C–H Activation

DOI: 10.1002/anie.200906870

Iron-Catalyzed Direct Arylation of Unactivated Arenes with Aryl Halides**

*Wei Liu, Hao Cao, and Aiwen Lei**

Cross-coupling reactions used to construct biaryl compounds mainly involve Ar^1X as an electrophile and Ar^2M as a nucleophile.[1] Recently, C–H bond activation has been used, where Ar^2H served as the nucleophile to react with Ar^1X (direct arylation of arenes).[2,3] This strategy efficiently avoids the disposal of stoichiometric amounts of metal waste generated from the organometallic reagent, ArM, in the traditional coupling manner.[2,3] Various transition metals have been reported as efficient catalysts for this transformation, for example, Pd,[4–11] Rh,[12–15] Ru,[16–18] Ir,[19,20] Cu,[21–27] and other transition metals.[28–30]

The application of inexpensive, non-toxic, commercially available, and environmentally benign iron complexes as catalysts in chemical syntheses has attracted much attention.[31,32] Recently, iron has been utilized extensively as a catalyst to promote the "traditional" cross-coupling between R^1X and R^2M.[33–41] Iron catalysts are also involved in many important transformations, such as Friedel–Crafts benzylation,[42,43] carbonylation,[44] oxidation[45,46] and other processes.[47–54]

Of great interest are the recently developed oxidative coupling reactions of Ar^1M with Ar^2H to generate $Ar^1–Ar^2$ products by employing Fe complexes as the catalysts. Nakamura and co-workers reported an elegant Fe-catalyzed oxidative coupling reaction between Ar^2H, which contain directing groups, and diaryl zinc reagents.[55,56] Yu and co-workers explored the oxidative reaction between Ar^2H and $Ar^1B(OH)_2$ using a stoichiometric amount of iron reagent.[57] Many other oxidative coupling reactions, which involve C–H activation using iron catalysts in the presence of stoichiometric amounts of oxidants, have also been reported.[58–61] However, to the best of our knowledge, no example of Fe-catalyzed cross-coupling between Ar^1X and Ar^2H has been reported (Scheme 1). Herein, we report the development of novel Fe-catalyzed cross-coupling reactions between electrophilic Ar^1X (X = I, Br, Cl) and unactivated Ar^2H coupling partners.

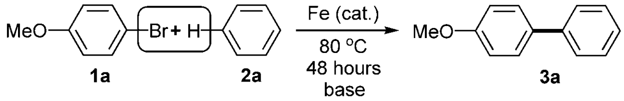
$$Ar^1–X + Ar^2–H \xrightarrow{[Fe]} Ar^1–Ar^2$$

Scheme 1. Iron-catalyzed direct arylation of arenes with aryl halides.

Initially, we chose 4-bromoanisole and unactivated benzene as the model substrates for surveying reaction parameters in the model reaction (Table 1). Commonly used inorganic bases, such as Li_2CO_3, Na_2CO_3, K_2CO_3, Cs_2CO_3, and K_3PO_4 were employed in the reaction, however, no conversion was observed at 80 °C for 48 hours in the presence of the iron salt. When NaO*t*Bu was employed, a trace amount of the direct arylation product was observed by GC/MS analysis. This outcome encouraged us to further examine the feasibility of this catalysis.

When LiHMDS (3.0 equiv) was added as a base, the desired product **3a** (16 % yield) was obtained in the presence

Table 1: Iron-catalyzed C–H bond activation: Screening of reaction conditions.[a]



