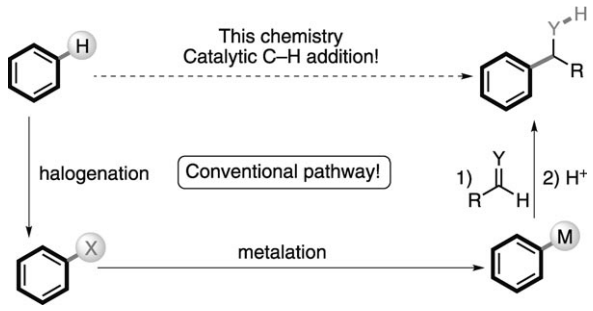
C–H Activation

DOI: 10.1002/anie.201007464

Rhodium-Catalyzed Direct Addition of Aryl C–H Bonds to *N*-Sulfonyl Aldimines**

*Yang Li, Bi-Jie Li, Wen-Hua Wang, Wei-Ping Huang, Xi-Sha Zhang, Kang Chen, and Zhang-Jie Shi**

Nucleophilic addition of highly reactive aryl Grignard reagents and other related organometallic reagents to carbonyl compounds and their derivatives is a fundamental and important reaction for the construction of C–C bonds. This approach has been well developed (since early last century) and broadly utilized to synthesize alcohol and amine compounds.[1] Traditionally, the requirement of organohalides as the starting materials to produce the active organometallic reagents causes environmental problems owing to their tedious and sluggish preparation (Scheme 1).[2] As a valuable complementary method, directed *ortho* metelation (DoM) of functionalized arene compounds has its advantages from a synthetic point of view.[3] Apart from their tedious preparation, both Grignard and DoM approached involve the manipulation of air-and moisture-sensitive reagents and the generation of unwanted salt waste. Recent Friedel–Crafts-type direct alkylation of electron-rich arene compounds have been developed. This reaction is catalyzed by a Lewis/Brønsted acid, however, a limited substrate scope and difficulty in regioselective control were encountered.[4] In comparison, transition metal complexes provide a broader outlook for the development of new transformations that may provide tunable reactivity and selectivity. The transition-metal-catalyzed addition of C–H bonds to alkene and alkyne derivatives have been extensively investigated.[5] Meanwhile, significant contributions have been made to the field by the addition of C–H bonds to carbonyl compounds and their derivatives, despite the demand for special additives or limited substrate scope.[6] Herein we demonstrated an "ideal" addition of "inert" aryl C–H bonds to C=N groups in the absence of any additives and without any undesirable waste under mild and neutral reaction conditions.[7]



Scheme 1. Rational design of direct C–H addition toward C=Y. Conventional arylation of C=Y through halogenations/metalation/nucleophilic addition-hydration sequence versus "ideal" direct C–H addition to C=Y, where Y = N or O. X = halogen.

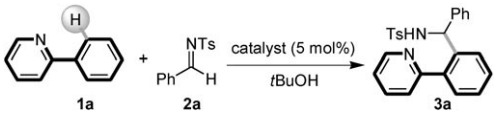
Our research was inspired by the recent progress on the rhodium/palladium-catalyzed addition of aryl boronic acid towards carbonyl compounds, in which the aryl–metal (metal = Pd or Rh) species was considered as a possible key intermediate formed by the transmetalation.[8] In principle, the high-valent aryl–metal species, either from direct cleavage of the C–H bond through electrophilic substitution or the transmetalation of organometallic reagents should exhibit similar reactivity. Because aromatic electrophilic metalation of arenes with/without directing groups and their applications in C–C and C–N bond formation have been well studied,[9] the use of Pd catalysis to investigate C–H addition to C=N bonds was highly preferred. Although numerous Pd catalysts were tested, the lack of desired product was disappointing. We finally gave up on a palladium-based system.

