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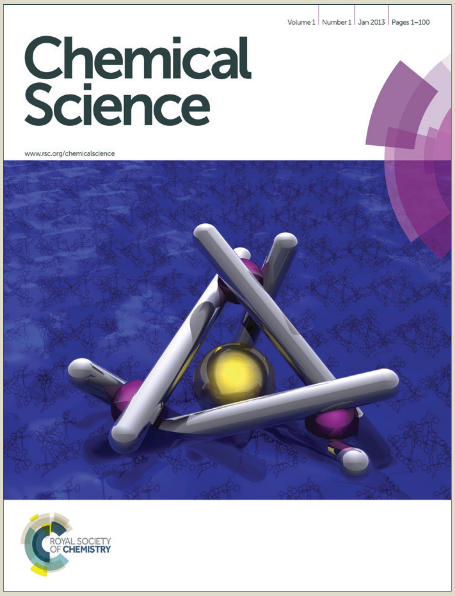

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ARTICLE

The First Chiral Diene-Based Metal-Organic Frameworks for Highly Enantioselective Carbon-Carbon Bond Formation Reactions

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We have designed the first chiral diene-based metal–organic framework (MOF), E_2-MOF, and postsynthetically metalated E_2-MOF with Rh(I) complexes to afford highly active and enantioselective single-site solid catalysts for C-C bond formation reactions. Treatment of E_2-MOF with $[RhCl(C_2H_4)_2]_2$ led to a highly enantioselective catalyst for 1,4-additions of arylboronic acids to α,β-unsaturated ketones, whereas treatment of E_2-MOF with $Rh(acac)(C_2H_4)_2$ afforded a highly efficient catalyst for the asymmetric 1,2-additions of arylboronic acids to aldimines. Interestingly, E_2-MOF•Rh(acac) showed higher activity and enantioselectivity than the homogeneous control catalyst, likely due to the formation of a true single-site catalyst in the MOF. E_2-MOF•Rh(acac) was also successfully recycled and reused at least seven times without loss of yield and enantioselectivity.

Introduction

In the past 15 years, metal-organic frameworks (MOFs) have emerged as a novel class of highly porous molecular materials with great potential for many applications, including gas storage,[1] chemical sensing,[2] biomedical imaging,[2a,3] drug delivery,[4] nonlinear optics,[5] and catalysis.[6] Although a number of excellent MOF-based catalytic systems have been developed recently,[7] examples of highly enantioselective asymmetric reactions catalyzed by MOFs are still limited despite their potential utility in the synthesis of high-value fine chemicals. Asymmetric MOF catalysts not only enable the recycling and reuse of expensive chiral ligands and precious metals, but also prevent the leaching of toxic metals into organic products which can be a significant issue for the pharmaceutical industry.

Since the first report of a MOF-based asymmetric catalyst with modest enantioselectivity in 2000,[8] a number of highly enantioselective MOF catalysts with Lewis acid reactivity have been designed, including Ti(IV)-BINOL-based MOFs[9] and Mn(III)- and Co(III)-salen-based MOFs.[10] To expand the scope of MOF-catalyzed asymmetric reactions, Lin and coworkers recently developed BINAP-based MOFs for a number of important asymmetric catalytic recations.[7g] However, the bulky BINAP and derivatives reduce the channel/cavity sizes of BINAP-MOFs and hinder their applications in asymmetric reactions involving sterically demanding transition states/intermediates. Herein we report the design and synthesis of the first chiral diene-based MOFs and their use in asymmetric C-C bond formation reactions (Fig. 1). With less steric demand than their BINAP predecessors, the diene-MOFs metalated with Rh(I) complexes are excellent catalysts with high activities and enantioselectivities for 1,4-additions of arylboronic acids to α,β-unsaturated ketones and 1,2-additions of arylboronic acids to aldimines.[11]

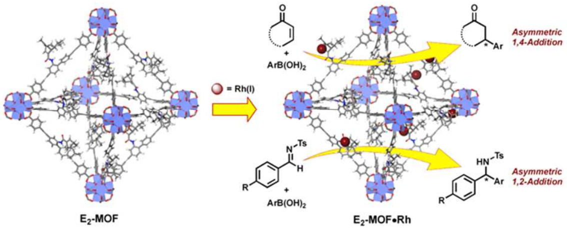

Fig. 1 Postsynthetically Rh-metalated E_2-MOF catalysts for asymmetric reactions.