Entry	[Fe] (mol %)	Ligand	Base	Benzene [mL]	Yield [%][b]
1	$FeCl_2$ (20)	none	LiHMDS	3	4
2	$FeBr_2$ (20)	none	LiHMDS	3	9
3	$FeCl_3$ (20)	none	LiHMDS	3	16
4	$FeCl_3$ (20)	bipy	LiHMDS	3	18
5	$FeCl_3$ (20)	TMEDA	LiHMDS	3	8
6	$FeCl_3$ (20)	$NH_2CH_2CH_2NH_2$	LiHMDS	3	14
7	$FeCl_3$ (20)	L-proline	LiHMDS	3	21
8	$FeCl_3$ (20)	$CH_3O(CH_2)_2OCH_3$	LiHMDS	3	6
9	$FeCl_3$ (20)	DMEDA	LiHMDS	3	66
10	$FeCl_3$ (20)	DMEDA	LiHMDS	4	75
11	$FeCl_3$ (20)	DMEDA	LiHMDS	5	66
12	**$FeCl_3$ (15)**	**DMEDA**	**LiHMDS**	**4**	**79**
13	$FeCl_3$ (10)	DMEDA	LiHMDS	4	66
14	$FeCl_3$ (15)	*t*BuNH$(CH_2)_2$NH*t*Bu	LiHMDS	4	76
15	$FeCl_3$ (15)	DMEDA	LiO*t*Bu	4	–
16	$FeCl_3$ (15)	DMEDA	NaO*t*Bu	4	trace
17	$FeCl_3$ (15)	DMEDA	KO*t*Bu	4	61
18	none	none	LiHMDS	4	–
19	none	DMEDA	LiHMDS	4	–

[a] Reactions were carried out with **1a** (0.5 mmol) and base (3.0 equiv) in benzene (3 mL, 34 mmol; 4 mL, 45 mmol; 5 mL, 56 mmol). [b] Yields were determined by GC analysis. TMEDA = *N,N,N',N'*-tetramethylethane-1,2-diamine. DMEDA = *N,N'*-dimethylethane-1,2-diamine, HMDS = hexamethyldisilazane, bipy = 2,2'-bipyridine.

---

[*] W. Liu, H. Cao, Prof. A. Lei
College of Chemistry and Molecular Sciences,
Wuhan University, Wuhan, Hubei, 430072 (China)
Fax: (+86) 27-6875-4067
E-mail: aiwenlei@whu.edu.cn
Prof. A. Lei
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai, 200032 (China)

[**] This work was supported by the National Natural Science Foundation of China (20772093, 20972118, and 20832003), and the Doctoral Fund of the Ministry of Education of China (20060486005).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906870.

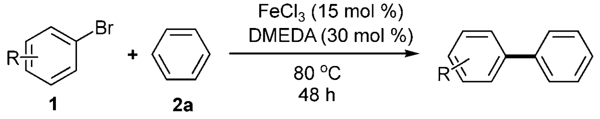
of $FeCl_3$ (20 mol %; Table 1, entry 3). Meanwhile, $FeCl_2$ and $FeBr_2$ were less efficient catalysts under the same reaction conditions (Table 1, entries 1 and 2). The nature of the base and the ligand was essential to influence the yield of the product (Table 1, entries 4–14). In the presence of DMEDA (40 mol %), the direct arylation of benzene was achieved in 66% yield (Table 1, entry 9), and this result showed that this particular diamine ligand was more efficient than others. Notably, the amount of benzene has some effect on this reaction. The best result (75 % yield) was obtained when the reaction was carried out in the presence of 4 mL of benzene (90 equiv; compare Table 1, entries 9–11). The effects of catalyst loading was also examined, and 15 mol % was the best and yielded **3a** in 79 % yield (compare Table 1, entries 10, 12, and 13). When LiHMDS was replaced with NaO*t*Bu or LiO*t*Bu, the reactions only produced trace amounts or no desired product, respectively (Table 1, entries 15 and 16). When KO*t*Bu was employed as the base, the desired product **3a** was obtained in 61 % yield (Table 1, entry 17). Moreover, the direct arylation of benzene was not observed at room temperature, and an increase to 60 °C led to poor conversion.

