation state of the Co center of In-Co(TBP)-MOF (see Figure S12). In-Co(TBP)-MOF was fitted to its corresponding crystal structure, with a Co–N bond length of 1.96 Å and a Co–O bond length of 1.96 Å (see Figures S15 and S16).

Catalytic hydration of alkynes forms carbonyl derivatives, which are key intermediates for both bulk and fine-chemical industries. Terminal alkynes are often used as substrates for the hydration reaction because they exclusively produce methyl ketones.[16] Previous studies have indicated that mercury(II) salts, such as HgO, are efficient catalysts for the hydration of alkynes with the assistance of acid. Because of the toxicity of mercury compounds, much effort has been devoted to exploring alternative catalysts based on transition metals, such as Pt,[17] Fe,[18] Pd,[19] Ir,[20] Ag,[21] Co,[22] and Au.[23] However, most of them exhibit lower reactivity and selectivity than mercury salts. Porphyrins and metalloporphyrins with biological, physical, chemical, and catalytic functionalities have been widely studied over the past decades. Because of their distinctive catalytic activities, cobalt(III) porphyrin complexes were found to be efficient homogeneous catalysts for the hydration of terminal alkynes.[22a]

In 2014, Naka and co-workers reported that a Co^{III} porphyrin complex, Na$_3$[Co(TPPS)], could catalyze the hydration of terminal alkynes.[22a] We decided to test this reaction using In-Co(TBP)-MOF, in which the TBP ligands were metallated by cobalt cations. To our delight, at a 0.1 mol % loading, In-Co(TBP)-MOF was extremely active, with 100 % conversion, while homogeneous controls, Na$_3$[Co(TPPS)] and Co^{III}(TBP), only resulted in 24 and 18.6 % conversion, respectively. Furthermore, Co(TBP)-MOF remained active at a very low catalyst loading (0.01 mol %), whereas the homogeneous analogue was totally inactive (Table 1, entries 3 and 6; Figure 2a). These results indicate that the reaction may involve two Co(TBP) complexes to allow cooperative activation. For In-Co(TBP)-MOF, two Co(TBP) units adjacent to each other were relatively fixed, thus a linear relationship was observed for conversions at different catalyst loadings. For the homogeneous control,

Table 1: Hydration of phenylacetylene.



Entry	Catalysts (mol %)	*t*	Conv. [%][a]
1	In-Co(TBP)-MOF (0.1)	12 h	95.2
2	In-Co(TBP)-MOF (0.1)	20 h	100
3	In-Co(TBP)-MOF (0.01)	7 d	92
4[b]	Na$_3$[Co(TPPS)] (0.1)	12 h	24
5	Co^{III}-(TBP) (0.1)	20 h	18.6
6	Co^{III}-(TBP) (0.01)	7 d	0
7	In-In(TBP)-MOF (0.2)	20 h	0
8	Zr-Co(TBP)-MOF (0.1)	20 h	2.0

[a] Conversions were determined by GC with undecane as an internal standard. [b] Ref. [22a].

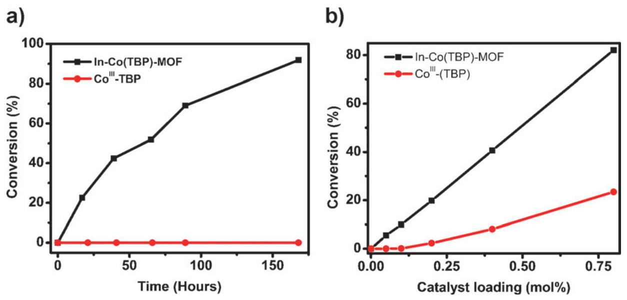
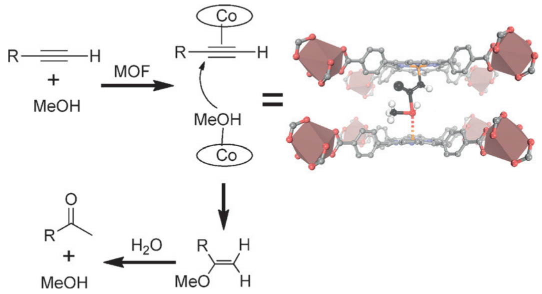