Chiral dienes have been applied to a broad range of asymmetric reactions since being reported independently by Hayashi[12] and Carreira.[13,14] In particular, asymmetric Rh-diene complexes provide powerful methods to construct chiral centers in C-C bond formations. For example, 1,4-additions of electron-deficient olefins and 1,2-addition of imines with arylboronic acids in the presence of rhodium and a chiral diene provide highly desirable synthetic methods to obtain the addition products with high yields and enantioselectivities.[15,16] In these reactions, Rh complexes of chiral dienes typically afford higher yields and enantiomeric excesses (ee's) than the corresponding Rh-BINAP complexes.

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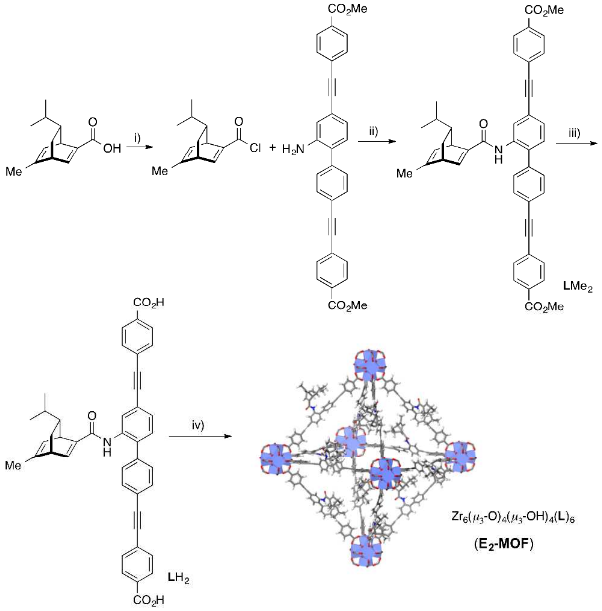
Results and discussion

We targeted the synthesis of the chiral diene-based MOF, E_2-MOF, based on the linear dicarboxylate ligand containing an orthogonal chiral diene group and the $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ secondary building unit (SBU). Zr MOFs of the UiO structure not only provide a highly tunable platform for designing functional materials but also are stable under a broad range of reaction conditions.[17] The diene ligand (**L**H_2) was synthesized from a known chiral diene-carboxylic acid compound (Scheme 1).[18] Upon treatment with oxalyl chloride, the corresponding acid chloride was reacted with the dicarboxylic ester possessing an orthogonal amino group to afford the methyl ester of the chiral diene (**L**Me_2) in 57% yield. Subsequent saponification of **L**Me_2 afforded enantiopure **L**H_2 in 77% yield. E_2-MOF was synthesized as colorless crystals in 42% yield by treating $ZrCl_4$ with 1 equiv of **L**H_2 and a small amount of trifluoroacetic acid (TFA) in dimethylformamide (DMF) at 70 °C for 5 d.



Scheme 1 Synthesis of **L**H_2. i) oxalyl chloride, CH_2Cl_2; ii) TEA, THF, 57% yield over 2 steps; iii) NaOH, THF, EtOH, 77% yield; iv) $ZrCl_4$, TFA, DMF, 70 °C, 5 d, 42% yield.

Single crystal X-ray diffraction revealed that E_2-MOF crystallizes in the $Fm\bar{3}m$ space group and adopts the UiO structure. The chiral diene moieties are randomly distributed in the framework and could not be located in the electron density map. The ^{1}H NMR spectra of digested E_2-MOF confirms that the chiral diene groups remain intact during the MOF crystal growth (Fig. S1 and S3, Supporting Information [SI]) and E_2-MOF has a formula of $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(L)_6$•143DMF•109$H_2O$. Thermogravimetric analysis indicated that E_2-MOF contains 73% solvent (Fig. S2, SI), suggesting a highly porous framework structure. However, nitrogen sorption measurements afforded negligible surface areas, presumably due to framework distortion upon solvent removal (Fig. S4 and S5, SI).[9c,19] The pore accessibility of E_2-MOF, E_2-MOF•RhCl, and E_2-MOF•Rh(acac) was demonstrated by dye absorption measurements which shows the uptake of 5.32 (112 wt%), 2.53 (98 wt%), and 4.47 (107 wt%) of Brilliant Blue R-250 per unit cell by E_2-MOF, E_2-MOF•RhCl, and E_2-MOF•Rh(acac), respectively (Fig. S7, SI).[9c]