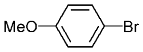
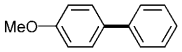
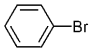
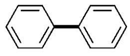
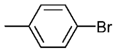
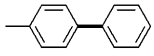
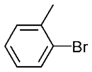
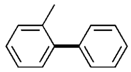
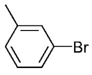
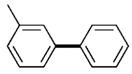
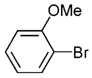
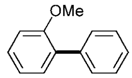
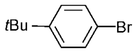
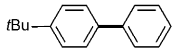
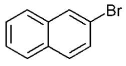
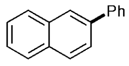
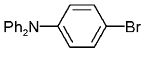
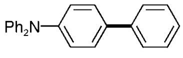
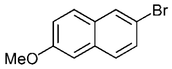
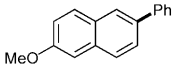
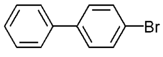
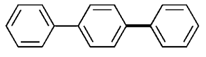
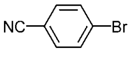
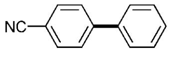
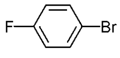
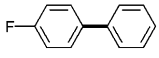
Control experiments revealed that no reaction was observed in the absence of $FeCl_3$ (Table 1, entries 18 and 19). To eliminate the contaminants which might potentially affect the catalysis, a different batch of Fe complex was employed. When high purity $FeCl_3$ (> 99.99 %, from Aldrich) was used under the standard conditions (15 mol % of $FeCl_3$, 30 mol % of DMEDA, 2.0 equiv of base), the yield remained unchanged (see the Supporting Information).[62] This result suggested that the C–H activation reaction was solely catalyzed by the Fe complex. When CuCl, CuBr, or CuI were tested as catalysts under the standard conditions, both conversion and yield became relatively low, thus indicating that Cu salts were much less effective catalysts in this reaction (for more details see the Supporting Information). These experiments further indicate that the Fe catalyst plays a crucial role in this aromatic C–H transformation.

With our optimized reaction conditions in hand, the scope of this direct arylation of benzene with various aryl halides was investigated (Table 2, Scheme 2, and Scheme 3). In general, the yields of the reactions with electron-rich aryl bromides were good (72 %–81 % yield; Table 2, entries 1–3, 5, 7, and 9) and were higher than those with the electron-deficient aryl bromides (Table 2, entries 11–13). 2-Naphthyl bromides **1h** and **1j** also underwent direct arylation smoothly and afforded the desired products in 70 % and 62 % yield, respectively (Table 2, entries 8 and 10). Aryl bromides with *ortho*-substituted groups led to lower yields (Table 2, entries 4 and 6).

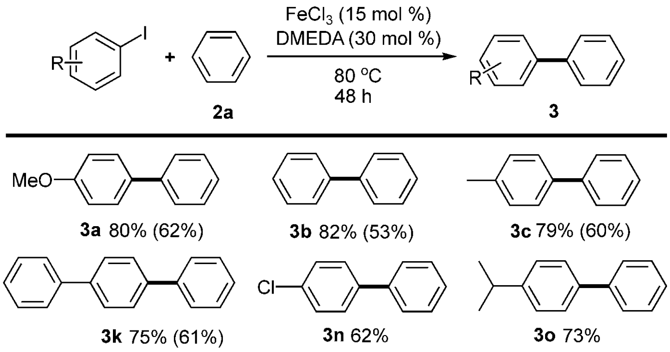
Aryl iodides containing electron-donating and electron-withdrawing groups reacted smoothly with benzene and gave the corresponding products in the range of yields (62 %–82 %; Scheme 2). Interestingly, in the direct arylation of benzene with aryl iodides reactions which employed KO*t*Bu as the base gave better yields compared with LiHMDS (Scheme 2). Notably, no homo-coupling products from the corresponding aryl halides were observed when using either aryl bromides or aryl iodides.

Table 2: Different aryl bromides coupling with benzene.[a]



Entry	Aryl halides		Product		Yield [%][b]
1	**1a**		**3a**		81
2	**1b**		**3b**		77
3	**1c**		**3c**		73
4	**1d**		**3d**		45
5	**1e**		**3e**		73
6	**1f**		**3f**		37
7	**1g**		**3g**		72
8	**1h**		**3h**		70
9	**1i**		**3i**		72
10	**1j**		**3j**		62
11	**1k**		**3k**		63
12	**1l**		**3l**		51
13	**1m**		**3m**		45

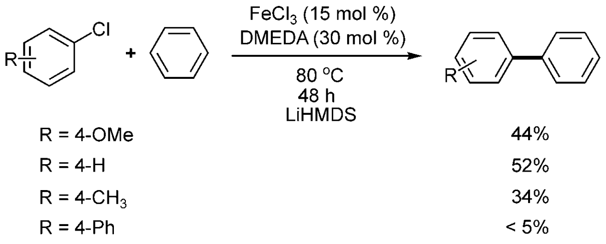
[a] Reactions were carried out with **1** (0.5 mmol) and LiHMDS (2.0 equiv) in benzene (4.0 mL, 45 mmol). [b] Yield of isolated product.



