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Synthesis and Catalytic Application of *N*-Heterocyclic Carbene Copper Complex Functionalized Conjugated Microporous Polymer

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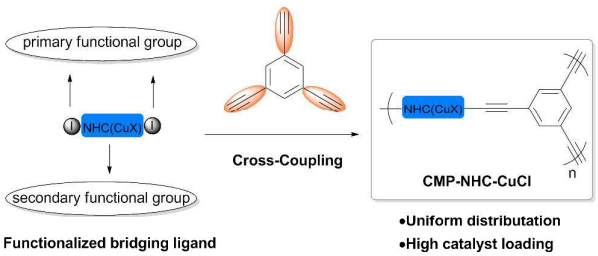
N-Heterocyclic carbene copper(I) complex functionalized conjugated microporous polymer (CMP-NHC-CuCl) was synthesized by palladium-catalyzed Sonogashira cross-coupling chemistry. The resulting CMP-NHC-CuCl proved to be good heterogeneous catalyst in hydrosilylation of functionalized terminal alkynes with boryldisiloxane to afford (β,β)-(*E*)-vinyldisiloxane with high stereoselectivity, and the catalyst could be used four times without obvious loss in catalytic activity. Moreover, CMP-NHC-CuCl was also efficient in catalyzing the hydrosilylation of CO_2 with triethoxysilane to form silyl formate under mild conditions.

Since *N*-heterocyclic carbene (NHC) copper complex was first reported by Arduengo and co-workers in 1993,[1] their applications have attracted broad attention in homogeneous catalysis,[2] especially for the hydrosilylation of carbonyl compounds producing the corresponding silyl compounds,[3] carbene transfer reactions generating the three-membered ring,[4] [3+2] cycloaddition of azides and alkynes enabling new triazole ring reaction[5] and Miscellaneous reaction providing the γ-selective allylic products[6]. Recently, the novel catalytic applications of NHC-Cu(I) complexes are emerging in various transformation of CO_2[2e-2g] such as the carboxylation of a variety of substrates[7], reduction of CO_2 into CO[8] or formic acid[9].

It is generally known that homogeneous catalytic processes usually suffer from some drawbacks, including the difficulty in the separation of catalysts, the purification of the product and the recovery of the expensive catalysts. Additionally, the residual metal in the products probably causes serious problems for the applications of bioactive substrates, particularly for medical purpose. The immobilization of homogeneous catalysts onto solid supports is an effective method to solve the above problems. In 2010, Zhang and co-workers successfully synthesized the novel poly-(NHC)CuCl, in which the main-chains contain a great amount of (NHC)CuCl units. The resultant poly-(NHC)CuCl was used to catalyze the transformation of CO_2 to carboxylic acids through C-H bond activation of terminal alkynes.[10] Shortly afterwards, Wang group developed the silica-supported NHC-Cu(II) catalyst for oxidative coupling of terminal alkynes with H-phosphonates, and no significant loss in the catalytic reactivity was observed after recycling six times.[11] More recently, a 3-D diamondoid metal organic framework using bis-NHC Cu(I) complex as a building block was successfully applied to catalyze the hydroboration of CO_2 to provide formamides.[12]

Conjugated microporous polymers[13], as a new class of porous materials with high synthetic diversification, have been used as promising solid supports in heterogeneous catalysis.[14] Main method for creating catalytically active CMPs is to design and synthesize the bridging ligands containing orthogonal functional groups, as shown in Scheme 1. The primary functional groups could be linked by suitable nodes to form extended networks, whereas the orthogonal secondary functional groups can then be employed to generate catalytic sites. Through this synthetic strategies, many CMPs containing Fe[14a], Re[14b], Rh[14b], Co[14e] and Zn[14f] complexes have been synthesized and applied for catalytic applications.



