RSC Advances

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2014, 4, 45838

Received 12th August 2014
Accepted 16th September 2014

DOI: 10.1039/c4ra08517e

www.rsc.org/advances

Monodisperse amorphous CuB_{23} alloy short nanotubes: novel efficient catalysts for Heck coupling of inactivated alkyl halides and alkenes†

Fan Yang,[ab] Shi Yan Fu,[ab] Wei Chu,*[c] Chun Li[ab] and Dong Ge Tong*[ab]

Heck-type coupling of inactivated alkyl halides and alkenes, catalyzed by amorphous CuB_{23} alloy short nanotubes, has been developed. Such couplings occur on the surfaces of nanotubes *via* a single-electron oxidative reaction. The results indicate that CuB_{23} nanotubes are efficient catalysts to replace Pd and Ni complexes for such Heck-type coupling.

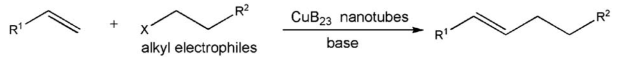
Introduction

Heck cross-coupling, which forms an intermolecular C–C bond between a halide or sulfonate electrophile and an alkene under mild conditions, is one of the most intensively studied organic reactions, because of its applications in many areas, including natural products and fine chemical syntheses.[1] Until now, most catalysts for Heck reactions have been based on Pd,[2] *e.g.*, Pd complexes and Pd nanoparticles. Among these Pd catalysts, soluble Pd compounds, generally phosphine–Pd complexes, are the most efficient catalysts for the Heck reaction.[2] However, Pd catalysts are very expensive, and the ligands in Pd complexes are generally toxic and therefore cannot be used. Catalysts based on Ni, Co, Cu, and Fe or their complexes have therefore recently been developed as novel catalysts to replace Pd catalysts.[3] However, none of these can rival Pd in synthetic versatility except Ni, especially in Heck-type reactions involving inactivated alkyl halides.[4] More efficient and cheaper catalysts for Heck reactions therefore need to be developed.

Recently, amorphous metal–boride (M–B) alloy catalysts with well-defined nanostructures have attracted much attention, because of their low cost and unusual properties such as isotropic structure, high concentration of coordinatively unsaturated sites, and chemical stability.[5] For example, Chen *et al.* used lyotropic liquid crystals with layered structures (formed by mixing nonionic and anionic surfactants) as templates to obtain M–B long nanotubes that gave excellent catalytic performances in hydrogenation reactions.[5a] Li, and Tong *et al.* prepared mesoporous M–B materials with good catalytic hydrogenation performances.[5b,c] M–B nanoflowers and hollow spheres with excellent performances in hydrolyzing metal borohydrides to produce H_2 have also been successfully prepared.[5d,e] Various M–B materials with superior catalytic performances, including yolk–shell nanostructures,[5f] hollow nanospindles,[5g] nanospheres,[5h] honeycombs,[5i] and nanowires,[5j] have also been reported. More recently, Li *et al.* developed Co–B nanospheres as efficient catalysts for Heck-type reactions.[6] Cu complexes can efficiently catalyze Heck-like cyclizations of oxime esters,[1c] and B-doped Cu catalysts have excellent catalytic activities in hydrogenation[7a] or dehydrogenation.[7b] Based on these results, we attempted to prepare an amorphous Cu–B alloy with a well-defined nanostructure as a novel catalyst with high activity for Heck-type reactions. To our knowledge, there have been no previous reports of the use of amorphous Cu–B alloys as catalysts in Heck reactions.

In this study, amorphous CuB_{23} alloy short nanotubes were prepared by a facile solution plasma method,[5h–j,8] and used to catalyze Heck reactions of inactivated alkyl halides, with good results (Scheme 1).

Fig. 1a shows a typical low-magnification image of CuB_{23} short nanotubes prepared by the reaction of $[Cu(NH_3)_4]^{2+}$ and KBH_4 in poly(ethylene glycol) solution, intrigued by a solution



Scheme 1 Heck cross-couplings involving inactivated alkyl halides.