3a 80% (62%)
3b 82% (53%)
3c 79% (60%)
3k 75% (61%)
3n 62%
3o 73%

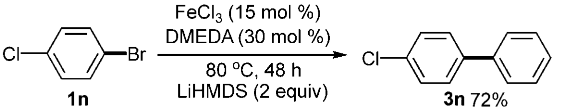
Scheme 2. Different aryl iodides coupling with benzene. Reactions were carried out using aryl iodide (0.5 mmol) and KO*t*Bu (3.0 equiv) in benzene (4.0 mL, 45 mmol). In parentheses, reactions were carried out using LiHMDS (2.0 equiv) in benzene (4.0 mL, 45 mmol).

In addition to aryl bromides and iodides, the applicability of more challenging aryl chlorides in this reaction was examined. The reaction of benzene chloride gave the desired coupling product (52% yield), and the reactions of p-MeC_6H_4Cl and p-$MeOC_6H_4Cl$ gave 34% and 44% yields, respectively (Scheme 3). Under the standard reaction conditions, ArCl bearing electron-withdrawing groups resulted in poor yields (< 5%; Scheme 3). Moreover, no reaction was observed using fluorobenzene as the electrophile under the same conditions.

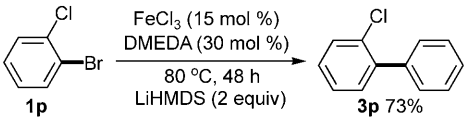


Scheme 3. Iron-catalyzed direct arylation of benzene with aryl chlorides. Reaction conditions: aryl chloride (0.5 mmol), LiHMDS (2.0 equiv), $FeCl_3$ (15 mol%), and DMEDA (30 mol%) in benzene (4.0 mL) at 80°C for 48 h.

Competitive experiments were carried out to probe the reactivity between the chloro and the bromo group. Aryl bromide was preferentially transformed, while the aryl chloride was tolerated at either the *para* or *ortho* position under the reaction conditions [Eq. (1) and (2)]. Both the reaction of p-ClC_6H_4Br and o-ClC_6H_4Br gave good yields, 72% and 73%, respectively.



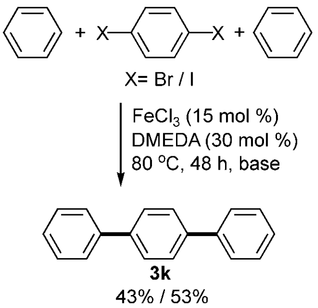
(1)



(2)

When 1,4-dibromobenzene or 1,4-diiodobenzene was treated with benzene in the presence of base (3 equiv), 1,4-diphenylbenzene was produced in 43% and 53% yields, respectively (Scheme 4).

The Fe-catalyzed direct arylation of substituted arenes with aryl bromides was investigated, and the results are listed in Table 3. The reaction between anisole and bromobenzene gave 69% combined yield of direct arylation product (three isomers, with a ratio of 64:24:12; Table 3, entry 2). Naphthalene could be arylated in moderate yields (65% and 68%, respectively; Table 3, entries 3 and 4), and produced a mixture of 1- and 2-substituted naphthalene derivatives. Direct arylation of toluene with 4-$MeOC_6H_4Br$ afforded the direct arylated product in 39% yield. Significantly, in the presence of Fe catalyst (15 mol%), ferrocene was successfully arylated with bromobenzene, and gave the corresponding monoarylated product (54% yield; Table 3, entry 5).



Scheme 4. Iron-catalyzed two-fold C—H bond activations. Reaction conditions: aryl bromide (0.5 mmol) or aryl iodide (0.5 mmol), LiHMDS (3.0 equiv) or KO*t*Bu (3.0 equiv) in benzene (4.0 mL) at 80°C for 48 h.