Scheme 1. Synthetic strategy of CMP-NHC-CuCl

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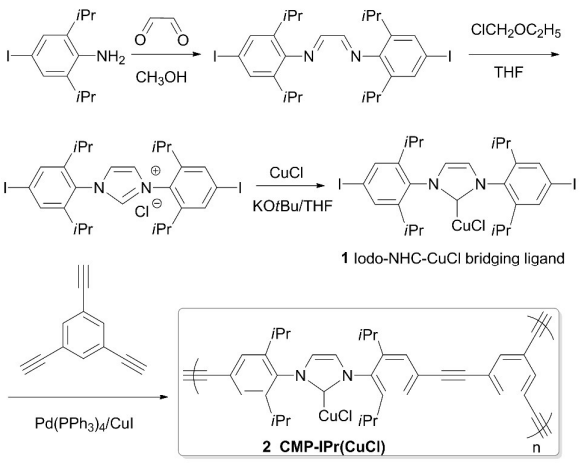
Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C cross-polarization magic-angel spinning NMR spectroscopy of *N*-Heterocyclic Carbene Copper Complex Functionalized Conjugated Microporous Polymer, kinetic studies and the characterization data of products. See DOI: 10.1039/x0xx00000x.

In this study, we firstly report the synthesis of a copper-coordinated conjugated microporous polymer (CMP-NHC-CuCl) by linking NHC-CuCl with 1,3,5-triethynylbenzene. The CMP-NHC-CuCl exhibits high activity towards the hydrosilylation of functionalized terminal alkynes to selectively synthesize (β,β)-(*E*)-vinyldisiloxane, as well as the chemical transformation of CO_2 to form silyl formate.

Results and Discussion

Due to its high air- and moisture-stability, IPrCuCl has the potential to be used as secondary functional group to construct copper complex functionalized CMPs.[15] Detailed synthetic routes are showed in Scheme 2. CMP-NHC-CuCl was synthesized by the Sonogashira cross coupling polycondensation of an iodo-NHC-CuCl **1** and 1,3,5-triethynylbenzene in the presence of Pd (0) and CuI as catalyst under alkaline conditions. According to the literature procedures,[13,14] polycondensation in toluene in the presence of triethylamine as base and Pd tetrakis-(triphenylphosphine) palladium (0) as palladium source allows for the preparation of CMP-NHC-CuCl **2** in an isolated yield of 86.7 %. The CMP-NHC-CuCl was insoluble in all solvents tested. After repeated rinse with water, CH_2Cl_2, methanol and acetone, CMP-NHC-CuCl was rigorously wash by Soxhlet extraction for 24 h with CH_2Cl_2, methanol and acetone, respectively, to remove any entrapped impurities, and then dried under vacuum for 24 h at 80 °C. The resultant CMP-IPr(CuCl) showed higher catalyst loading and more accessible catalytic centers based on the iodo-NHC-CuCl linkers.

The morphology of CMP-NHC-CuCl was investigated by scan electron microscopy (SEM) and transmittance electron microscopy (TEM) measurements. SEM image in Figure 1a displayed that CMP-NHC-CuCl consists of submicro spheres, while TEM image in Figure 1b revealed the presence of nanometer-scale pores (≈0.4 nm in diameter) on the polymer surface. The porous properties of the networks were investigated by nitrogen adsorption analyses at 77.3 K. The



Scheme 2. Synthetic route of CMP-NHC-CuCl

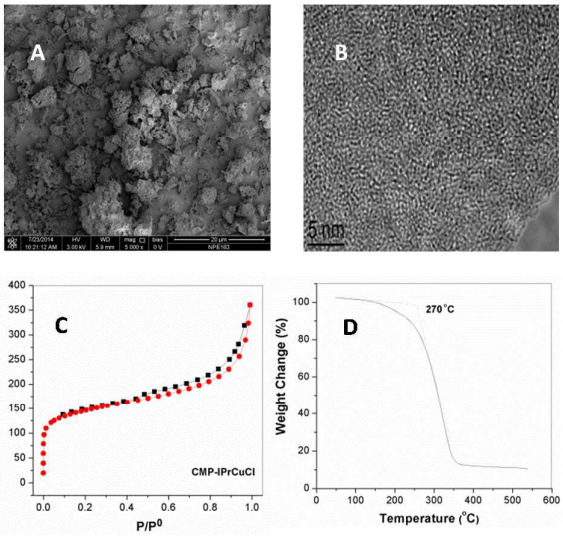
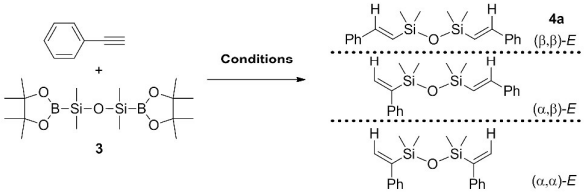