We therefore focused on Rh catalysis because of its credible reactivity in the addition of aryl boronic acid to aldehydes[8a] and imines,[10] as well as direct C–H transformations.[11] Thus, 2-phenylpyridine (**1a**)[9t] and PhCH=NTs (**2a**) were selected as model substrates. Different Rh species, including Rh^{I}, Rh^{II}, and Rh^{III} complexes, were screened (Table 1). Fortunately, we found that $[\{Cp^*RhCl_2\}_2]$[12] in the presence of silver salts,[13] $AgSbF_6$, for example, gave a reasonable yield and the structure of the final product **3a** was characterized by single-crystal X-ray crystallography[14] (entry 3). The prepared Rh^{III} precursor $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ is more practical and exhibited better efficiency (entry 4). Apart from *t*BuOH and the many other solvents tested, toluene gave a moderate yield for this transformation (entry 5). Moreover, extension of the reaction time did not enhance the reaction's efficiency. Meanwhile, a decrease of

[*] Dr. Y. Li, B.-J. Li, Dr. W.-H. Wang, Dr. W.-P. Huang, X.-S. Zhang, K. Chen, Prof. Dr. Z.-J. Shi
Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education
College of Chemistry and Green Chemistry Center
Peking University, Beijing 100871 (China)
Fax: (+86) 10-6276-0890
Prof. Dr. Z.-J. Shi
State Key Laboratory of Organometallic Chemistry
Chinese Academy of Sciences, Shanghai 200032 (China)
E-mail: zshi@pku.edu.cn
Homepage: http://www.chem.pku.edu.cn/zshi/

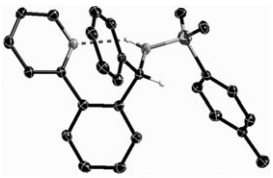
[**] Support of this study by the NSFC (No. 20672006, 20821062, 20832002, 20925207, 21002001, GZ419) and the "973" Project from the MOST of China (2009CB825300) is gratefully acknowledged.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201007464.

Table 1: Rhodium-catalyzed C–H addition to *p*-tolylsulfonylbenzaldimine under various reaction condition.[a]



Entry	Catalyst	T [°C]	t [h]	Yield [%][b]
1	–	90	6	0
2	$[\{Cp^*RhCl_2\}_2]$	90	6	0
3	$[\{Cp^*RhCl_2\}_2]$, $AgSbF_6$	90	10	73
4	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	10	84
5[c]	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	10	64
6	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	6	68
7	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	15	81
8	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	70	15	52
9	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	80	15	71
10[d]	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	80	15	64
11	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	100	15	75
12	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	120	15	65
13[e]	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	48	70
14[f]	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	10	71

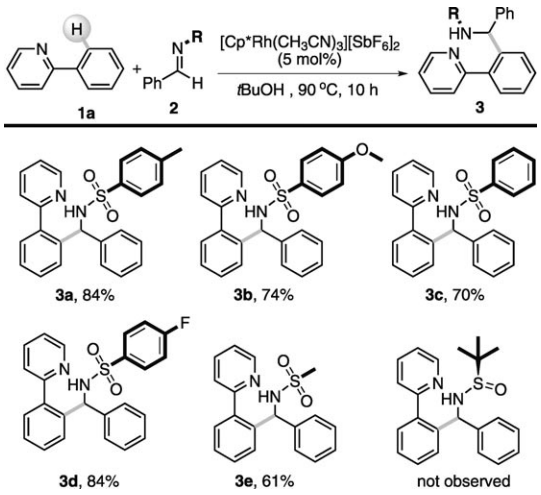
[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), *t*BuOH (1.0 mL), under N_2 in a sealed reaction tube. [b] Yield of isolated product. [c] Toluene (1.0 mL) was used as the solvent. [d] 1.5 equivalents of **2a** was used. [e] 1.0 mol% of catalyst was used. [f] The reaction was carried out under air. Cp* = pentamethylcyclopentadienyl, Ts = 4-toluenesulfonyl. See ORTEP drawing of **3a** below. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are omitted for clarity.