---

[a] *Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China. E-mail: tongdongge@163.com; Fax: +86 28 8407 9074*

[b] *State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Chengdu University of Technology, Chengdu 610059, China*

[c] *College of Chemical Engineering, Sichuan University, Chengdu 610065, China. E-mail: chuwei1965@foxmail.com; Fax: +86 28 8540 3397*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra08517e

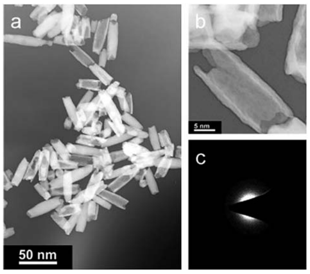
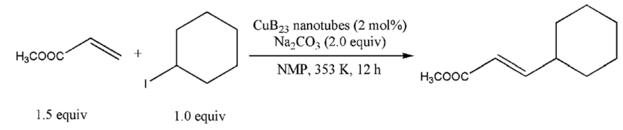


Fig. 1 (a) Low magnification STEM image; (b) enlarged STEM image; (c) SAED pattern of the as-prepared CuB_{23} short nanotubes. The scale bar for (b) is 5 nm.

Table 1 CuB_{23}-short-nanotubes-catalyzed cross-coupling of cyclohexyl iodide and methyl acrylate

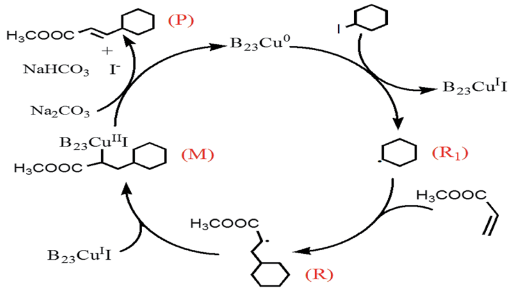


Entry	Deviation from conditions described above	Yield[a]/%
1	None	91
2	THF instead of NMP	<2
3	$PhCF_3$ instead of NMP	62
4	DMF instead of NMP	74
5	K_3PO_4 instead of Na_2CO_3	65
6	Na_3PO_4 instead of Na_2CO_3	53
7	K_2CO_3 instead of Na_2CO_3	71
8	NaOH instead of Na_2CO_3	66
9	KOH instead of Na_2CO_3	59
10	333 K instead of 353 K	26
11	2.0 equiv. of methyl acrylate	94
12	1.5 equiv. of cyclohexyl iodide	67
13	Commercial nano B	<2
14	Nano CuO catalyst	<2
15	Nano Cu_2O catalyst	<2
16	Commercial nano Cu catalyst	7
17	Conventional Cu–B catalyst	18
18	Reaction in the dark	78
19	1.0 equiv. of cyclohexyl bromide	91
20	1.0 equiv. of cyclohexyl chloride	7
21	Cu(2-ethylhexanonate)$_2$ (ref. 1*c*)	34
22	$PdCl_2$(dppf)[4a]	68
23	Co–B nanospheres[6]	30
24	Ni(cod)$_2$ (ref. 12*a*)	70
25	Co(acac)$_2$ (ref. 12*b*)	51
26	Fe(acac)$_3$ (ref. 12*c*)	35
27	Pd–UiO67 (ref. 12*d*)	48
28	Pd@XH[12e]	52
29	$AgNO_3$/NXS[12f]	23

[a] Calculated by ^{1}H NMR spectroscopy of the crude reaction mixtures using an internal standard.

plasma. From Fig. 1a, it can be seen that CuB_{23} short nanotubes were obtained on a large scale and with a uniform size distribution. The enlarged transmission electron microscopy (TEM) image (Fig. 1b) shows that the nanotubes had an average length of 50 nm and diameter of 10 nm. The average wall thickness was about 2 nm. Electron diffraction analysis of the CuB_{23} nanotubes showed that they are noncrystalline, based on the observed halos (Fig. 1c). Further evidence comes from the X-ray diffraction (XRD) patterns of samples heated at different temperatures in an Ar atmosphere (Fig. S1a–c†). It can be seen that the as-prepared CuB_{23} nanotubes are poorly crystalline or amorphous. After annealing in an Ar atmosphere at 573 K for 2 h, crystalline CuB_{23} (JCPDS-71-01-02) was obtained (Fig. S1c†). The inductively coupled plasma atomic emission spectroscopy (ICP-AES) results show that the B/Cu ratio of CuB_{23} nanotubes is 23.01, which is almost the same as that of conventional CuB_{23} (22.99). The Brunauer–Emmett–Teller surface area of the CuB_{23} nanotubes is 84.7 $m^2\ g^{-1}$, which is higher than that of a conventional irregular CuB_{23} alloy (23.2 $m^2\ g^{-1}$; Fig. S2 and S3†). The formation of homogeneous alloy nanoparticles was confirmed by black cross-sectional compositional line analyses in high-angle annular dark-field-scanning TEM (STEM) experiments (Fig. S4a and b†), and energy-dispersive X-ray spectroscopy (EDS) performed at different points (Fig. S4c–e†). The results showed that the short nanotubes are composed of Cu and B. X-ray photoelectron spectroscopy (XPS; Fig. S5a–c†) showed that the Cu and B species in the CuB_{23} short nanotubes are present in the elemental state.[9] The shift in the binding energy of B species relative to pure B (187.1 eV) indicates that electrons are partly transferred from B to the vacant d-orbital of Cu, resulting in electron-rich Cu species in CuB_{23} nanotubes. These electron-enriched Cu sites are favorable for the Heck coupling reaction between inactivated alkyl halides and alkenes.[7,10] To the best of our knowledge, this is the first example of CuB_{23} short nanotubes prepared using a solution plasma process (such nanostructures have not been reported previously).