Figure 1. Synthetic route of CMP-NHC-CuCl SEM (a) and TEM (b) images of CMP-NHC-CuCl. (c) N_2 sorption isotherm at 77.3 K (●= adsorption; ▯= desorption). (d) TGA of CMP-NHC-CuCl under N_2 atmosphere. Ramp rate = 5 °C/min

BET surface area was found to be 388 m^2g^{-1} (the Langmuir surface area is 580 m^2g^{-1}) and the total volumes were 0.56 cm^3g^{-1} at P/P^0 = 0.99. As shown in Figure 1c, the adsorption isotherm displayed a notable nitrogen gas uptake at low relative pressure (P/P_0<0.01) reflecting an abundant micropore structure.[16] The TGA curve in Figure 1d reveals a stability of the materials at least up to 270 °C.

Considering the excellent thermal stability of CMP-IPr(CuCl)

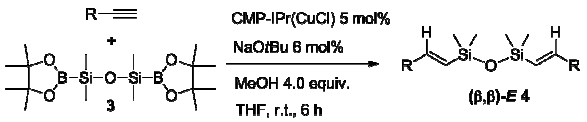
Table 1. CMP-NHC-CuCl catalyzed hydrosilylation of phenylacetylene with boryldisiloxane 3.[a]

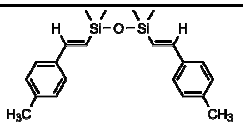
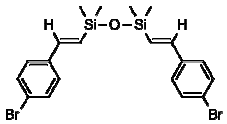
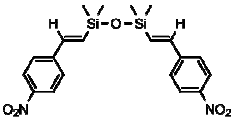
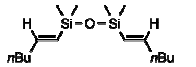
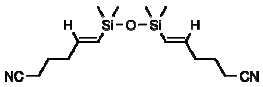
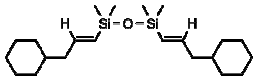
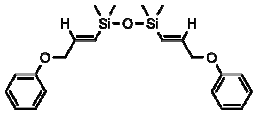
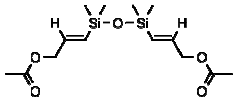
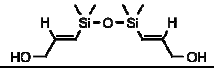


Entry	Cat. (mol%)	Time (h)	Yield (%)[b]	Selectivity (β,β/α,β/α,α)[c]
1	1	2	34	>99:1:<1
2	2	2	50	>99:1:<1
3	5	2	79	>99:1:<1
4	5	6	92	>99:1:<1

[a] Reaction conditions: Si-B reagent (77.2 mg, 0.2 mmol), phenylacetylene (40.8 mg, 0.4 mmol), CMP-IPr(CuCl), NaO*t*Bu (1.2 equiv. to the amount of [Cu]), MeOH (65 μL, 1.6 mmol, 4.0 equiv.), THF (1 mL), room temperature, unless otherwise noted. [b] Yield of isolated product. [c] Determined by analysis of the crude mixture.

Table2. Scope in terminal alkynes. [a]



Entry	Product		Yield (%)[b]
1		**4b**	90
2		**4c**	82
3		**4d**	75
4		**4e**	91
5		**4f**	90
6		**4g**	88
7		**4h**	75
8		**4i**	80
9[c]		**4j**	87