3a

the yield was observed by shortening the reaction time (compare entries 6 and 7). Raising the temperature induced the dialkylation, and lowering the temperature diminished the yield (entries 8–12). The amount of imine substrate could be lowered to 1.5 equivalents, while the efficiency of the reaction was slightly decreased (entry 10). The present addition reaction can also be carried out with good efficiency in the presence of 1.0 mol% of catalyst **4** by simply lengthening the reaction time (48 h; entry 13). Notably, this transformation is easily handled under air and is potentially applicable in large-scale synthesis despite a small decrease in the yield (71% yield; entry 14). Most importantly, in this transformation nothing is required besides the catalyst and solvent to facilitate the addition as desired.

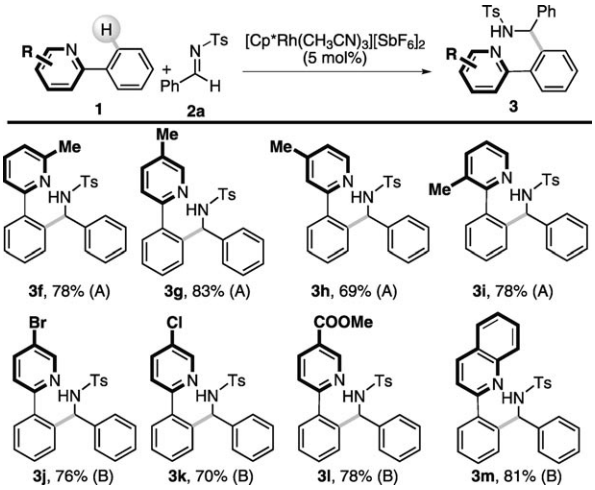
Under the optimized reaction conditions, the reactivity of different sulfonylbenzaldimine derivatives was investigated (Scheme 2). Various *N*-arylsulfonyl substrates were tested and all of them exhibited good reactivities, no matter whether electron-withdrawing or electron-donating groups are introduced to the aryl group. For example, *N*-4-methoxyphenyl-, 4-phenyl-, and 4-fluorophenylsulfonyl aldimines showed good to excellent reactivities (**3b**, **3c**, and **3d**). However, alkylsulfonylbenzaldimines, for example mesylbenzaldimine, led to relatively lowered efficiency (**3e**). Other than *N*-sulfonyl



Scheme 2. Addition of the C–H bond of **1a** to different benzaldimines **2**. Reaction conditions: **1a** (0.25 mmol), **2** (0.50 mmol), *t*BuOH (1.0 mL). The yield of isolated product is reported.

aldimine, various electron-withdrawing groups, including sulfinyl, carbamyl, and phosphoryl, completely inhibited this transformation. This outcome might arise from their relatively lower inductive effect to decrease the electrophilicity of the corresponding imines.

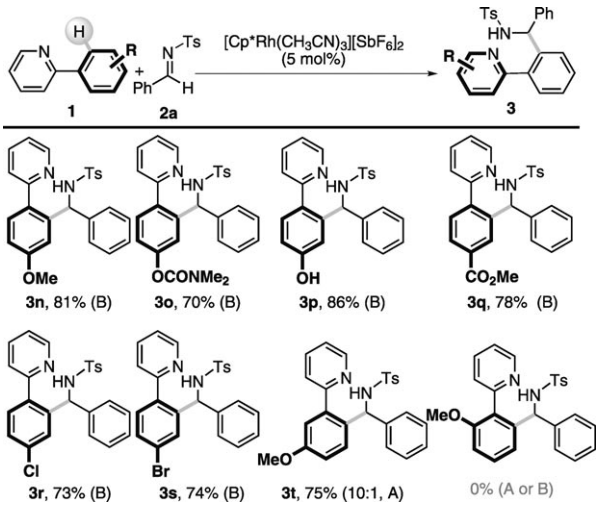
We further explored the arene substrates. First, various pyridinyl directing groups were investigated. It was found that the electronic nature of the substituents on the pyridine ring did not play a key role (Scheme 3). With either electron-donating or -withdrawing groups, for example methyl (**3f–3i**), halide (**3j** and **3k**), and ester groups (**3l**), the reactions proceeded smoothly. Notably, the tolerance of the halides (**3j** and **3k**) offers the opportunity for further functionalization. The tolerance of this reaction for steric bulkiness on the pyridine ring was also tested. To our satisfaction, all the reactions with a methyl group at the 3- to 6-positions of the