Postsynthetic metalation of E_2-MOF was carried out by treatment with 1 equiv of $[RhCl(C_2H_4)_2]_2$ or 1 equiv of $Rh(acac)(C_2H_4)_2$, (based on the Rh equivalent with respect to the **L** equivalents in E_2-MOF, SI; acac is acetylacetonate). Powder X-ray diffraction (PXRD) studies indicated that E_2-MOF•RhCl and E_2-MOF•Rh(acac) remained crystalline and adopted the same structure as the original E_2-MOF (Fig. 2a). Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the extent of metalation in E_2-MOF based on the Rh to Zr ratios. E_2-MOF•RhCl achieved 66% metalation whereas E_2-MOF•Rh(acac) only had 13% of the **L** ligands metalated.

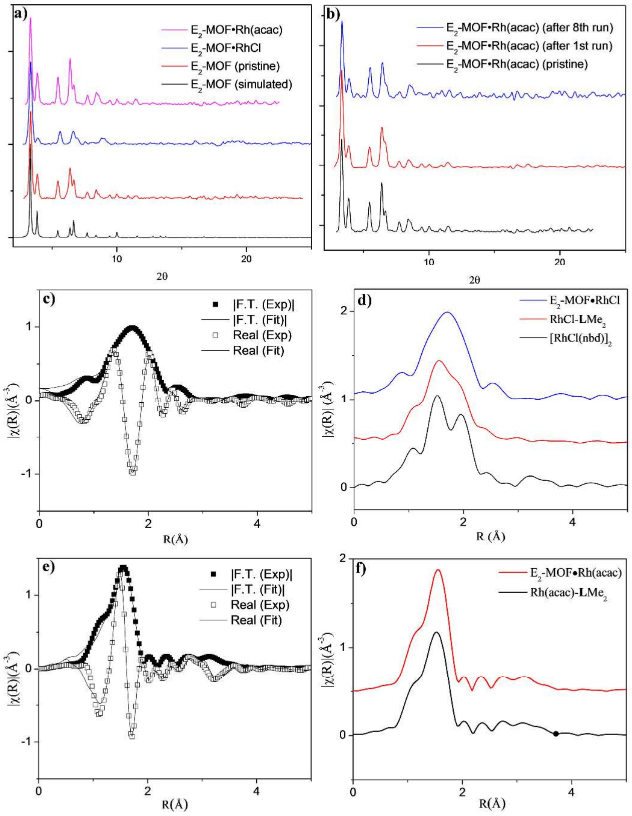


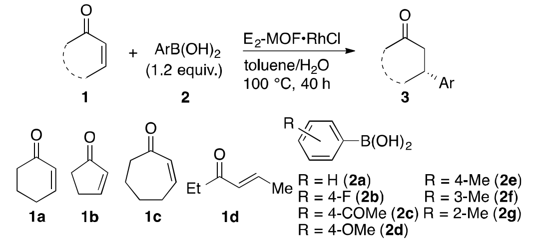
Fig. 2 a) PXRD patterns of pristine E_2-MOF (simulated from the CIF file, black; experimental, red), and freshly prepared E_2-MOF•RhCl (blue) and E_2-MOF•Rh(acac) (pink). b) PXRD patterns of pristine E_2-MOF•Rh(acac) (black) and E_2-MOF•Rh(acac) recovered from 1,2-addition reactions (after 1st run (red) and 8th run (blue)). c) EXAFS data (squares) and best fits(lines) for E_2-MOF•RhCl. Data are displayed in *R*-space containing both magnitude of Fourier Transform and real components. An *R*-factor of 0.01 was obtained for the fit. d) A comparison of EXAFS data for E_2-MOF•RhCl, RhCl(**L**Me_2), and the $[RhCl(nbd)]_2$ dimer. e) EXAFS data (squares) and best fits (lines) for E_2-MOF•Rh(acac). An *R*-factor of 0.016 was obtained for the fit. f) A comparison of EXAFS data for E_2-MOF•Rh(acac) and Rh(acac)-**L**Me_2.