The results for the catalysis of the Heck reaction with CuB_{23} short nanotubes are shown in Table 1. The yields of the corresponding products were moderate to good. The experiments indicated that 2 mol% of the catalyst was sufficient to catalyze the reaction. Solvents such as trifluoromethylbenzene ($PhCF_3$), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were used as reaction media. The results show that THF was not effective in this reaction (Table 1, entry 2). $PhCF_3$ and DMF (Table 1, entries 3 and 4) gave low yields; NMP gave the best results (Table 1, entry 1). A basic environment was also important for this Heck reaction; almost all our experiments confirmed this. Common bases, namely K_3PO_4, Na_3PO_4, Na_2CO_3, K_2CO_3, NaOH, and KOH, were tested; Na_2CO_3 was found to be the best, and was therefore selected as the base for subsequent experiments (Table 1, entries 5–9). The most suitable temperature was 80 °C. Lowering the reaction temperature to 60 °C resulted in a significant decrease in the reaction efficiency (Table 1, entry 10). A slight excess of methyl acrylate was favorable in this cross-coupling (2 equiv.; Table 1, entry 11), but reactions using a slight excess of cyclohexyl iodide gave lower yields (Table 1, entry 12). If the CuB_{23} short nanotubes were filtered out after reaction for 2 h, no conversion of cyclohexyl iodide was observed (Fig. S6†), confirming that this reaction occurred on the CuB_{23} nanotube surfaces, because

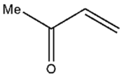
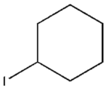
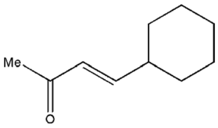
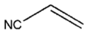
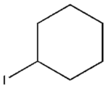
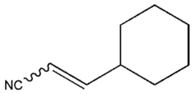
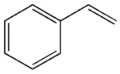
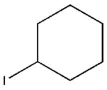
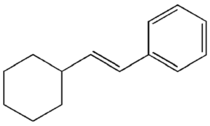
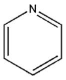
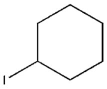
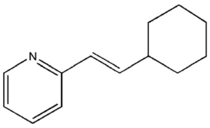
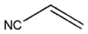
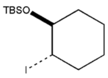
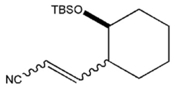


Scheme 2 Plausible catalytic processes for the CuB$_{23}$-short-nanotubes-catalyzed alkyl-Heck-type cross-coupling between cyclohexyl iodide and methyl acrylate.