Scheme 3. Investigation of substituted pyridinyl directing groups. Reaction conditions A: **1** (0.25 mmol), **2a** (0.5 mmol), *t*BuOH (0.5–1.0 mL), 10 h; reaction conditions B: **1** (0.25 mmol), **2a** (0.5 mmol), toluene (0.5 mL), 48 h. The yield of isolated product is reported.

pyridine ring exhibited excellent reactivities (**3f–3i**), thus showing high tolerance for steric hindrance. Moreover, the quinodinyl unit can be successfully used as a directing group with the quinodinyl motif remaining untouched (**3m**).

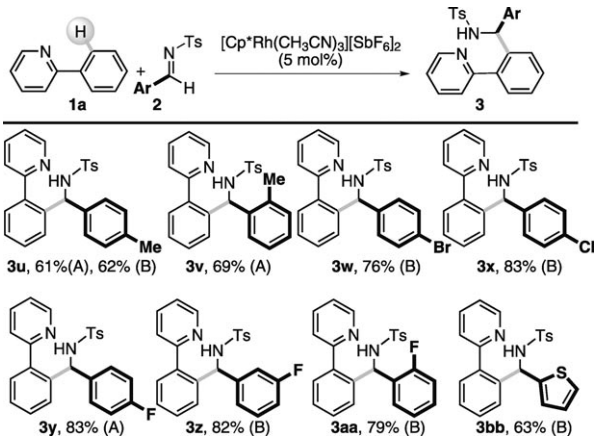
The investigation of the phenyl unit of the arene substrate also showed broad functional group compatibility (Scheme 4). With either electron-donating or -withdrawing groups, for example methoxy (**3n**), carbamate (**3o**), and ester groups (**3q**), the reactions proceeded very smoothly in good to excellent yields. This transformation also showed good



Scheme 4. Investigation of functional group compatibility of substituents on the phenyl group of **1**. Reaction conditions A: arene (0.25 mmol), *N*-sulfonyl aldimine (0.5 mmol), *t*BuOH (1.0 mL), 10 h; reaction conditions B: arene (0.25 mmol), *N*-sulfonyl aldimine (0.5 mmol), toluene (0.5–1.0 mL), 32–48 h. The yield of isolated product is reported.

regio- and chemoselectivity, and a single product was produced from *para*-substituted substrates (**3n–3s**). Meanwhile, the *meta*-methoxy-substituted substrate gave two products in a 10:1 ratio where the reaction was under steric control (**3t**; structure of the major product is shown in Scheme 4). Importantly, the arene substrate with an unprotected hydroxy group was also compatible and the desired product was isolated in excellent yield (**3p**). The variety of functional groups on these products provide a great opportunity for further functionalization with various methods.[15] However, the *ortho*-methoxy-substituent product terminated the transformation, which supposedly resulted from the chelating ability of the substrates.