Due to the positional disorder and incomplete metalation of the diene moiety, the Rh coordination environments could not be determined by traditional crystallographic techniques. X-ray absorption fine structure (XAFS) spectroscopy at the Rh K-edge was used to investigate the local coordination environment of Rh in E_2-MOF•RhCl, E_2-MOF•Rh(acac), Rh-metalated **L**Me_2, and the dimeric $[RhCl(nbd)]_2$ standard. Data were processed and analyzed using the Athena and Artemis programs of the IFEFFIT package based on FEFF 6. E_2-MOF•RhCl was fitted with a monomeric model where the Rh coordination sphere is occupied by norbornadiene, chloride, and a THF molecule (Fig. 2c). The spectra for $[RhCl(nbd)]_2$ was fitted by the corresponding crystal structure (Fig. S13). Compared to the spectra for E_2-MOF•RhCl, a significant peak was observed in *R*-space at ~2 Å which is largely attributable to a second Rh-Cl direct scattering path; amplitude from Rh-Rh direct scattering paths can also be observed at ~3.2 Å (Fig. 2d). The RhCl-**L**Me_2 system was best fitted with a combination of monomeric (~85%) and dimeric (~15%) models (Fig. S15, SI), which was confirmed by ^{1}H NMR spectroscopy (Fig. S18, SI). E_2-MOF•Rh(acac) and Rh(acac)-**L**Me_2 were fitted with a reported crystal struture where the Rh coordination sphere is occupied by a diene and an acac ligand.[18a] There is little difference between E_2-MOF•Rh(acac) and Rh(acac)-**L**Me_2 in their EXAF spectra (Fig. 2f) presumably due to the similarity of one chelating diene and two bridging diene on each Rd center in EXAFS, but ^{1}H NMR of Rh(acac)-**L**Me_2 indicated that the Rh(acac)-**L**Me_2 contained a complex mixture inlcuding oligomeric/polymeric species in the homogeneous control (Fig. S19, SI). These results indicate that E_2-MOF•RhCl is a true single-site catalyst by prohibiting any such dimer formation owing to site isolation.[7a-7j,20]

E_2-MOF•RhCl is a highly effective catalyst for 1,4-additions of arylboronic acids to α,β-unsaturated ketones. The reaction of 2-cyclohexenone (**1a**) with phenylboronic acid (**2a**) in the presence of 0.01 mol% E_2-MOF•RhCl gave the addition product in 97% yield and 95% ee (Table 1, entry 1). At 0.005 mol% Rh loading, the reaction proceeded to give the addition product in 67% yield and 94% ee, leading to a high turnover number (TON) of 13400 (entry 2). In comparison, the 1,4-addition reaction with 0.005 mol% Rh of E_2-MOF•Rh(acac) gave the addition product in 46% yield with 93% ee. These results are comparable with those of the homogeneous control catalyst (Table 1, entry 3). As expected, the catalytic activity of E_2-MOF•RhCl is much higher than BINAP-MOF•RhCl (Table 1, entries 2 vs 4). E_2-MOF•RhCl catalyzed 1,4-addition reactions have a broad substrate scope for both arylboronic acids and α,β-unsaturated ketones. Both electron donating groups and electron withdrawing groups can be installed to the aromatic ring of arylboronic acids, giving the addition products in high yields and high ee's (Table 1, entries 5–8). The addition of arylboronic acids having a substituent at the *meta* and *ortho* position also proceeded (Table 1, entries 9 and 10). For α,β–unsaturated ketones, the reactions proceeded with five-membered ring and seven-membered ring substrates (Table 1, entries 11 and 12) as well as with a linear ketone (Table 1, entry 13). Heterogeneity of the 1,4-addition reaction was confirmed by ICP-MS, which indicates the leaching of only small amounts of Rh (1.3%) and Zr (<0.01%) into the solution. However, the recovered E_2-MOF•RhCl showed reduced catalytic activity (Scheme S1, SI), which might be due to the gradual loss of MOF crystallinity during the course of the reaction (Fig. S19, SI). Consistent with this, E_2-MOF Soaked in 1M HCl, water, or 1M NaOH for 40 h lost crystallinity as judged by PXRD (Fig S6, SI).

Asymmetric 1,2-addition of arylboronic acids to aldimines proceeded in the presence of E_2-MOF•Rh(acac).[21] At 0.2 mol% Rh loading, the reaction gave the addition product in 55% yield and 98% ee (Table 2, entry 1). Quantitative yield of the addition product was obtained at 3 mol% Rh loading (Table 2, entry 3). Interestingly, E_2-MOF•Rh(acac) performed better than the homogeneous control catalyst both in terms of yields and ee's. For the homogeneous control, the product yield can be increased by increasing the catalyst loading but at the expense of the obtained ee's. The ee's of the E_2-MOF•Rh(acac)-catalyzed reactions remained constant at different catalyst loadings. This striking difference can be attributed to the desirable site isolation provided by the MOF, which exclusively affords the desired monomeric Rh species; in contrast, the homogeneous control can form a dimeric/oligomeric species which might be less enantioselective. This monomer/dimer equilibrium was proved by EXAFS and ^{1}H NMR studies for the RhCl(**L**Me_2) system (Fig. 2d and 3a).