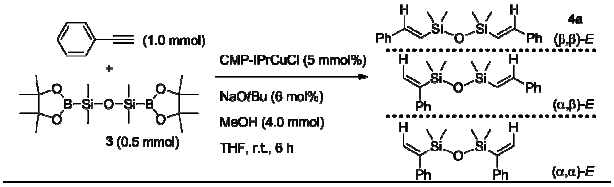
[a](β,β)-(*E*)-vinyldisiloxanes 4b-4j obtained from their corresponding terminal alkynes using CMP-IPr(CuCl) as heterogeneous catalyst. General conditions: Si-B reagent (0.2 mmol, terminal alkyne (0.4 mmol), CMP-IPr(CuCl) (5 mol%) NaO^{t}Bu (6 mol%), MeOH (1.6 mmol), THF (1 mL), RT, 6 h, unless otherwise noted. [b] Yield of isolated product; (β,β)/(α,β)/(α,α)>99:1:<1, as determined by analysis of the crude mixture by ^{1}H-NMR spectroscopy. [c] No additional MeOH.

and the successful incorporation of IPr(CuCl) into this network, the catalytic behaviour of CMP-IPr(CuCl) was investigated in detail. Firstly, the hydrosilylation of terminal alkynes with boryldisiloxane was chosen as a model reaction to selectively synthesize functionalized vinylsilanes. Our previous study on NHC copper(I) catalyzed hydrosilylation had shown that IPr(CuCl) complex was effective catalyst system to transform *terminal* alkynes employing 1,1,3,3-Tetramethyl-1,3-(pinacolboryl) disiloxane **3** as silicon source to (β,β)-(*E*)-vinyldisiloxane **4a** as the sole detectable isomer with perfect regio- and stereoselectivity under mild conditions (room temperature, 2 h).[17] CMP-IPr(CuCl) displayed excellent dispersion ability in THF. To out delight, CMP-IPr(CuCl) proved to be an effective catalyst for the hydrosilylation of phenylacetylene with **3**, and all results are shown in table 1. The reaction could proceed smoothly in the 1 mol% CMP-IPr(CuCl) at room temperature, affording (β,β)-(*E*)-**4a** with an isolated yield of 34% within 2 h (entry 1). It is worth noting that the stereoselectivity of CMP-IPr(CuCl) is comparable to those of homogeneous catalyst and only (β,β)-(*E*)-**4a** was produced with high regio-and site-selectivity, confirmed by the analysis of the crude mixture by ^{1}H-NMR spectroscopy. When the catalyst loading was increased 5 mol%, the yield of (β,β)-(*E*)-**4a** reached to 79% at the same conditions (entry 3). Moreover, the highest yield (92%) could be obtained by the prolonged reaction time of 6 h (entry 4).

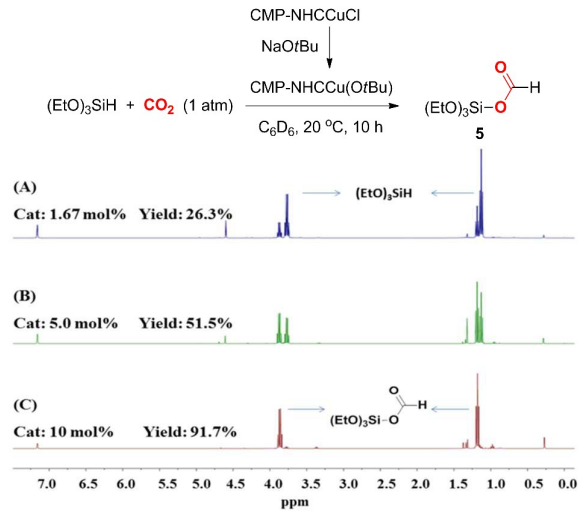
Furthermore, several types of terminal alkynes were subjected to the catalytic reaction with boryldisiloxane 3 in order to evaluate the scope of the present transformation, and the results are summarized in Table 2. Functional groups such as methyl-, bromo- and nitro- groups at the para position of the aromatic ring were tolerated in the reaction, although electron withdrawing substituents retarded the reaction rate (4b-4d). Other substrates with a variety of functional groups, such as alkyl, cyano, ether, ester, were tolerated in these reaction (4e-4i), giving the corresponding (β,β)-(*E*)-vinyldisiloxanes in good to excellent yields with no observable byproduct formation. The reaction with propargyl alcohol did not require the use of additional MeOH. The desired product 4j could be obtained by hydrolysis and SiO_2 flash chromatography purification.[17]

Since CMP-IPr(CuCl) is stable and insoluble in common organic solvents, the investigation of the recycle use of CMP-IPr(CuCl) is very convenient. After the hydrosilylation reaction was completed, the reaction mixture was filtered to collect the

Table 3. Recycle test of CMP-IPr(CuCl) in the hydrosilylation of phenylacetylene with boryldisiloxane **3**.