Figure 2. a) Plot of conversion vs. time using 0.01 mol % In-Co(TBP)-MOF and Co^{III}-(TBP). b) Plot of conversion vs. catalyst loading using In-Co(TBP)-MOF and Co^{III}-(TBP). Reaction time: 2 hours.

the possibility of two Co(TBP) complexes meeting each other decreased at a lower catalyst concentration, resulting in a nonlinear relation between conversion and catalyst loading (Figure 2b).

When isostructural In-In(TBP)-MOF was used, no conversion was observed, ruling out the contribution from $[In(COO)_4]^-$ SBUs (Table 1, entry 7). More importantly, Zr-Co(TBP)-MOF, which has a similar topology to MOF-545 or PCN-222,[24] served as a good control to demonstrate our proposed cooperative mechanism, since its Co-to-Co distance is 11.0 Å within its trigonal channel or 36.6 Å within its hexagonal channel, greater than that of In-Co(TBP)-MOFs (see Figure S17). Because of its larger channel/pore size, which enables faster diffusion of substrates and products, Zr-Co(TBP)-MOF was expected to have a higher catalytic activity if a monometallic activation pathway was dominant. However, only 2% conversion was achieved when Zr-Co-(TBP)-MOF was used for the hydration of phenylacetylene at the same catalyst loading as In-Co(TBP)-MOF or homogeneous Co^{III}(TBP) (Table 1, entry 8), further supporting the bimetallic activation mechanism for In-Co(TBP)-MOF.

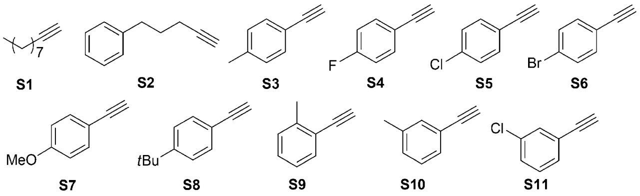
Herein we propose that our reaction involves a cooperative mechanism: Co(TBP) serves as a Lewis acid to activate the terminal alkyne by π-coordination while the adjacent Co(TBP) coordinates to MeOH to make it more nucleophilic (Scheme 1). The Co^{III}-coordinated MeOH attacks the activated alkyne to afford methyl vinyl ether, which is hydrolyzed by water to give a ketone as the final product and to regenerate MeOH.



Scheme 1. Proposed mechanism for cooperative activation in Co(TBP)-catalyzed hydration of alkynes.

We further investigated the substrate scope of alkyne hydration. In-Co(TBP)-MOF displayed excellent activity of hydration over a wide range of aliphatic and aromatic terminal alkynes (Table 2). Aromatic alkyne derivatives with either electron-donating or electron-withdrawing substituents at the *para* position reacted smoothly to afford the desired methyl ketone products (entries 3–8). For the substrate **S10**, no hydration took place using either MOF or homogeneous catalysts (entries 10 and 11). The steric clash between the methyl group of 3-methylphenylacetylene and the phenyl group of Co(TBP) upon coordination led to diminished catalytic activity (Figure 3a). Similarly, little conversion was observed for **S11** (Table 2, entry 12). These data further demonstrate that the alkyne was activated by Co(TBP) through π-coordination.

Table 2: Hydration of terminal alkynes.



Entry	Substrate	Catalyst (mol%)	t [d]	Yield [%][a]
1	**S1**	In-Co(TBP)-MOF (0.2)	2	98
2	**S2**	In-Co(TBP)-MOF (0.2)	2	93
3	**S3**	In-Co(TBP)-MOF (0.1)	1	92
4	**S4**	In-Co(TBP)-MOF (0.1)	1	95
5	**S5**	In-Co(TBP)-MOF (0.1)	1	100
6	**S6**	In-Co(TBP)-MOF (0.1)	1	90 (86[b])
7	**S7**	In-Co(TBP)-MOF (0.1)	1	95
8	**S8**	In-Co(TBP)-MOF (0.1)	1	94
9	**S9**	In-Co(TBP)-MOF (0.1)	3	97
10	**S10**	In-Co(TBP)-MOF (0.1)	3	0
11	**S10**	Co^{III}-TBP (0.1)	3	0
12	**S11**	In-Co(TBP)-MOF (0.1)	1	2.5

[a] Yields were determined by ^1H NMR spectroscopy using nitromethane as an internal standard. [b] Yield of isolated product.