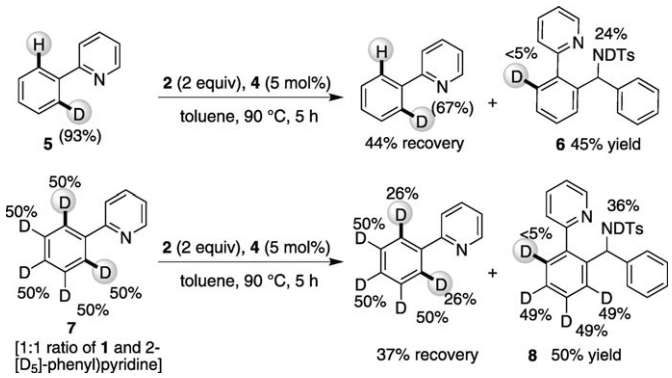
Finally, various *p*-tolylsulfonylarylaldimine compounds were investigated (Scheme 5). We found that the steric bulkiness does not play a significant role. For example, 4-tolylaldimine (**3u**) shows comparable reactivity with 2-tolylaldimine (**3v**). Also, the electron-withdrawing group (**3w–3aa**) should increase the reactivity and vice versa (**3u–v**), probably as a result of the enhancement of the electrophilicity of the sulfonylimine group. A heterocyclic substrate was also suitable for this addition reaction (**3ab**). Notably, the efficiency of the transformation for different substrates was



Scheme 5. Investigation of different aryl *N*-sulfonyl aldimines **2** in C–H addition. Reaction conditions A: arene (0.25 mmol), *N*-sulfonyl aldimine (0.5 mmol), *t*BuOH (0.5–1.0 mL), 10–48 h; reaction conditions B: arene (0.25 mmol), *N*-sulfonyl aldimine (0.5 mmol), toluene (0.5 mL), 48 h. The yield of isolated product is reported.

directly related to the solvent—this finding cannot be satisfactorily explained at this stage.

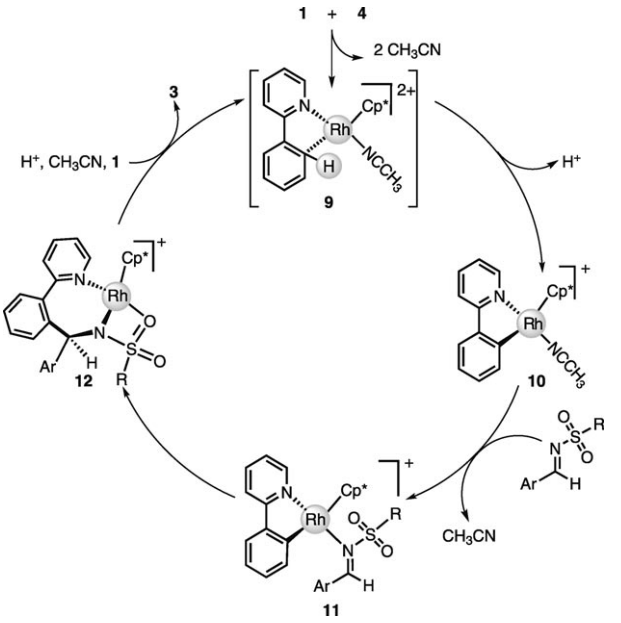
To further investigate the mechanism, intra- and intermolecular isotopic studies were performed in dried toluene (Scheme 6). During the intramolecular reaction, the content



Scheme 6. Intramolecular and intermolecular isotopic reactions.

of deuterium in the recovered 2-([D]-phenyl)pyridine (**5**) was decreased from 93% to 67%, and the content of deuterium in the NH(D)Ts group was 24% in **6**. Intermolecularly, the content of deuterium at the 2- and 6-positions of the phenyl group in 2-([D_5]-phenyl)pyridine (**7**) was decreased from 50% to 26%. Interestingly, no obvious deuterium contents at the 6-position of the phenyl group in product **8** were observed. The content of deuterium in NH(D)Ts group was 36%. All these data offer strong evidence to show that the first step of C–H cleavage is reversible.