homogeneous catalysis by Cu species leached into the solution could be ruled out. No product was formed in the presence of B, CuO, or Cu$_2$O (Table 1, entries 13–15), which confirms that metallic Cu was the active site. The catalytic role of electron-enriched Cu sites was confirmed by the Cu 2p$_{3/2}$ binding energy shifts from Cu^0, Cu$^{\mathrm{I}}$, and Cu$^{\mathrm{II}}$ to Cu^0 during the reaction, shown by *in situ* XPS measurements (Fig. S7†). This means that the coupling occurs on the surfaces of the CuB$_{23}$ short nanotubes, and is a single-electron oxidative process. Time-of-flight secondary-ion mass spectrometry analyses of the catalyst in the initial reaction stage indicated that I atoms could bond with the surfaces of the CuB$_{23}$ short nanotubes to form B–Cu–I, based on the appearance of CuI$^+$ (m/z = 190, 192), BI$^+$ (m/z = 137, 138), and CuBI$^+$ (m/z = 200, 201, 202, 203) peaks (Fig. S8a–c†). Furthermore, without the presence of Na$_2$CO$_3$ during the reaction, Cu–R (Fig. S8d,† m/z = 231, 233) and CuBI$^+$ (m/z = 200, 201, 202, 203) were formed, indicating that R groups and I atoms bonded with Cu-active sites to form M (Scheme 2) on the surfaces of the CuB$_{23}$ short nanotubes during the reaction (Fig. S8d and e†). Na$_2$CO$_3$ therefore plays a key role in forming the final product of the Heck reaction (Fig. S8e†). Based on these results, we propose that the heterogeneous Heck cross-coupling catalyzed by our CuB$_{23}$ short nanotubes proceeds *via* the pathway shown in Scheme 2. First, Cu^0 on the surfaces of the CuB$_{23}$ nanotubes is oxidized by giving away one electron to alkyl halides. As a result, the carbon-centered radical R$_1$ (Scheme 2) and B–Cu$^{\mathrm{I}}$–I formed. Second, alkene addition to the carbon-centered radical R$_1$ forms the radical R, and then R bonds with B–Cu$^{\mathrm{I}}$–I on the CuB$_{23}$ nanotube surfaces to form the alkyl Cu(II) species M. Finally, base-assisted β-hydride elimination from the alkyl Cu(II) species M gives the cross-coupling product P (Scheme 2). However, the exact mechanism of the CuB$_{23}$-short-nanotube-catalyzed alkyl-Heck-type cross-coupling is not clear; further studies involving theoretical calculations are needed, and are currently underway.

The product yields obtained using Cu and conventional CuB$_{23}$ catalysts were inferior to those achieved using CuB$_{23}$ short nanotubes (Table 1, entries 16 and 17). The better performance of CuB$_{23}$ relative to that of Cu is attributed to electron-enriched Cu sites, identified using XPS, which are favorable for oxidative addition of metallic Cu to a carbon–halogen bond.[6,10] Additionally, the performance of Cu–B short

Table 2 CuB$_{23}$-short-nanotubes-catalyzed cross-coupling of cyclohexyl iodide and different alkenes

Entry	Alkenes	Alkyl iodide	Product	Yield^{a,b}/%
1				65 30^c 41^d
2				77 (86 : 14 E : Z) 73^c (29 : 71 E : Z) 72^d (69 : 31 E : Z)
3				87 80^c 80^d
4				59 39^c 44^d
5			 50:50 d.r.	76 (33 : 66 E : Z) 66^c (33 : 66 E : Z) 55^d (33 : 66 E : Z)

^{a} Yields of isolated product. ^{b} Product ratios were determined by ^{1}H NMR spectroscopy of crude reaction mixtures. TBS = *tert*-butyldimethylsilyl. ^{c} PdCl$_2$(dppf) catalyst.[4a] ^{d} Ni(cod)$_2$ catalyst.[12a]

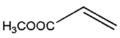
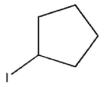
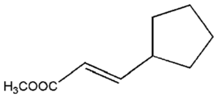
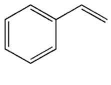
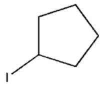
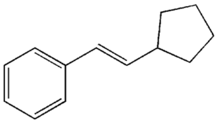
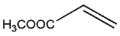
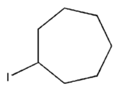
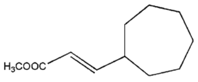
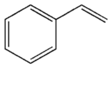
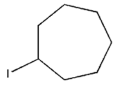
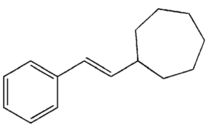
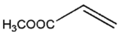
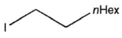
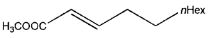
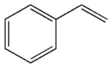
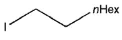
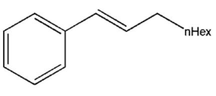
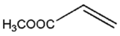
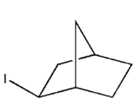
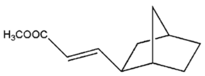
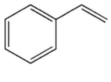
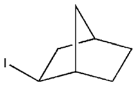
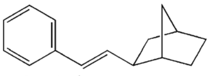
nanotubes (active surface area $S_{Cu} = 47.3\ m^2\ g^{-1}$) is better than that of conventional CuB_{23} ($S_{Cu} = 10.9\ m^2\ g^{-1}$) because their unique structure facilitates mass transfer and increases the accessibility of active sites to reactant molecules during heterogeneous catalysis.[1d,5,11] Also, the reaction proceeded in the dark (Table 1, entry 18). The catalyst showed high activities in the Heck couplings of cyclohexyl bromide and cyclohexyl iodide (Table 1, entries 1 and 19). Cyclohexyl chloride had low activity in the reaction (Table 1, entry 20). The catalytic performance of our CuB_{23} nanotubes was also compared with that of recently reported Heck-coupling catalysts (Table 1, entries 21–29).[12] Based on the yield, the catalytic performance of our CuB_{23} nanotubes is superior to those catalysts.