If the reaction proceeded through a benzyne pathway, when substituted aryl bromide such as **1a** was employed, two products would be generated. However, the reactions of various substituted aryl bromides with benzene all produced the sole corresponding direct arylation products (Table 2), which clearly ruled out the benzyne mechanism. The isotope effect of the reaction was examined. The reaction was conducted under the standard conditions using 4-bromoanisole (**1a**) coupling with equimolar amounts of benzene and $[D_6]$benzene (see the Supporting Information). The labeling experiment yielded **3a** and deuterated **3a** in the ratio of 5:3 ($k_H/k_D = 1.7$).

In summary, we have successfully developed the first novel Fe-catalyzed direct arylation of unactivated arenes with a broad range of aryl halides, including aryl chlorides, bromides, and iodides, through C—H bond activation to prepare biaryl compounds. The choice of the base and ligand are essential to the success of this Fe-catalyzed direct arylation of unactivated arenes. Further studies on the mechanism are actively underway, and will be reported in due course.

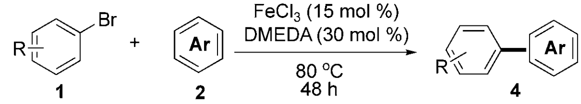
Experimental Section

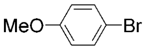
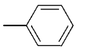
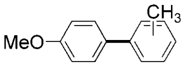
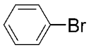
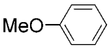
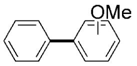
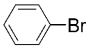
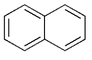
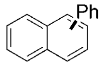
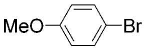
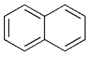
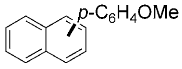
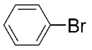
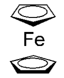
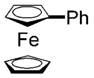
General procedure: Benzene (4.0 mL), DMEDA (13.2 mg, 0.15 mmol), and 4-bromoanisole (93.5 mg, 0.5 mmol) were added to a Schlenk tube charged with $FeCl_3$ (12.1 mg, 0.075 mmol) and LiHMDS (167 mg, 1.0 mmol) under an argon atmosphere at RT. The resulting reaction mixture was stirred at 80°C for 48 h. After cooling to RT, the mixture was quenched and extracted with ethyl acetate (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, concentrated under reduced pressure, and then purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:100) to yield the desired product as a white solid (74.5 mg, 81% yield).

Received: December 6, 2009
Published online: February 16, 2010

Keywords: aryl halides · biaryls · C—H activation · cross-coupling · iron

Table 3: Different aryl bromides coupling with unactivated arenes.[a]



Entry	Aryl halides	Arene	Product	Yield [%][b]
1[c]			**4a** 	39 (*o*/*m*/*p*= 47:34:19)
2[d]			**4b** 	69 (*o*/*m*/*p*= 64:24:12)
3[e]			**4c** 	65 (α/β= 61:39)
4[e]			**4d** 	68 (α/β= 69:31)
5[f]			**4f** 	54

[a] Reactions were carried out using **1** (0.5 mmol) and LiHMDS (2.0 equiv). [b] The ratio of regioisomers was determined by GC/MS analysis. [c] Reaction was carried out using 4-bromoanisole (0.5 mmol) in toluene (4.0 mL). [d] Reaction was carried out using PhBr (0.5 mmol) in anisole (40 mmol). [e] Reaction was carried out in naphthalene (30 mmol). [f] Reaction was carried out using ferrocene (20 mmol) in benzene (2.0 mL).

---

[1] A. de Meijere, F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed., Wiley-VCH, Weinheim, **2004**.

[2] D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238.

[3] G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447–2464.

[4] D. A. Candito, M. Lautens, *Angew. Chem.* **2009**, *121*, 6841–6844; *Angew. Chem. Int. Ed.* **2009**, *48*, 6713–6716.

[5] L. C. Campeau, M. Parisien, A. Jean, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 581–590.

[6] L. C. Campeau, M. Parisien, M. Leblanc, K. Fagnou, *J. Am. Chem. Soc.* **2004**, *126*, 9186–9187.

[7] L. C. Campeau, S. Rousseaux, K. Fagnou, *J. Am. Chem. Soc.* **2005**, *127*, 18020–18021.

[8] M. Lafrance, C. N. Rowley, T. K. Woo, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 8754–8756.

[9] B. S. Lane, M. A. Brown, D. Sames, *J. Am. Chem. Soc.* **2005**, *127*, 8050–8057.