On the basis of these preliminary studies, the mechanism of this transformation is proposed as Scheme 7. The transformation is initiated by the coordination of the nitrogen atom of 2-phenylpyridine (**1a**) to the cationic Rh center, followed by an electrophilic substitution to produce the C–Rh complexes **10**, and is accompanied a release of one equivalent



Scheme 7. Proposed mechanism of aryl C–H addition to the C=N bond of aryl *N*-sulfonyl aldimines.

of proton (H^+). After the ligand exchange from acetonitrile to sulfonylaldimine, the coordinating complex **11** forms. Then the nucleophilic addition (or C=N insertion) takes place to form the N–Rh species **12**. The seven-membered rhodacycle **12** is protonated by the acid that is generated in situ at the initiating step, thus producing the desired product **3**. This final step is accompanied by the regeneration of the active catalyst to facilitate the catalytic cycle. Thus, external additives are not needed to facilitate this catalytic cycle.

In conclusion, we have developed an "ideal" rhodium-catalyzed selective C–H activation and subsequent nucleophilic addition to *N*-sulfonyl arylaldimines. In this reaction, the inert arene substrates played the role as a surrogate for aryl Grignard reagents to facilitate the direct addition to C=N groups in the absence of any additives and waste production (the excess *N*-sulfonyl aldimine can be recovered). The reaction can be carried out under mild conditions without the requirement of special techniques. This transformation is potentially applicable in laboratory and industrial synthesis. The use of a chelating ligand also offers the potential for asymmetric catalysis. Most importantly, this process may provide a new direction for direct C–H addition to C=O/N motifs—where C–H bonds become efficient nucleophiles to produce alcohols and secondary amines in an efficient and clean manner. Thus, our approach provides the possibility for state-of-art examples of sustainable transformations.

Experimental Section

General procedure: To a Schlenck tube were added [Cp*Rh-$(CH_3CN)_3$][SbF_6]$_2$ (10.4 mg, 0.0125 mmol), **1** (0.25 mmol), **2** (0.50 mol), *t*BuOH (0.5–1.0 mL) or toluene (0.5–1.0 mL). The reaction mixture was stirred in the sealed tube at 90 °C under N_2 in a Wattecs Parallel Reactor for 10–48 h. After cooling to RT, the solvent was removed in vacuo and the residue was purified by chromatography on silica gel (eluent: hexanes/EtOAc/CH_2Cl_2 7:1:1–4:1:1) to afford **3** as a white solid.

Received: November 28, 2011
Published online: January 26, 2011

Keywords: addition reactions · catalysis · C–H activation · rhodium · sulfonyl aldimines

[1] a) G. S. Silverman, P. E. Rakita, *Handbook of Grignard Reagents*, Marcel Dekker, New York, **1996**; b) H. G. Richey, Jr., *Grignard Reagents: New Development*, Wiley, Chichester, **2000**; c) S. Kobayashi, H. Ishitani, *Chem. Rev.* **1999**, *99*, 1069–1094.

[2] A. R. Katritzky, R. J. K. Taylor, *Comprehensive Organic Functional Group Transformations II*, Elsevier, Dordrecht, **2004**, Chapter 2, pp. 561–593.

[3] a) V. Snieckus, *Chem. Rev.* **1990**, *90*, 879–933; b) M. C. Whisler, S. MacNeil, V. Snieckus, P. Beak, *Angew. Chem.* **2004**, *116*, 2256–2276; *Angew. Chem. Int. Ed.* **2004**, *43*, 2206–2225; c) C. J. Rohbogner, G. C. Clososki, P. Knochel, *Angew. Chem.* **2008**, *120*, 1526–1530; *Angew. Chem. Int. Ed.* **2008**, *47*, 1503–1507; d) S. H. Wunderlich, M. Kienle, P. Knochel, *Angew. Chem.* **2009**, *121*, 7392–7396; *Angew. Chem. Int. Ed.* **2009**, *48*, 7256–7260; e) M. Jaric, B. A. Haag, A. Unsinn, K. Karaghiosoff, P. Knochel, *Angew. Chem.* **2010**, *122*, 5582–5586; *Angew. Chem. Int. Ed.* **2010**, *49*, 5451–5455.