Table 1 Asymmetric 1,4-additions of arylboronic acids to α,β-unsaturated ketones with E_2-MOF•RhCl and homogeneous catalysts[a]

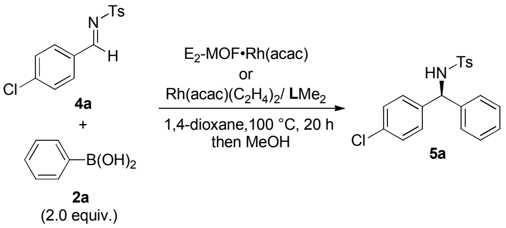


entry	enone	aryl boronic acid	catalyst loading (mol% Rh)	yield (%)[b]	ee (%)[c]	TON
1	**1a**	**2a**	0.01	97	95	9700
2	**1a**	**2a**	0.005	67	94	13400
3[d]	**1a**	**2a**	0.005	70	91	14000
4[e]	**1a**	**2a**	0.005	3	–[f]	600
5	**1a**	**2b**	0.025	90	94	3600
6	**1a**	**2c**	0.05	80	91	1600
7	**1a**	**2d**	0.01	84	96	8400
8	**1a**	**2e**	0.05	87	95	1740
9	**1a**	**2f**	0.05	84	94	1680
10	**1a**	**2g**	0.05	82	74	1640
11	**1b**	**2a**	0.1	82	90	820
12[g]	**1c**	**2a**	0.1	93	70	930
13[g]	**1d**	**2a**	0.25	84	90	336

[a] Reaction conditions: **1** (1 equiv.), **2** (1.2 equiv.), toluene, H_2O at 100 °C for 40 h. [b] Isolated yield. [c] Determined by chiral HPLC. [d] $[RhCl(C_2H_4)_2]_2$ and

LMe$_2$ were used as catalyst. [e] BINAP-MOF•RhCl was used as catalyst. [f] Not determined. [g] 2.0 equiv of PhB(OH)$_2$.

Table 2 Asymmetric 1,2-Addition of aldimine **4a** with E$_2$-MOF•Rh(acac) and homogeneous control catalyst[a]

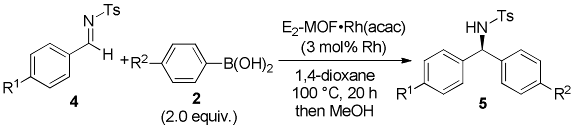


entry	catalyst	catalyst loading	yield (%)[b]	ee (%)[c]	TON
1	E$_2$-MOF•Rh(acac)	0.2 mol%	55	98	275
2	E$_2$-MOF•Rh(acac)	0.6 mol%	71	98	118
3	E$_2$-MOF•Rh(acac)	3 mol%	99	98	33
4	Rh(acac)/**L**Me$_2$	0.2 mol%	11	94	55
5	Rh(acac)/**L**Me$_2$	0.6 mol%	55	89	92
6	Rh(acac)/**L**Me$_2$	3 mol%	87	83	29

[a] **4a** (1.0 equiv.), **2a** (2.0 equiv.), catalyst, 1,4-dioxane, 100 °C, 20 h. [b] NMR yield based on internal standard. [c] Determined by chiral HPLC analysis. Ts = *p*-toluenesulfonyl

E$_2$-MOF•Rh(acac)-catalyzed 1,2-addition reactions have a broad substrate scope for both arylboronic acids and aldimines to give addition products with excellent ee's (ranging from 97% to >99%). The reaction works with aldimines and arylboronic acids having electron donating groups or electron withdrawing groups (Table 3, entries 1–6).

Table 3 Asymmetric Addition of Arylboronic Acids to *N*-Tosylaldimines[a]



entry	R^1	R^2	yield (%)[b]	ee (%)[c]	TON
1	Cl (**4a**)	H (**2a**)	99	98	33
2	Cl (**4a**)	F (**2b**)	95	99	32
3	Cl (**4a**)	OMe (**2d**)	80	97	27
4	H (**4b**)	F (**2b**)	97	99	32
5	H (**4b**)	OMe (**2d**)	96	97	32
6	OMe (**4c**)	H (**2a**)	98	99	33
7	OMe (**4c**)	F (**2b**)	99	>99	33

[a] **4** (1.0 equiv.), **2** (2.0 equiv.), E$_2$-MOF•Rh(acac) (3 mol% Rh), 1,4-dioxane, 100 °C, 20 h. [b] NMR yield based on internal standard. [c] Determined by chiral HPLC analysis.