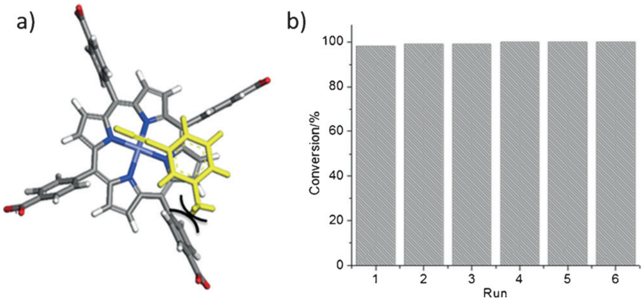


Figure 3. a) Proposed steric clash between the methyl group of 3-methylphenylacetylene and the phenyl group of Co(TBP). b) Plot of conversions (%) at various runs in the hydration of phenylacetylene.

We found that In-Co(TBP)-MOF could be recycled by simple centrifugation and reused at least six times without obvious loss in the catalytic activity (Figure 3b). PXRD of the recovered In-Co(TBP)-MOF was identical to that of the pristine catalyst, thus indicating the stability of the MOF catalyst during catalytic reactions.

In conclusion, a series of porous twofold interpenetrated metal-metalloporphyrin frameworks were synthesized and applied to the hydration of terminal alkynes. Controlled loading of the transition-metal cations into the MOFs supplied the opportunity to study the catalytic mechanism in the hydration of terminal alkynes. The twofold interpenetration brings catalytically active metalloporphyrin centers adjacent to each other, allowing cooperative activation, which results in excellent efficiency compared to their homogeneous analogues. Zr-Co(TBP)-MOF, isostructural In-In(TBP)-MOF, and the homogeneous reaction were examined to confirm the proposed cooperative catalytic mechanism. This work highlights how MOFs can participate in cooperative catalysis in organic synthesis and provides a new strategy for constructing efficient heterogeneous catalysts.

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[1] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. OKeeffe, O. M. Yaghi, *Science* **2002**, *295*, 469; b) L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294; c) M. P. Suh, H. J. Park, T. K. Prasad, D. W. Lim, *Chem. Rev.* **2012**, *112*, 782; d) X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey, M. Schröder, *Angew. Chem. Int. Ed.* **2006**, *45*, 7358; *Angew. Chem.* **2006**, *118*, 7518.

[2] a) J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477; b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724; c) Z. Zhang, Y. Zhao, Q. Gong, Z. Li, J. Li, *Chem. Commun.* **2013**, *49*, 653.

[3] a) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450; b) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248; c) C. Wang, M. Zheng, W. Lin, *J. Phys. Chem. Lett.* **2011**, *2*, 1701; d) G. Q. Kong, S. Ou, C. Zou, C. D. Wu, *J. Am. Chem. Soc.* **2012**, *134*, 19851; e) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*, 1196; f) D. T. Genna, A. G. Wong-Foy, A. J. Matzger, M. S. Sanford, *J. Am. Chem. Soc.* **2013**, *135*, 10586; g) H. Fei, J. Shin, Y. S. Meng, M. Adelhardt, J. Sutter, K. Meyer, S. M. Cohen, *J. Am. Chem. Soc.* **2014**, *136*, 4965; h) K. Mo, Y. Yang, Y. Cui, *J. Am. Chem. Soc.* **2014**, *136*, 1746; i) M. Zhao, S. Ou, C. D. Wu, *Acc. Chem. Res.* **2014**, *47*, 1199; j) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C. Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011; k) J. A. Johnson, X. Zhang, T. C. Reeson, Y. S. Chen, J. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 15881; l) W.-Y. Gao, M. Chrzanowski, S. Ma, *Chem. Soc. Rev.* **2014**, *43*, 5841.