Run	Yield (%)	Selectivity (%)		
		(β,β)-*E*	(α,β)-*E*	(α,α)-*E*
1st	92	>99	<1	<1
2nd	90	>99	<1	<1
3rd	90	>99	<1	<1
4th	89	>99	<1	<1



Scheme 3. CMP-IPrCuCl catalyzed hydrosilylation of CO_2.

catalyst for the next round of hydrosilylation of phenylacetylene with boryldisiloxane **3**. As shown in table 3, CMP-NHC-CuCl exhibited excellent stability, and was recycled for four times, without obvious loss in catalytic activity.

Chemical transformation of CO_2, as an inexpensive, abundant, nontoxic and renewable C1 feedstock, always attract extensive attention worldwide of the scientists, especially in the areas of environment and chemistry.[18] The NHC-copper alkoxide complex IPrCu(O*t*Bu) have recently been reported to catalyze the hydrosilylation of CO_2 with triethoxysilane, affording the silyl formate at room temperature under 1 atm CO_2.[5a] IPrCu(O*t*Bu) complex is readily prepared from the corresponding chloride through the reaction with sodium *tert*-butoxide.[19] Therefore, we further investigated the diverse activity of CMP-IPr(CuCl) to catalyze the hydrosilylation of CO_2 in the presence of catalytic amount of NaO*t*Bu, and the results are shown in Scheme 3. The hydrosilylation was performed with 1.67 mol% CMP-IPr(CuCl), although the product yield (**A** 26.3%) was lower than that when IPrCu(O*t*Bu) complex as homogeneous catalyst[9a]. However, the product yield could be significantly increased to 51.5% (**B**) and 91.7% (**C**), respectively, by increasing CMP-IPrCuCl concentration to 5 mol% and 10 mol%, respectively. In order to clarify this process, the reaction order in [CMP-IPrCuCl] was further studied by means of in-situ FTIR (See supporting Information, Figure S4-S9). The results showed that the reaction is first-order in [CMP-IPrCuCl], so the rate of the silyl formate was obviously affected by the catalyst concentration.

Conclusions

In summary, we have reported the first example of IPr(CuCl) functionalized conjugated microporous polymer, CMP-IPr(CuCl). CMP-IPr(CuCl) has been found to be efficient heterogeneous catalysts for the hydrosilylation of terminal alkynes with good substrate tolerance and could be reused at least four times without a significant loss in catalytic efficiency. Further investigations of the catalytic diversity showed that CMP-IPr(CuCl) also was efficient in catalyzing the hydrosilylation of CO_2 to afford the silyl formate under mild conditions.

Experimental Section

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a dry nitrogen atmosphere or an Innovative Technology glovebox under Ar. NMR spectra were recorded on a Bruker Avance II 400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. Infra-red spectra (IR) were recorded using a Nicolet NEXUS FT-IR spectrophotometer.THF and d^6-benzene were purified by distilling from sodium/benzophenone under a N_2 atmosphere. iodo-NHC-CuCl **1** [20] and 1,1,3,3-tetramethyl-1,3-(pinacolboryl) disiloxane **3** [17] were synthesized according the responding literatures. Commerically available terminal alkynes and triethoxysilane were used without further purification.