The scope of our CuB_{23}-nanotube-catalyzed Heck cross-coupling reaction with respect to alkenes (Table 2) and inactivated alkyl iodides (Table 3) was also investigated. Cyclohexyl iodide reacted with methyl vinyl ketone, acrylonitrile, styrene, and 2-vinylpyridine to provide the corresponding products in moderate to good yields (Table 2, entries 1–4). To investigate the electron pathway over the CuB_{23} short nanotubes, we studied the diastereoselectivity of the reaction of *trans*-2-(*tert*-butyldimethylsilyloxy)-1-iodocyclohexane with acrylonitrile (Table 2, entry 5). A 50 : 50 ratio of *cis* to *trans* coupling products was obtained, which confirmed the proposed single-electron pathway for coupling over CuB_{23} short nanotubes (Scheme 2).[4a]

The data in Table 3 indicate that our CuB_{23} short nanotubes also had high activities towards cyclopentyl iodide, cycloheptyl iodide, and iodooctane, as well as cyclohexyl iodide (Table 3, entries 1–6). The coupling of *exo*-2-norbornyl iodide with alkenes exhibited high diastereoselectivities (>95 : 5 d.r.; Table 3, entries 7 and 8), which further confirmed the proposed single-electron pathway for coupling over CuB_{23} short nanotubes (Scheme 2).[4a] The reaction yields (Tables 2 and 3) show that the catalytic performance of our CuB_{23} short nanotubes is superior to those of the most effective catalysts: Pd[4a] and Ni complexes[12a] in Heck coupling of inactivated alkyl iodides and alkenes (Tables 2 and 3). Considering the price difference among CuB_{23}, Pd and Ni complexes, our CuB_{23} short nanotubes are more cost effective.

Fig. 2 shows the recycling performance of CuB_{23} short nanotubes. Our sample could be used 10 times with only a slight loss of activity (8%). ICP-AES analysis shows that no Cu or

Table 3 CuB_{23}-short-nanotubes-catalyzed cross-coupling of alkene with different alkyl iodide

Entry	Alkene	Alkyl iodide	Product	Yield[a,b]/%
1				77 (79 : 21 $E : Z$) 57[c] (61 : 39 $E : Z$) 77[d](84 : 16 $E : Z$)
2				73 (88 : 12 $E : Z$) 56[c] (86 : 14 $E : Z$) 65[d] (86 : 14 $E : Z$)
3				82 72[c] 69[d]
4				80 72[c] 76[d]
5		 	 	78 57[c] 62[d]
6		 		57 40[c] 50[d]
7			 > 95:1 d.r.	83 (86 : 14 $E : Z$) 72[c] (86 : 14 $E : Z$) 69[d] (86 : 14 $E : Z$)
8			 > 95:1 d.r.	82 (91 : 9 $E : Z$) 76[c] (88 : 12 $E : Z$) 67[d] (86 : 14 $E : Z$)

[a] Yields of isolated product. [b] Product ratios were determined by ^1H NMR spectroscopy of crude reaction mixtures. [c] $PdCl_2(dppf)$ catalyst.[4a] [d] $Ni(cod)_2$ catalyst.[12a]

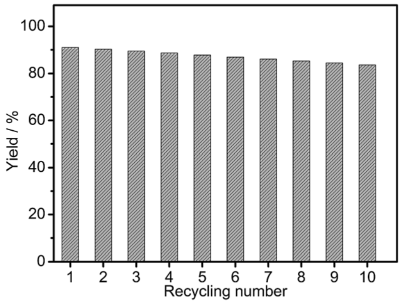


Fig. 2 Cycling performance of CuB_{23} short nanotubes for cross-coupling of cyclohexyl iodide and methyl acrylate. Reaction conditions: a catalyst containing 0.01 mmol CuB_{23} short nanotubes, cyclohexyl iodide (5.0 mmol), methyl acrylate (7.5 mmol), Na_2CO_3 (10.0 mmol), NMP (10 mL), $T = 353$ K, $t = 12$ h, stirring rate = 800 rpm.