[4] a) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511; b) C. Wang, T. Zhang, W. Lin, *Chem. Rev.* **2012**, *112*, 1084.

[5] a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105; b) Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, *43*, 5815; c) K. C. Stylianoum, R. Heck, S. Y. Chong, J. Bacsa, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2010**, *132*, 4119.

[6] J. Della Rocca, D. Liu, W. Lin, *Acc. Chem. Res.* **2011**, *44*, 957.

[7] a) W. J. Rieter, K. M. Pott, K. M. L. Taylor, W. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 11584; b) K. M. L. Taylor-Pashow, J. D. Rocca, Z. Xie, S. Tran, W. Lin, *J. Am. Chem. Soc.* **2009**, *131*, 14261; c) R. C. Huxford, K. E. deKrafft, W. S. Boyle, D. Liu, W. Lin, *Chem. Sci.* **2012**, *3*, 198; d) C. He, K. Lu, D. Liu, W. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 5181.

[8] a) G. Givaja, P. Amo-Ochoa, C. Gomez-Garcia, F. Zamora, *Chem. Soc. Rev.* **2012**, *41*, 115; b) T. C. Narayan, T. Miyakai, S. Seki, M. Dincă, *J. Am. Chem. Soc.* **2012**, *134*, 12932; c) M. Yoon, K. Suh, S. Natarajan, K. Kim, *Angew. Chem. Int. Ed.* **2013**, *52*, 2688; *Angew. Chem.* **2013**, *125*, 2752; d) D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Er, C. R. Wade, C. K. Brozek, A. Aspuru-Guzik, M. Dincă, *J. Am. Chem. Soc.* **2014**, *136*, 8859.

[9] a) C. Wang, Z. Xie, K. E. deKrafft, W. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 13445; b) T. Zhang, W. Lin, *Chem. Soc. Rev.* **2014**, *43*, 5982; c) Z.-M. Zhang, T. Zhang, C. Wang, Z. Lin, L.-S. Long, W. Lin, *J. Am. Chem. Soc.* **2015**, *137*, 3197.

[10] a) S. H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563; b) L. Ma, J. M. Falkowski, C. Abney, W. Lin, *Nat. Chem.* **2010**, *2*, 838; c) F. Song, C. Wang, J. M. Falkowski, L. Ma, W. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 15390; d) J. M. Falkowski, T. Sawano, T. Zhang, G. Tsun, Y. Chen, J. V. Lockard, W. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 5213.

[11] a) K. Manna, T. Zhang, M. Carboni, C. W. Abney, W. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 13182; b) K. Manna, T. Zhang, W. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 6566; c) N. C. Thacker, Z. Lin, T. Zhang, J. C. Gilhula, C. W. Abney, W. Lin, *J. Am. Chem. Soc.* **2016**, *138*, 3501.

[12] a) C. Zhu, G. Yuan, X. Chen, Z. Yang, Y. Cui, *J. Am. Chem. Soc.* **2012**, *134*, 8058; b) T. Zhang, F. Song, W. Lin, *Chem. Commun.* **2012**, *48*, 8766.

[13] a) N. Sträter, W. N. Lipscomb, T. Klabunde, B. Krebs, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2024; *Angew. Chem.* **1996**, *108*, 2158; b) E. K. van den Beuken, B. L. Feringa, *Tetrahedron* **1998**, *54*, 12985; c) N. C. Gianneschi, P. A. Bertin, S. T. Nguyen, C. A. Mirkin, L. N. Zakharov, A. L. Rheingold, *J. Am. Chem. Soc.* **2003**, *125*, 10508; d) M. Wiester, P. A. Ulmann, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2011**, *50*, 114; *Angew. Chem.* **2011**, *123*, 118.