[4] a) M. B. Smith, *Organic Synthesis*, McGraw-Hill, New York, **1994**, p. 1313; b) M. Bandini, A. Melloni, A. Umani-Ronchi, *Angew. Chem.* **2004**, *116*, 560–566; *Angew. Chem. Int. Ed.* **2004**, *43*, 550–556; c) T. B. Poulsen, K. A. Jørgensen, *Chem. Rev.* **2008**, *108*, 2903–2915.

[5] For representative examples, see: a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, *366*, 529–531; b) C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura, Y. Fujiwara, *Science* **2000**, *287*, 1992–1995; c) K. Cheng, B. Yao, J. Zhao, Y. Zhang, *Org. Lett.* **2008**, *10*, 5309–5312; d) T. Fukutani, N. Umeda, K. Hirano, T. Satoh, M. Miura, *Chem. Commun.* **2009**, 5141–5143; e) J. Chen, G. Song, C.-L. Pan, X. Li, *Org. Lett.* **2010**, *12*, 5426–5429; f) Y. Boutadla, D. L. Davies, O. Al-Duaij, J. Fawcett, R. C. Jones, K. Singh, *Dalton Trans.* **2010**, *39*, 10447–10457; g) D. J. Schipper, M. Hutchinson, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6910–6911; h) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326–18339; for reivews, see: i) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1769; j) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212–11222; k) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655.

[6] a) Y. Fukumoto, K. Sawada, M. Hagihara, N. Chatani, S. Murai, *Angew. Chem.* **2002**, *114*, 2903–2905; *Angew. Chem. Int. Ed.* **2002**, *41*, 2779–2781; b) Y. Kuninobu, Y. Nishina, C. Nakagawa, K. Takai, *J. Am. Chem. Soc.* **2006**, *128*, 12376–12377; c) B. Zhao, X. Lu, *Org. Lett.* **2006**, *8*, 5987–5990; d) Y. Kuninobu, Y. Nishina, T. Takeuchi, K. Takai, *Angew. Chem.* **2007**, *119*, 6638; *Angew. Chem. Int. Ed.* **2007**, *46*, 6518; e) K. Tsuchikama, Y.-K. Hashimoto, K. Endo, T. Shibata, *Adv. Synth. Catal.* **2009**, *351*, 2850–2854; f) B. Qian, S. Guo, J. Shao, Q. Zhu, L. Yang, C. Xia, H. Huang, *J. Am. Chem. Soc.* **2010**, *132*, 3650–3651; g) B.-J. Li, Z.-J. Shi, *Chem. Sci.* **2010**, DOI: 10.1039/c0sc00419g.

[7] During the review of our manuscipt, a very similar study was published, A. S. Tsai, M. E. Tauchert, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2011**, DOI: 10.1021/ja109562x.

[8] a) M. Sakai, M. Ueda, N. Miyaura, *Angew. Chem.* **1998**, *110*, 3475–3477; *Angew. Chem. Int. Ed.* **1998**, *37*, 3279–3281; b) T. Yamamoto, T. Ohta, Y. Ito, *Org. Lett.* **2005**, *7*, 4153–4155; c) G. Liu, X. Lu, *J. Am. Chem. Soc.* **2006**, *128*, 16504–16505; d) S. Lin, X. Lu, *J. Org. Chem.* **2007**, *72*, 9757–9760; e) C. Qin, H. Wu, J.

Cheng, X. Chen, M. Liu, W. Zhang, W. Su, J. Ding, *J. Org. Chem.* **2007**, *72*, 4102 – 4107; f) N. Miyaura, *Synlett* **2009**, 2039 – 2350.