B leaching occurs, which rules out the loss of active phases after repetitive use. Moreover, the STEM, selected area electron diffraction, and XRD results indicate that no crystallinity or structural changes occur for the CuB_{23} short nanotubes after repeated use (Fig. S9 and S10a†). It appears that B oxidation on the active surface of CuB_{23} is responsible for the deactivation, as shown by EDS (Fig. S10b†) and XPS (Fig. S11†). In particular, the boron oxide film results in a decrease in S_{Cu} from 47.3 $m^2\ g^{-1}$ to 43.2 $m^2\ g^{-1}$, as it blocks the Cu-active sites and reduction of the Cu electron density.

Conclusions

In summary, we have prepared amorphous CuB_{23} alloy short nanotubes for the first time, using a solution plasma process, and successfully used this catalyst in the Heck coupling of inactivated alkyl halides and alkenes. We showed that amorphous CuB_{23} alloy short nanotubes can replace Pd and Ni complexes for Heck coupling of inactivated alkyl iodides and alkenes. Furthermore, alkyl bromides were tolerated. The CuB_{23}-short-nanotubes-catalyzed protocol proceeds *via* coupling on the surfaces of the nanotubes, by single-electron oxidative reactions. More importantly, the catalyst is cheaper than Pd and Ni catalysts and no ligands are needed. Work to extend the use of this new catalyst in organic synthesis is underway in our laboratory.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21376033), the Sichuan Youth Science and Technology Innovation Research Team Funding Scheme (2013TD0005), the Cultivating programme of Middle aged backbone teachers (HG0092), the Cultivating programme for Excellent Innovation Team of Chengdu University of Technology (HY0084) and Innovative Experimental Items for College Students of Sichuan Province (SZH1106CX04).

Notes and references

1 (*a*) M. Oestreich, *Angew. Chem., Int. Ed.*, 2014, **53**, 2282; (*b*) M. R. Harris, M. O. Konev and E. R. Jarvo, *J. Am. Chem. Soc.*, 2014, **136**, 7825; (*c*) A. Faulkner, N. J. Race, J. S. Scott and J. F. Bower, *Chem. Sci.*, 2014, **5**, 2416; (*d*) H. Li, C. C. C. J. Seechurn and T. J. Colacot, *ACS Catal.*, 2012, **2**, 1147; (*e*) A. Balanta, C. Godard and C. Claver, *Chem. Soc. Rev.*, 2011, **40**, 4973; (*f*) J. M. Liu, X. G. Peng, W. Sun, Y. W. Zhao and C. G. Xia, *Org. Lett.*, 2008, **10**, 3933; (*g*) B. Baruwati, D. Guin and S. V. Manorama, *Org. Lett.*, 2007, **9**, 5377; (*h*) J.-P. Corbet and G. Mignani, *Chem. Rev.*, 2006, **106**, 2651; (*i*) P. D. Stevens, G. F. Li, J. D. Fan, M. Yen and Y. Gao, *Chem. Commun.*, 2005, 4435; (*j*) C. S. Consorti, F. R. Flores and J. Dupont, *J. Am. Chem. Soc.*, 2005, **127**, 12054; (*k*) *Metal-Catalyzed Cross-Coupling Reactions, 2nd Completely Rev. and Enlarged Ed*, ed. A. de Meijere and F. Diederich, Wiley-VCH, Weinheim, 2004; (*l*) O. Mongin, L. Porres, L. Moreaux, J. Merta and M. Blanchard-Desce, *Org. Lett.*, 2002, **4**, 719; (*m*) I. Paterson, R. D. M. Davies and R. Marquez, *Angew. Chem., Int. Ed.*, 2001, **40**, 603; (*n*) L. Brunsveld, E. W. Meijer, R. B. Prince and J. S. Moore, *J. Am. Chem. Soc.*, 2001, **123**, 7978; (*o*) J. Li, A. Ambroise, S. I. Yang, J. R. Diers, J. Seth, C. R. Wack, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Am. Chem. Soc.*, 1999, **121**, 8927; (*p*) R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146.