[10] N. Lebrasseur, I. Larrosa, *J. Am. Chem. Soc.* **2008**, *130*, 2926–2927.

[11] G. L. Turner, J. A. Morris, M. F. Greaney, *Angew. Chem.* **2007**, *119*, 8142–8146; *Angew. Chem. Int. Ed.* **2007**, *46*, 7996–8000.

[12] S. Proch, R. Kempe, *Angew. Chem.* **2007**, *119*, 3196–3199; *Angew. Chem. Int. Ed.* **2007**, *46*, 3135–3138.

[13] A. M. Berman, J. C. Lewis, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 14926–14927.

[14] J. C. Lewis, A. M. Berman, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 2493–2500.

[15] S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748–11749.

[16] L. Ackermann, A. Althammer, R. Born, *Angew. Chem.* **2006**, *118*, 2681–2685; *Angew. Chem. Int. Ed.* **2006**, *45*, 2619–2622.

[17] I. Özdemir, S. Demir, B. Cetinkaya, C. Gourlaouen, F. Maseras, C. Bruneau, P. H. Dixneuf, *J. Am. Chem. Soc.* **2008**, *130*, 1156–1157.

[18] F. Požgan, P. H. Dixneuf, *Adv. Synth. Catal.* **2009**, *351*, 1737–1743.

[19] K. Fujita, M. Nonogawa, R. Yamaguchi, *Chem. Commun.* **2004**, 1926–1927.

[20] B. Join, T. Yamamoto, K. Itami, *Angew. Chem.* **2009**, *121*, 3698–3701; *Angew. Chem. Int. Ed.* **2009**, *48*, 3644–3647.

[21] H. Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2007**, *129*, 12404–12405.

[22] H. Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128–1129.

[23] H. O. Do, R. M. K. Khan, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 15185–15192.

[24] D. B. Zhao, W. H. Wang, F. Yang, J. B. Lan, L. Yang, G. Gao, J. S. You, *Angew. Chem.* **2009**, *121*, 3346–3350; *Angew. Chem. Int. Ed.* **2009**, *48*, 3296–3300.

[25] R. J. Phipps, N. P. Grimster, M. J. Gaunt, *J. Am. Chem. Soc.* **2008**, *130*, 8172–8173.

[26] R. J. Phipps, M. J. Gaunt, *Science* **2009**, *323*, 1593–1597.

[27] S. Yotphan, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2009**, *11*, 1511–1514.

[28] Y. Nakao, N. Kashihara, K. S. Kanyiva, T. Hiyama, *J. Am. Chem. Soc.* **2008**, *130*, 16170–16171.

[29] O. Kobayashi, D. Uraguchi, T. Yamakawa, *Org. Lett.* **2009**, *11*, 2679–2682.

[30] J. Canivet, J. Yamaguchi, I. Ban, K. Itami, *Org. Lett.* **2009**, *11*, 1733–1736.

[31] S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363–3367; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321.

[32] C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254.

[33] B. D. Sherry, A. Fürstner, *Acc. Chem. Res.* **2008**, *41*, 1500–1511.

[34] D. Bézier, C. Darcel, *Adv. Synth. Catal.* **2009**, *351*, 1732–1736.

[35] R. Loska, C. M. R. Volla, P. Vogel, *Adv. Synth. Catal.* **2008**, *350*, 2859–2864.

[36] M. Carril, A. Correa, C. Bolm, *Angew. Chem.* **2008**, *120*, 4940–4943; *Angew. Chem. Int. Ed.* **2008**, *47*, 4862–4865.

[37] O. Bistri, A. Correa, C. Bolm, *Angew. Chem.* **2008**, *120*, 596–598; *Angew. Chem. Int. Ed.* **2008**, *47*, 586–588.

[38] A. Correa, C. Bolm, *Angew. Chem.* **2007**, *119*, 9018–9021; *Angew. Chem. Int. Ed.* **2007**, *46*, 8862–8865.

[39] A. Correa, M. Carril, C. Bolm, *Angew. Chem.* **2008**, *120*, 2922–2925; *Angew. Chem. Int. Ed.* **2008**, *47*, 2880–2883.