[14] a) J. Park, S. Hong, *Chem. Soc. Rev.* **2012**, *41*, 6931; b) A. E. Allen, D. W. C. MacMillan, *Chem. Sci.* **2012**, *3*, 633.

[15] CCDC CCDC numbers 1485691 and 1485692 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[16] a) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079; b) M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem. Int. Ed.* **2004**, *43*, 3368; *Angew. Chem.* **2004**, *116*, 3448; c) L. Hintermann, A. Labonne, *Synthesis* **2007**, 1121; d) W. E. Brenzovich, *Angew. Chem. Int. Ed.* **2012**, *51*, 8933; *Angew. Chem.* **2012**, *124*, 9063.

[17] a) W. Hiscox, P. W. Jennings, *Organometallics* **1990**, *9*, 1997; b) P. W. Jennings, J. W. Hartman, W. C. Hiscox, *Inorg. Chim. Acta* **1994**, *222*, 317; c) L. W. Francisco, D. A. Moreno, J. D. Atwood, *Organometallics* **2001**, *20*, 4237.

[18] a) J. P. Damiano, M. Postel, *J. Organomet. Chem.* **1996**, *522*, 303; b) X. F. Wu, D. Bezier, C. Darcel, *Adv. Synth. Catal.* **2009**, *351*, 367.

[19] a) Y. Fukuda, H. Shiragami, K. Utimoto, H. Nozaki, *J. Org. Chem.* **1991**, *56*, 5816; b) C. Xu, W. Du, Y. Zeng, B. Dai, H. Guo, *Org. Lett.* **2014**, *16*, 948.

[20] T. Hirabayashi, Y. Okimoto, A. Saito, M. Morita, S. Sakaguchi, Y. Ishii, *Tetrahedron* **2006**, *62*, 2231.

[21] a) K. T. Venkateswara Rao, P. S. S. Prasad, N. Lingaiah, *Green Chem.* **2012**, *14*, 1507; b) M. B. T. Thuong, A. Mann, A. Wagner, *Chem. Commun.* **2012**, *48*, 434.

[22] a) T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, *J. Am. Chem. Soc.* **2013**, *135*, 50; b) S. Wang, C. Miao, W. Wang, Z. Lei, W. Sun, *ChemCatChem* **2014**, *6*, 1612; c) J. Lu, J. Dimroth, M. Weck, *J. Am. Chem. Soc.* **2015**, *137*, 12984.

[23] a) Y. Fukuda, K. Utimoto, *J. Org. Chem.* **1991**, *56*, 3729; b) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem. Int. Ed.* **1998**, *37*, 1415; *Angew. Chem.* **1998**, *110*, 1475; c) E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, *Angew. Chem. Int. Ed.* **2002**, *41*, 4563; *Angew. Chem.* **2002**, *114*, 4745; d) R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, *J. Am. Chem. Soc.* **2003**, *125*, 11925; e) C. Y. Zhou, P. W. H. Chan, C. M. Che, *Org. Lett.* **2006**, *8*, 325; f) N. Marion, R. S. Ramon, S. P. Nolan, *J. Am. Chem. Soc.* **2009**, *131*, 448; g) A. Almássy, C. E. Nagy, A. C. Bényei, F. Joó, *Organometallics* **2010**, *29*, 2484; h) A. Cavarzan, A. Scarso, P. Sgarbossa, G. Strukul, J. N. H. Reek, *J. Am. Chem. Soc.* **2011**, *133*, 2848; i) L. Li, S. B. Herzon, *J. Am. Chem. Soc.* **2012**, *134*, 17376; j) D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen, X. Shi, *J. Am. Chem. Soc.* **2012**, *134*, 9012; k) Y. Xu, X. Hu, J. Shao, G. Yang, Y. Wu, Z. Zhang, *Green Chem.* **2015**, *17*, 532.

[24] a) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, *Angew. Chem. Int. Ed.* **2012**, *51*, 10307; *Angew. Chem.* **2012**, *124*, 10453; b) W. Morris, B. Volosskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart, O. M. Yaghi, *Inorg. Chem.* **2012**, *51*, 6443.

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