2 (*a*) L. Xu, M. J. Hilton, X. Zhang, P.-O. Norrby, Y.-D. Wu, M. S. Sigman and O. Wiest, *J. Am. Chem. Soc.*, 2014, **136**, 1960; (*b*) C. Wu and J. (Steve) Zhou, *J. Am. Chem. Soc.*, 2014, **136**, 650; (*c*) Y. M. A. Yamada, Y. Yuyama, T. Sato, S. Fujikawa and Y. Uozumi, *Angew. Chem., Int. Ed.*, 2014, **53**, 127; (*d*) J.-H. Fan, W.-T. Wei, M.-B. Zhou, R.-J. Song and J.-H. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 6650; (*e*) P. Liu, Z. Dong, Z. Ye, W.-J. Wang and B.-G. Li, *J. Mater. Chem. A*, 2013, **1**, 15469; (*f*) C. C. C. J. Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, *Angew. Chem., Int. Ed.*, 2012, **51**, 5062; (*g*) A. Molnar, *Chem. Rev.*, 2011, **111**, 2351; (*h*) K. S. Bloome, R. L. McMahen and E. J. Alexanian, *J. Am. Chem. Soc.*, 2011, **133**, 20146; (*i*) T. Mino, Y. Shirae, Y. Sasai, M. Sakamoto and T. Fujita, *J. Org. Chem.*, 2006, **71**, 6834; (*j*) N. E. Leadbeater, *Chem. Commun.*, 2005, 2881; (*k*) C. M. Frech, L. J. W. Shimon and D. Milstein, *Angew. Chem., Int. Ed.*, 2005, **44**, 1709; (*l*) J. C. Garcia-Martinez, R. Lezutekong and R. M. Crooks, *J. Am. Chem. Soc.*, 2005, **127**, 5097; (*m*) M. T. Reetz and J. G. Vries, *Chem. Commun.*, 2004, 1559; (*n*) D. Gelman and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2003, **42**, 5993; (*o*) R. Narayanan and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2003, **125**, 8340; (*p*) M. T. Reetz and E. Westermann, *Angew. Chem., Int. Ed.*, 2000, **39**, 165; (*q*) M. T. Reetz, G. Lohmer and R. Schwickardi, *Angew. Chem., Int. Ed.*, 1998, **37**, 481; (*r*) M. T. Reetz and G. Lohmer, *Chem. Commun.*, 1996, 1921; (*s*) M. T. Reetz, W. Helbig, S. A. Quaiser, U. Stimming, N. Breuer and R. Vogel, *Science*, 1995, **267**, 367.

3 (*a*) T. Nishikata, Y. Noda, R. Fujimoto and T. Sakashita, *J. Am. Chem. Soc.*, 2013, **135**, 16372; (*b*) C. Liu, S. Tang, D. Liu,

J. Yuan, L. Zheng, L. Meng and A. Lei, *Angew. Chem., Int. Ed.*, 2012, **51**, 3638; (*c*) H. Qi, W. Zhang, X. Wang, H. Li, J. Chen, K. Peng and M. Shao, *Catal. Commun.*, 2009, **10**, 1178; (*d*) P. Zhou, Y. Li, P. Sun, J. Zhou and J. Bao, *Chem. Commun.*, 2007, 1418; (*e*) W. Affo, H. Ohmiya, T. Fujioka, Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, Y. Imamura, T. Mizuta and K. Miyoshi, *J. Am. Chem. Soc.*, 2006, **128**, 8068; (*f*) M. Moreno-Manas and R. Pleixats, *Acc. Chem. Res.*, 2003, **36**, 638; (*g*) J. Terao, H. Watabe, M. Miyamoto and N. Kambe, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 2209; (*h*) Y. Ikeda, T. Nakamura, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2002, **124**, 6514; (*i*) S. Iyer and V. V. Thakur, *J. Mol. Catal. A: Chem.*, 2000, **157**, 275.

4 (*a*) C. M. McMahon and E. J. Alexanian, *Angew. Chem., Int. Ed.*, 2014, **53**, 5974; (*b*) Y. Zou and J. Zhou, *Chem. Commun.*, 2014, **50**, 3725; (*c*) Q. Qian, Z.-h. Zang, Y. Chen, W.-q. Tong and H.-g. Gong, *Mini-Rev. Med. Chem.*, 2013, **13**(6), 802; (*d*) A. C. Bissember, A. Levina and G. C. Fu, *J. Am. Chem. Soc.*, 2012, **134**, 14232; (*e*) A. Millán, L. Á. Cienfuegos, D. Miguel, A. G. Campaña and J. M. Cuerva, *Org. Lett.*, 2012, **14**, 5984; (*f*) M. E. Weiss, L. M. Kreis, A. Lauber and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2011, **50**, 11125; (*g*) K. S. Bloome and E. J. Alexanian, *J. Am. Chem. Soc.*, 2010, **132**, 12823; (*h*) L. Firmansjah and G. C. Fu, *J. Am. Chem. Soc.*, 2007, **129**, 11340; (*i*) S. A. Lebedev, V. S. Lopatina, E. S. Petrov and I. P. Beletskaya, *J. Organomet. Chem.*, 1988, **344**, 253.