[9] a) S. S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298 – 2311; *Angew. Chem. Int. Ed.* **1998**, *37*, 2180 – 2192; b) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808 – 1822; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698 – 1712; c) S. Murai, *Activation of Unreactive Bonds and Organic Synthesis*, Springer, Berlin, **1999**, pp. 48 – 78; d) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507 – 514; e) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861 – 2903; f) G. Dyker, *Handbook of C–H Transformations. Applications in Organic Synthesis*, Wiley-VCH, Weinheim, **2005**; g) L.-C. Campeau, K. Fagnou, *Chem. Commun.* **2006**, 1253 – 1264; h) A. R. Dick, M. S. Sanford, *Tetrahedron* **2006**, *62*, 2439 – 2462; i) R. G. Bergman, *Nature* **2007**, *446*, 391 – 393; j) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174 – 238; k) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173 – 1193; l) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417 – 424; m) J. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013 – 1025; n) B.-J. Li, S.-D. Yang, Z.-J. Shi, *Synlett* **2008**, 949 – 957; o) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196 – 5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094 – 5115; p) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074 – 1086; q) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976 – 10011; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792 – 9826; r) J.-Q. Yu, Z.-J. Shi, *C–H Activation, Topics in Current Chemistry, Vol. 292*, Springer, Berlin, **2010**; s) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147 – 1169; t) L. Ackermann, *Chem. Commun.* **2010**, *46*, 4866 – 4877.

[10] a) M. Ueda, N. Miyaura, *J. Organomet. Chem.* **2000**, *595*, 31 – 35; b) M. Kuriyama, T. Soeta, X. Hao, Q. Chen, K. Tomioka, *J. Am. Chem. Soc.* **2004**, *126*, 8128 – 8129; c) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2004**, *126*, 13584 – 13585.

[11] a) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748 – 11749; b) X. Zhao, Z. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 8136 – 8137; c) M. Kim, J. Kwak, S. Chang, *Angew. Chem.* **2009**, *121*, 9097 – 9101; *Angew. Chem. Int. Ed.* **2009**, *48*, 8935 – 8939; d) T. K. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565 – 10569; e) F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9982 – 9983.

[12] a) C. Scheeren, F. Maasarani, A. Hijazi, J.-P. Djukic, M. Pfeffer, *Organometallics* **2007**, *26*, 3336 – 3345; b) L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 12414 – 12419; c) L. Li, W. W. Brennessel, W. D. Jones, *Organometallics* **2009**, *28*, 3492 – 3500.

[13] T. Nishikata, Y. Yamamoto, N. Miyaura, *Angew. Chem.* **2003**, *115*, 2874 – 2876; *Angew. Chem. Int. Ed.* **2003**, *42*, 2768 – 2770.

[14] CCDC 793688 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] A. R. Katritzky, R. J. K. Taylor, *Comprehensive Organic Functional Group Transformations II*, Elsevier, Dordrecht, **2004**; for recent studies, see: a) D.-G. Yu, B.-J. Li, Z.-J. Shi, *Acc. Chem. Res.* **2010**, *43*, 1486 – 1495; b) M. Tobisu, T. Shimasaki, N. Chatani, *Angew. Chem.* **2008**, *120*, 4944; *Angew. Chem. Int. Ed.* **2008**, *47*, 4866; c) A. Antoft-Finch, T. Blackburn, V. Snieckus, *J. Am. Chem. Soc.* **2009**, *131*, 17750; d) B.-T. Guan, Y. Wang, B.-J. Li, D.-G. Yu, Z.-J. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 14468; e) K. W. Quasdorf, X. Tian, N. K. Garg, *J. Am. Chem. Soc.* **2008**, *130*, 14422; f) Z. Li, S.-L. Zhang, Y. Fu, Q.-X. Guo, L. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 8815; g) B.-J. Li, Y.-Z. Li, X.-Y. Lu, J. Liu, B.-T. Guan, Z.-J. Shi, *Angew. Chem.* **2008**, *120*, 10278; *Angew. Chem. Int. Ed.* **2008**, *47*, 10124.