Synthesis of CMP-IPr(CuCl). iodo-IPr(CuCl) (368 mg, 0.5 mmol), 1,3,5-triethynylbenzene (75 mg, 0.50 mmol), tetrakis-(triphenylphosphine) palladium (0) (30 mg, 0.025 mmol) and CuI (20 mg, 0.10 mmol) were dissolved in a mixture of toluene (2.5 mL) and triethylamine (1.25 mL). The reaction mixture was heated to 80 °C and stirred for 72 h. The mixture was cooled to room temperature, and the insoluble precipitated network polymer was filtered and washed three times with dichloromethane, water and methanol (30 mL×3) respectively to remove the unreacted substrates. Further purification of the polymer was carried out using a Soxhlet extraction with water, CH_2Cl_2, methanol and acetone (1:1:1:1) for 24 h. The product was dried under vacuum with the temperature of 80 °C for 24 h and isolated as a yellow powder (Yield: 286 mg, 86.7%). IR (KBr): 2961, 2928, 2863, 1626, 1595, 1436, 1387, 882 cm^{-1}. Elemental combustion analysis (%) Calcd for $C_{41}H_{37}N_2Cu$ (based on 100% reaction of Iodo group): C: 74.64, H 6.11, N 4.25, Cu 9.63; Found: C 71.43, H 5.77, N 4.05. The copper content of CMP-IPr(CuCl) was determined to be 1.4 mmol/g based on ICP analysis.

General procedure for CMP-IPr(CuCl) catalyzed hydrosilylation of terminal alkynes with Si-B 3. In a glovebox, a vial was charged with CMP-IPr(CuCl) (14.2 mg, 5 mol %), NaO*t*Bu (2.3 mg, 6 mol%) and THF (1 mL). After 30 min stirring at room temperature, phenylacetylene (40.8 mg, 0.4 mmol), 1,1,3,3-tetramethyl-1,3-(pinacolboryl)disiloxane **3** (77.2 mg, 0.2 mmol) and methanol (65 µL, 1.6 mmol, 4.0 equiv.) were sequentially added to the solution, then continue to stir at room temperature for 6 hours. After removal of the solvents under reduced pressure, the crude product was purified by silica gel column chromatography (hexane) to afford **4a** as a colourless liquid (92% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.4 Hz, 4 H), 7.39 (t, *J* = 7.4 Hz, 4 H), 7.33 (t, *J* = 7.4 Hz, 2 H), 7.05 (d, *J* = 19.2 Hz, 2 H), 6.54 (d, *J* = 19.2 Hz, 2 H), 0.36 (s, 12 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.66, 138.45, 128.85, 128.50, 126.88, 1.23.

General procedure for CMP-IPr(CuCl) catalyzed hydrosilylation of CO_2 with $(EtO)_3SiH$. In a glovebox, a 5 mL vial was charged with CMP-IPr(CuCl) (21.5 mg, 10 mol %), NaO^tBu (3.5 mg, 12 mol%), $(EtO)_3SiH$ (49.2 mg, 0.3 mmol) and C_6D_6 (1.5 mL) respectively. After 10 minutes stirring at room temperature, the resulting mixture was transferred from glovebox into a 100 mL Schlenk flask with a CO_2 balloon. The reaction was carried out at room temperature for 10 hours with continuous stirring. Then, the yield was determined by ^1H NMR of the crude reaction mixture. **5** (yield: 91.7%). **^1H NMR** (400 MHz, C_6D_6): δ 7.71 (s, 1H), 3.84 (q, *J* = 6.9 Hz, 6H), 1.10 (t, *J* = 6.9 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): 158.21, 60.15, 18.02.