5 (*a*) Y. Zhu, F. P. Liu, W. P. Ding, X. F. Guo and Y. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 7211; (*b*) H. Li, H. X. Yang and H. X. Li, *J. Catal.*, 2007, **251**, 233; (*c*) D. G. Tong, W. Chu, Y. Y. Luo, H. Chen and X. Y. Ji, *J. Mol. Catal. A: Chem.*, 2007, **269**, 149; (*d*) D. G. Tong, X. Han, W. Chu, H. Chen and X. Y. Ji, *Mater. Res. Bull.*, 2008, **43**, 1327; (*e*) H. Ma, W. Q. Ji, J. Z. Zhao and J. Chen, *J. Alloys Compd.*, 2008, **474**, 584; (*f*) H. Li, D. Q. Zhang, G. S. Li, Y. Xu, Y. F. Lu and H. X. Li, *Chem. Commun.*, 2010, **46**, 791; (*g*) D. G. Tong, X. L. Zeng, W. Chu, D. Wang and P. Wu, *J. Mater. Sci.*, 2010, **45**, 2862; (*h*) D. G. Tong, X. L. Zeng, W. Chu, D. Wang and P. Wu, *Mater. Res. Bull.*, 2010, **45**, 442; (*i*) D. G. Tong, W. Chu, P. Wu and L. Zhang, *RSC Adv.*, 2012, **2**, 2369; (*j*) F. Yang, Y. Z. Li, W. Chu, C. Li and D. G. Tong, *Catal. Sci. Technol.*, 2014, **4**, 3168.

6 Z. Zhu, J. Ma, L. Xu, L. Xu, H. Li and H. Li, *ACS Catal.*, 2012, **2**, 2119.

7 (*a*) A. Yin, J. Qu, X. Guo, W.-L. Dai and K. Fan, *Appl. Catal., A*, 2011, **400**, 39; (*b*) A. K. Figen, *Int. J. Hydrogen Energy*, 2013, **38**, 9186.

8 (*a*) M. A. Bratescu, S.-P. Cho, O. Takai and N. Saito, *J. Phys. Chem. C*, 2011, **115**(50), 24569; (*b*) P. Wu, J. H. Sun, Y. Y. Huang, G. F. Gu and D. G. Tong, *Mater. Lett.*, 2012, **82**, 191; (*c*) J. Kang, O. L. Li and N. Saito, *Nanoscale*, 2013, **5**, 6874; (*d*) B. Sun, *Discharge plasma in liquid and its applications*, Press of Science, Beijing, 2013; (*e*) D. G. Tong, W. Chu, P. Wu, G. F. Gu and L. Zhang, *J. Mater. Chem. A*, 2013, **1**, 358; (*f*) D. G. Tong, D. M. Tang, W. Chu, G. F. Gu and P. Wu, *J. Mater. Chem. A*, 2013, **1**, 6425; (*g*) Y. J. He, J. F. Peng, W. Chu, Y. Z. Li and D. G. Tong, *J. Mater. Chem. A*, 2014, **2**, 1721.

9 *Reference: Manual for Operator for PHI PC Windows Software Version 1.2b*, Physical Electronic Division, Perkin-Elmer.

10 C. S. Consorti, F. R. Flores and J. Dupont, *J. Am. Chem. Soc.*, 2005, **127**, 12054.

11 Q. Xin and M. F. Luo, *Technique for Modern Catalysis*, Science Press, Beijing, 2009.

12 (*a*) Y.-C. Hong, P. Gandeepan, S. Mannathan, W. T. Lee and C.-H. Cheng, *Org. Lett.*, 2014, **16**, 2806; (*b*) L. Ackermann, *J. Org. Chem.*, 2014, DOI: 10.1021/jo501361k; (*c*) L. Ilies, T. Matsubara, S. Ichikawa, S. Asako and E. Nakamura, *J. Am. Chem. Soc.*, 2014, DOI: 10.1021/ja5066015; (*d*) L.-y. Chen, S. Rangan, J. Li, H.-f. Jiang and Y.-w. Li, *Green Chem.*, 2014, **16**, 3978; (*e*) W. Chen, L.-x. Zhong, X.-w. Peng, K. Wang, Z.-f. Chen and R.-c. Sun, *Catal. Sci. Technol.*, 2014, **4**, 1426; (*f*) S. Dharuman and Y. D. Vankar, *Org. Lett.*, 2014, **16**, 1172.