Several experiments proved that E$_2$-MOF•Rh(acac) is a true heterogeneous and reusable catalyst. First, the MOF catalyst (6 mol% Rh) could be recycled and reused for at least 7 times without loss of yield and ee (Fig. 3b). Second, the crystallinity of the MOF catalyst recovered from the 1st and 8th runs was still maintained as the PXRD of the recovered catalyst remained the same as the freshly prepared E$_2$-MOF•Rh(acac) (Fig. 2b). Third, ICP-MS analysis showed negligible leaching of Rh (0.49%) and Zr (0.07%) during the reaction. Fourth, the progress of the reaction was stopped by removing the MOF catalyst from the reaction mixture, indicating that the supernatant is inactive in catalyzing the 1,2-addition reactions (Scheme S3, SI).

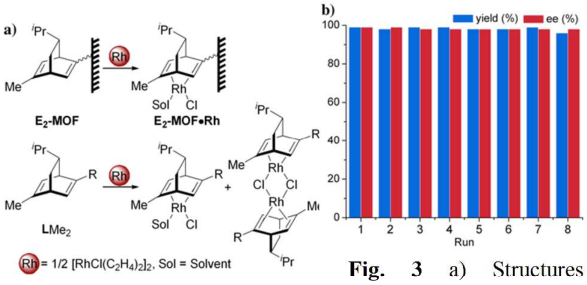


Fig. 3 a) Structures of rhodium-coordinated diene complexes in MOF catalyst and the homogeneous control catalyst. b) Plot of yield (%) and ee (%) of 1,2-addition product at various runs in the recycle and reuse of E$_2$-MOF•Rh(acac) (6 mol% Rh) for 1,2-addition of aldimine **4a** with phenylboronic acid (**2a**).

Conclusions

We have developed catalytically active chiral Rh-diene-based MOFs for asymmetric C-C formation reactions. The metalated MOFs catalyzed 1,4-addition of α,β-unsaturated ketones and arylboronic acid with a TON of 13400 and 1,2-addition of aldimines and arylboronic acid with excellent enantioselectivity (up to >99% ee). E$_2$-MOF•Rh(acac) showed higher activity and enantioselectivity than the homogeneous control catalyst owing to the formation of a single-site catalyst in the MOF, and was reused for at least 7 times without loss of yield and ee. Our work thus establishes metalated diene-MOFs as highly active and enantioselective single-site solid catalysts for the construction of carbon-carbon bonds.

Acknowledgements

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Notes and references

1 (*a*) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.* 2012, **112**, 782-835; (*b*) M. Dincă and J. R. Long, *Angew. Chem., Int. Ed.* 2008, **47**, 6766-6779; (*c*) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.* 2005, **44**, 4670-4679.

2 (*a*) D. Liu, K. Lu, C. Poon and W. Lin, *Inorg. Chem.* 2014, **53**, 1916-1924; (*b*) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.* 2012, **112**, 1105-1125; (*c*) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.* 2012, **112**, 1126-1162; (*d*) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.* 2009, **38**, 1330-1352.

3 W. Lin, W. J. Rieter and K. M. L. Taylor, *Angew. Chem., Int. Ed.* 2009, **48**, 650-658.

4 (*a*) P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.* 2012, **112**, 1232-1268; (*b*) J. D. Rocca, D. Liu and W. Lin, *Acc. Chem. Res.* 2011, **44**, 957-968; (*c*) R. C. Huxford, J. D. Rocca and W. Lin, *Curr. Opin. Chem. Biol.* 2010, **14**, 262-268.

5 (*a*) C. Wang, T. Zhang and W. Lin, *Chem. Rev.* 2012, **112**, 1084-1104; (*b*) O. R. Evans and W. Lin, *Acc. Chem. Res.* 2002, **35**, 511-522.

6 (*a*) J. Gascon, A. Corma, F. Kapteijn and F. X. Llabrés i Xamena, *ACS Catal.* 2014, **4**, 361-378; (*b*) M. Zhao, S. Ou and C.-D. Wu, *Acc. Chem. Res.* 2014, **47**, 1199-1207; (*c*) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.* 2012, **112**, 1196-1231; (*d*) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.* 2009, **38**, 1248-1256; (*e*) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.* 2009, **38**, 1450-1459.