Acknowledgements

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Notes and references

1 A. J. Arduengo, H. V. Rasika Dias, J. C. Calabrese, F. Davidson, *Organometallics,* 1993, **12**, 3405-3409.
2 For review, see: (a) P. L. Arnold, *Heteroat. Chem*., 2002, **13**, 534-539. (b) S. Díez-González, S. P. Nolan, *Synlett*., 2007, **14**, 2158-2167. (c) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.,* 2009, **109**, 3612-3676. (d) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.,* 2009, **109**, 3561-3598. (e) L. Zhang, Z. Hou, *Pure Appl. Chem.,* 2012, **48**, 1705-1712. (f) L. Zhang, Z. Hou, *Chem. Sci.,* 2013, **4**, 3395-3403. (g) F. Lazerg, F. Nahra, C. S. J. Cazin, *Coord. Chem. Rev.,* 2015, **293-294**, 48-79.
3 (a) H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics,* 2004, **23**, 1157-1160. (b) S. Díez- González, H. Kaur, F. K. Zinn, E. D. Stevens, S. P. Nolan, *J. Org. Chem.,* 2005, **70**, 4784-4796.
4 (a) M. R. Fructos, T. R. Belderrain, M. C. Nicasio, S. P. Nolan, H. Kaur, M. M. Díaz-Requejo, P. J. Pérez, *J. Am. Chem. Soc.,* 2004, **126**, 10846-10847. (b) B. M. Trost, G. Dong, *J. Am. Chem. Soc.,* 2006, **128**, 6054-6055.
5 (a) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.,* 2001, **40**, 2004-2021; *Angew. Chem.,* 2001, **113**, 2056-2075 (b) S. Diez-Gonzalez, E. D. Stevens, S. P. Nolan, *Chem. Commun.,* 2008, 4747-4749. (c) J.-M. Collinson, J. D. E. T. Wilton-Ely, S. Díez-González, *Chem. Commun.,* 2013, **49**, 11358-11360.
6 (a) S. Tominaga, Y. Oi, T. Kato, D. K. An, S. Okamoto, *Tetrahedron Lett.,* 2004, **45**, 5585-5588. (b) K.-s. Lee, M. K. Brown, A. W. Hird, A. H. Hoveyda, *J. Am. Chem. Soc.,* 2006, **128**, 7182-7184. (c) D. Martin, S. Kehrli, M. d'Augustin, H. Clavier, M. Mauduit, A. Alexakis, *J. Am. Chem. Soc.,* 2006, **128**, 8416-8417. (d) Brown, M. K.; May, T. L.; Baxter, C. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.,* 2007, **46**, 1097-1100; *Angew. Chem.* 2007, **119**, 1115-1118.
7 (a) T. Ohishi, M. Nishiura, Z. Hou, *Angew. Chem., Int. Ed*., 2008, **47**, 5792-5795; *Angew. Chem.,* 2008, **120**, 5876-5879. (b) L. Zhang, J. Cheng, T. Ohishi, Z. Hou, *Angew. Chem., Int. Ed*., 2010, **49**, 8670-8673; *Angew. Chem.,* 2010, **122**, 8852-8855. (c) T. Ohishi, L. Zhang, M. Nishiura, Z. Hou, *Angew. Chem., Int. Ed*., 2011, **50**, 8114-8117; *Angew. Chem.,* 2011, **123**, 8264-8267. (d) T. Fujihara, T. Xu, K. Semba, J. Terao, Y. Tsuji, *Angew. Chem., Int. Ed*., 2011, **50**, 523-527; *Angew. Chem.,* 2011, **123**, 543-547. (e) W.-Z. Zhang, W.-J. Li, X. Zhang, H. Zhou, X.-B. Lu, *Org. Lett.,* 2010, **12**, 4748-4751. (f) L. Zhang, J. Cheng, B. Carry, Z. Hou, *J. Am. Chem. Soc*., 2012, **134**, 14314-14317.
8 (a) D. S. Laitar, P. Muller, J. P. Sadighi, *J. Am. Chem. Soc*., 2005, **127**, 17196-17197. (b) C. Kleeberg, M. S. Cheung, Z. Lin, T. B. Marder, *J. Am. Chem. Soc*., 2011, **133**, 19060-19063.
9 (a) L. Zhang, J. Cheng, Z. Hou, *Chem. Commun.,* 2013, **49**, 4782-4784. (b) R. Shintani, K. Nozaki, *Organometallics,* 2013, **32**, 2459-2462.
10 D. Yu, Y. Zhang, *PNAS*, 2010, **107**, 20184-20189.
11 Y. Yang, R. M. Rioux, *Green Chem.,* 2014, **16**, 3916-3925.