[40] C. M. Rao Volla, P. Vogel, *Angew. Chem.* **2008**, *120*, 1325–1327; *Angew. Chem. Int. Ed.* **2008**, *47*, 1305–1307.

[41] X. F. Wu, C. Darcel, *Eur. J. Org. Chem.* **2009**, 4753–4756.

[42] M. Bandini, M. Tragni, A. Umani-Ronchi, *Adv. Synth. Catal.* **2009**, *351*, 2521–2524.

[43] I. Iovel, K. Mertins, J. Kischel, A. Zapf, M. Beller, *Angew. Chem.* **2005**, *117*, 3981–3985; *Angew. Chem. Int. Ed.* **2005**, *44*, 3913–3917.

[44] K. M. Driller, H. Klein, R. Jackstell, M. Beller, *Angew. Chem.* **2009**, *121*, 6157–6160; *Angew. Chem. Int. Ed.* **2009**, *48*, 6041–6044.

[45] F. G. Gelalcha, G. Anilkumar, M. K. Tse, A. Brueckner, M. Beller, *Chem. Eur. J.* **2008**, *14*, 7687–7698.

[46] F. Shi, M. K. Tse, Z. P. Li, M. Beller, *Chem. Eur. J.* **2008**, *14*, 8793–8797.

[47] W. Liu, A. W. Lei, *Tetrahedron Lett.* **2008**, *49*, 610–613.

[48] M. Itazaki, K. Ueda, H. Nakazawa, *Angew. Chem.* **2009**, *121*, 3363–3366; *Angew. Chem. Int. Ed.* **2009**, *48*, 3313–3316.

[49] W. Han, A. R. Ofial, *Chem. Commun.* **2009**, 5024–5026.

[50] N. S. Shaikh, S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 2531–2535; *Angew. Chem. Int. Ed.* **2008**, *47*, 2497–2501.

[51] S. Prateeptongkum, I. Jovel, R. Jackstell, N. Vogl, C. Weckbecker, M. Beller, *Chem. Commun.* **2009**, 1990–1992.

[52] K. Kohno, K. Nakagawa, T. Yahagi, J. C. Choi, H. Yasuda, T. Sakakura, *J. Am. Chem. Soc.* **2009**, *131*, 2784–2785.

[53] J. Kischel, I. Jovel, K. Mertins, A. Zapf, M. Beller, *Org. Lett.* **2006**, *8*, 19–22.

[54] There is an interesting discussion of whether Fe or Cu is the true catalytic species for the formation of C–N, C–O, or C–S bonds. (Ref. [62]).

[55] J. Norinder, A. Matsumoto, N. Yoshikai, E. Nakamura, *J. Am. Chem. Soc.* **2008**, *130*, 5858–5859.

[56] N. Yoshikai, A. Matsumoto, J. Norinder, E. Nakamura, *Angew. Chem.* **2009**, *121*, 2969–2972; *Angew. Chem. Int. Ed.* **2009**, *48*, 2925–2928.

[57] J. Wen, J. Zhang, S. Y. Chen, J. Li, X. Q. Yu, *Angew. Chem.* **2008**, *120*, 9029–9032; *Angew. Chem. Int. Ed.* **2008**, *47*, 8897–8900.

[58] Z. P. Li, L. Cao, C. J. Li, *Angew. Chem.* **2007**, *119*, 6625–6627; *Angew. Chem. Int. Ed.* **2007**, *46*, 6505–6507.

[59] Z. P. Li, R. Yu, H. J. Li, *Angew. Chem.* **2008**, *120*, 7607–7610; *Angew. Chem. Int. Ed.* **2008**, *47*, 7497–7500.

[60] Y. Z. Li, B. J. Li, X. Y. Lu, S. Lin, Z. J. Shi, *Angew. Chem.* **2009**, *121*, 3875–3878; *Angew. Chem. Int. Ed.* **2009**, *48*, 3817–3820.

[61] C. X. Song, G. X. Cai, T. R. Farrell, Z. P. Jiang, H. Li, L. B. Gan, Z. J. Shi, *Chem. Commun.* **2009**, 6002–6004.

[62] S. L. Buchwald, C. Bolm, *Angew. Chem.* **2009**, *121*, 5694–5695; *Angew. Chem. Int. Ed.* **2009**, *48*, 5586–5587.