7 (*a*) K. Manna, T. Zhang, F. X. Greene and W. Lin, *J. Am. Chem. Soc.* 2015, **137**, 2665-2673; (*b*) C. M. McGuirk, M. J. Katz, C. L. Stern, A. A. Sarjeant, J. T. Hupp, O. K. Farha and C. A. Mirkin, *J. Am. Chem. Soc.* 2015, **137**, 919-925; (*c*) H. Fei and S. M. Cohen, *J. Am. Chem. Soc.* 2015, **137**, 2191-2194; (*d*) M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.* 2014, **136**, 15861-15864; (*e*) K. Manna, T. Zhang, M. Carboni, C. W. Abney and W. Lin, *J. Am. Chem. Soc.* 2014, **136**, 13182-13185; (*d*) K. Manna, T. Zhang and W. Lin, *J. Am. Chem. Soc.* 2014, **136**, 6566-6569; (*f*) H. Fei, J. Shin, Y. S. Meng, M. Adelhardt, J. Sutter, K. Meyer and S. M. Cohen, *J. Am. Chem. Soc.* 2014, **136**, 4965-4973; (*g*) J. M. Falkowski, T. Sawano, T. Zhang, G. Tsun, Y. Chen, J. V. Lockard and W. Lin, *J. Am. Chem. Soc.* 2014, **136**, 5213-5216; (*h*) K. Mo, Y. Yang and Y. Cui, *J. Am. Chem. Soc.* 2014, **136**, 1746-1749; (*i*) J. Canivet, S. Aguado, Y. Schuurman and D. Farrusseng, *J. Am. Chem. Soc.* 2013, **135**, 4195; (*j*) D. T. Genna, A. G. Wong-Foy, A. J. Matzger and M. S. Sanford, *J. Am. Chem. Soc.* 2013, **135**, 10586-10589; (*k*) M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.* 2014, **136**, 15861-15864; (*l*) D. T. Genna, A. G. Wong-Foy, A. J. Matzger and M. S. Sanford, *J. Am. Chem. Soc.* 2013, **135**, 10586-10589; (*m*) Y. Liu, S. Liu, S. Liu, D. Liang, S. Li, Q. Tang, X. Wang, J. Miao, Z. Shi and Z. Zheng, *ChemCatChem* 2013, **5**, 3086-3091.

8 J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature* 2000, **404**, 982-986.

9 (*a*) C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.* 2005, **127**, 8940-8941; (*b*) C.-D. Wu and W. Lin, *Angew. Chem., Int. Ed.* 2007, 46, 1075-1078; (*c*) L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nat. Chem.* 2010, **2**, 838-846; (*d*) S. Regati, Y. He, M. Thimmaiah, P. Li, S. Xiang, B. Chen and J. C.-G. Zhao, *Chem. Commun.* 2013, **49**, 9836-9838.

10 (*a*) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chem. Comm.* 2006, 2563-2565; (*b*) F. Song, C. Want, J. M. Falkowski, L. Ma and W. Lin, *J. Am. Chem. Soc.* 2010, **132**, 15390-15398; (*c*) F. Song, C. Wang and W. Lin, *Chem. Commun.* 2011, **47**, 8256-8258; (*d*) A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.* 2011, **133**, 13252-13255; (*e*) J. M. Falkowski, C. Wang, S. Liu and W. Lin, *Angew. Chem., Int. Ed.* 2011, **50**, 8674-8678; (*f*) A. M. Shultz, O. K. Farha, D. Adhikari, A. A. Sarjeant, J. T. Hupp and S. T. Nguyen, *Inorg. Chem.* 2011, **50**, 3174-3176; (*g*) C. Zhu, G. Yuan, X. Chen, Z. Yang and Y. Cui, *J. Am. Chem. Soc.* 2012, **134**, 8058-8061.

11 Chiral diene-based covalent organic framework was recently reported and used for rhodium-catalyzed 1,4-addition reaction at modest TONs and ee's. J. Dong, Y. Liu and Y. Cui, *Chem. Commun.* 2014, **50**, 14949-14952.