12 A. Burgun, R. S. Crees, M. L. Cole, C. J. Doonan, C. J. Sumby, *Chem. Commun.,* 2014, **50**, 11760-11763.
13 (a) J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem., Int. Ed*., 2007, **46**, 8574-8578; *Angew. Chem.,* 2007, **119**, 8728-8732. (b) J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak, A. I. Cooper, *J. Am. Chem. Soc.,* 2008, **130**, 7710-7720. (c) R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams, A. I. Cooper, *Macromolecules,* 2010, **43**, 8524-8530. (d) D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.,* 2012, **112**, 3959-4015.
14 (a) L. Chen, Y. Yang, D. Jiang, *J. Am. Chem. Soc*., 2010, **132**, 9138-9143. (b) J.-X. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y. Z. Khimyak, J. Xiao, S. J. Higgins, D. J. Adams, A. I. Cooper. *Angew. Chem., Int. Ed*., 2011, **50**, 1072-1075; *Angew. Chem.,* 2011, **123**, 1104-1107. (c) H. C. Cho, H. S. Lee, J. Chun, S. M. Lee, H. J. Kim, S. U. Son, *Chem. Commun.,* 2011, **47**, 917-919. (d) C. Zhang, J.-J Wang, Y. Liu, H. Ma, X.-L. Yang, H.-B. Xu, *Chem. Eur. J.,* 2013, **19**, 5004-5008. (e) Y. Xie, T.-T. W, X.-H. Liu, K. Zou, W.-Q. Deng, *Nat. Commun.,* 2013, **4**, 1960. (f) Y. Xie, T.-T. W, R.-X. Yang, N.-Y. Huang, K. Zou, W.-Q. Deng, *ChemSusChem,* 2014, **7**, 2110-2114. (g) K. K. Tanabe, M. S. Ferrandon, N. A. Siladke, S. J. Kraft, G. Zhang, J. Niklas, O. G. Poluektov, S. J. Lopykinski, E. E. Bunel, T. R. Krause, J. T. Miller, A. S. Hock, S. T. Nguyen, *Angew. Chem., Int. Ed*., 2014, **53**, 12055-12058; *Angew. Chem.,* 2014, **126**, 12251-12254. (h) V. M. Suresh, S. Bonakala, H. S. Atreya, S. Balasubramanian, T. K. Maji, *ACS Appl. Mater. Interfaces,* 2014, **6**, 4630-4637.
15 F. Cisnetti, C. Gibard, A. Gautier, *J. Organomet. Chem.,* 2015, **782**, 22-30.
16 (a) Z. Zhang, Y. Chen, S. He, J. Zhang, X. Xu, Y. Yang, F. Nosheen, F. Saleem. W. He, X. Wang, *Angew. Chem., Int. Ed.,* 2014, **53**, 12517-12521; *Angew. Chem.,* 2014, **126**, 12725-12729. (b) H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, O. M. Yaghi, *J. Am. Chem. Soc.,* 2014, **136**, 4369-4381.
17 H. Zhou, Y.-B. Wang, *ChemCatChem,* 2014, **6**, 2512.
18 (a) S. Zhang, Y. Chen, F. Li, X. Lu, W. Dai, R. Mori, *Catal. Today,* 2006, **115**, 61-69. (b) X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.,* 2012, **441**, 1462-1484. (c) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, *Chem. Rev.,* 2013, **113**, 6621-6658. (d) A. Dibenedetto, A. Angelini, P. Stufano, *J. Chem. Technol. Biotechnol.,* 2014, **89**, 334-353. (e) G. Fiorani, W. Guo. A. W. Kleij, *Green Chem.,* 2015, **17**, 1375-1389. (f) B. Yu, L.-N. He, *ChemSusChem,* 2015, **8**, 52-62.
19 N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics,* 2004, **23**, 3369-3371.

20 (a) J. Chun, I. G. Jung, H. J. Kim, M. Park, M. S. Lah, S. U. Son. *Inorg. Chem.,* 2009, **48**, 6353-6355. (b) J. Chun, H. S. Lee, I. G. Jung, S. W. Lee, H. J. Kim, S. U. Son, *Organometallics,* 2010, **29**, 1518-1521. (c) A. Hospital, C. Gibard, C. Gaulier, L. Nauton, V. Théry, M. El-Ghozzi, D. Avignant, F. Cisnetti, A. Gautier, *Dalton Trans.,* 2012, **41**, 6803-6812.