12 T. Hayashi, K. Ueyama, N. Tokunaga and K. Yoshida, *J. Am. Chem. Soc.* 2003, **125**, 11508-11509.

13 C. Fischer, C. Defieber, T. Suzuki and E. M. Carreira, *J. Am. Chem. Soc.* 2004, **126**, 1628-1629.

14 C. Defieber, H. Grützmacher and E. M. Carreira, *Angew. Chem., Int. Ed.* 2008, **47**, 4482-4502.

15 (*a*) R. Shintani, Y. Tsutsumi, M. Nagaosa, T. Nishimura and T. Hayashi, *J. Am. Chem. Soc.* 2009, **131**, 13588-13589; (*b*) T. Nishimura, J. Wang, M. Nagaosa, K. Okamoto, R. Shintani, F. Kwong, W. Yu, A. S. C. Chan and T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 464-465; (*c*) R. Shintani, M. Takeda, T. Nishimura and T. Hayashi, *Angew. Chem., Int. Ed.* 2010, **49**, 3969-3971; (*d*) T. Nishimura, Y. Takiguchi and T. Hayashi, *J. Am. Chem. Soc.* 2012, **134**, 9086-9089.

16 (*a*) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani and T. Hayashi, *J. Am. Chem. Soc.* 2004, **126**, 13584-13585; (*b*) R. Shintani, M. Takeda, T. Tsuji and T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 13168-13169; (*c*) Z. Cui, H.-J. Yu, R.-F. Yang, W.-Y. Gao, C.-G. Feng and G.-Q. Lin, *J. Am. Chem. Soc.* 2011, **133**, 12394-12397; (*d*) T. Nishimura, A. Noishiki, G. C. Tsui and T. Hayashi, *J. Am. Chem. Soc.* 2012, **134**, 5056-5059; (*e*) Y. Luo, H. B. Hepburn, N. Chotsaeng and H. W. Lam, *Angew. Chem., Int. Ed.* 2012, **51**, 8309-8313; (*f*) T. Nishimura, A. Noishiki, Y. Ebe and T. Hayashi, *Angew. Chem., Int. Ed.* **2013**, *52*, 1777-1780.

17 (*a*) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.* 2008, **130**, 13850-13851; (*b*) M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.* 2010, **22**, 6632-6640.

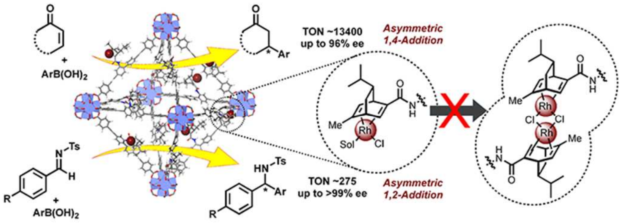
18 (*a*) K. Okamoto, T. Hayashi and V. H. Rawal, *Chem. Commun.* 2009, 4815-4817; (*b*) G. Pattison, G. Piraux and H. W. Lam, *J. Am. Chem. Soc.* 2010, **132**, 14373-14375.

19 G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.* 2005, **38**, 217-225.

20 (*a*) P. V. Dau and S. M. Cohen, *Inorg. Chem.* 2015, **54**, 3134-3138; (*b*) Y.-R. Lee; Y.-M. Chung and W.-S. Ahn, *RSC Adv.* 2014, **4**, 23064-23067; (*c*) Y. Yang, H.-F. Yao, F.-G. Xi, E.-Q. Gao, *J. Mol. Catal. A: Chem.* 2014, **390**, 198-205; (*d*) T. Toyao, M. Fujiwaki, Y. Horiuchi and M. Matsuoka, RSC Adv. 2013, 3, 21582-21587; (*e*) B. Li, Y. Zhang, D. Ma, L. Li, G. Li, G. Li, Z. Shi and S. Feng, *Chem. Commun.* 2012, **48**, 6151-6153; (*f*) P. Wu, J. Wang, Y. Li, C. He, Z. Xie and C. Duan, *Adv. Funct. Mater.* 2011, **21**, 2788-2794; (*g*) R. Srirambalaji, S. Hong, R. Natarajan, M. Yoon, R. Hota, Y. Kim, Y. Ho Ko and K. Kim, *Chem. Commun.* 2012, **48**,

11650-11652; (h) F. Vermoortele, R. Ameloot, A. Vimont, C. Serre and D. De Vos, *Chem. Commun.* 2011, **47**, 1521-1523.
21 The 1,2-addition reaction did not proceed with E_2-MOF•RhCl.

TOC Graphic:



The first chiral rhodium-diene-based metal–organic frameworks are highly active and enantioselective catalysts for C–C bond formation reactions.