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C–F Activation

Iridium-Catalyzed Synthesis of Diaryl Ethers by Means of Chemoselective C–F Bond Activation and the Formation of B–F Bonds

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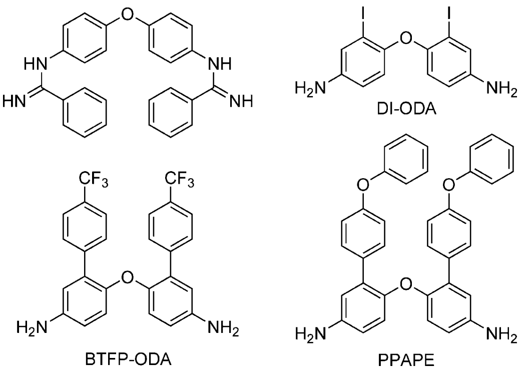
Abstract: Transition-metal-catalyzed C–F activation, in comparison with C–H activation, is more difficult to achieve and therefore less fully understood, mainly because carbon–fluorine bonds are the strongest known single bonds to carbon and have been very difficult to cleave. Transition-metal complexes are often more effective at cleaving stronger bonds, such as C(sp^2)–X versus C(sp^3)–X. Here, the iridium-catalyzed C–F activation of fluorarenes was achieved through the use of bis(pinacolato)diboron with the formation of the B–F bond and self-coupling. This strategy provides a convenient method with which to convert fluoride aromatic compounds into symmetrical diaryl ether compounds. Moreover, the chemoselective products of the C–F bond cleavage were obtained at high yields with the C–Br and C–Cl bonds remaining.

Introduction

The past decade has seen the extremely rapid growth of C–H activation, which is considered to be an innovative, environmentally benign synthetic tool. The reason for this acceptance is that such procedures provide economical routes, achievable in steps, to the desired or natural compounds from simple starting materials.[1] Compared with C–H activation, transition-metal-catalyzed C–F activation[2] is more difficult to achieve and less fully understood,[3] mainly because carbon–fluorine bonds are the strongest known single bonds to carbon and have been very difficult to cleave.[4] Scientists have devoted great efforts to this matter.[5] Several kinds of transition-metal complexes have proved to be effective with respect to C–F activation.[6] Although some articles that describe C–F activation that involves stoichiometric iridium complexes have been published,[7] to our knowledge there have been few reports on catalytic C–F activation with iridium as a catalyst. A typical example is the Ir-catalyzed reduction of fluorobenzene with a silane reagent by Brookhart and Yang.[8a] Other transition metals have been reported for more complex transformations of C–F bonds.[8b]

Symmetrical diaryl ether polymers are very important and increasingly interesting on account of their application in the aerospace and microelectronics industries, principally in the form of films or moldings. This is attributable to their excellent thermal stability, electric properties, and chemical resistance.[9] Many synthetic methods thus far reported have shown that symmetrical diaryl ethers are important building blocks for large varieties of natural and artificial products (Scheme 1).



Scheme 1. Some typical natural and artificial diaryl ethers.

Transition-metal-catalyzed C–O bond coupling from C–X bonds and phenolic derivatives has always been useful as a method for the construction of diaryl ether molecules.[10] Recently, scientists have made great efforts in this area. Various transition metals (e.g., Fe, Cu, and Pd) have been shown to be effective in regard to C–O coupling. Monnier, Taillefer, and Man et al. reported the efficient and versatile sol–gel immobilized copper catalyst for the Ullmann arylation of phenols.[11]

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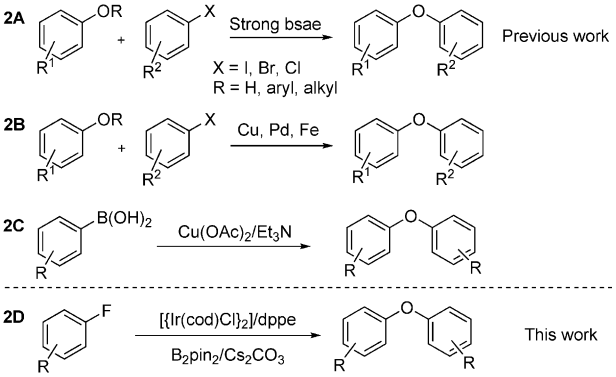
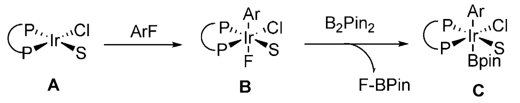
Yang and Xu et al. reported the coupling reaction with magnetic copper–ferrite nanoparticles as catalysts.[12] Bolm and coworkers reported the $FeCl_3$-catalyzed C–O coupling of phenols with aryl iodides;[13] and later Buchwald and Bolm et al. studied the iron-catalyzed C–O coupling reaction in the presence of trace amounts of copper.[14] Similar results have been described by Likhar et al. using Fe_3O_4 mesoporouspolyaniline as a catalyst.[15] Concurrently, several other groups (Singh, Olofsson, Zolfigol, Obora, and so forth) have published their results in this area.[16] Despite the aforementioned excellent examples, these reactions usually require high temperatures, harsh conditions, or expensive starting materials (Scheme 2). Herein, we report that iridium-catalyzed C–F activation has been realized through the use of bis(pinacolato)diboron (B_2pin_2) as a reagent with the formation of the B–F bond and homocoupling of aryl fluorides with the incorporation of an oxygen atom.



Scheme 2. Several methods of synthesis of diaryl ethers.

We have recently shown that the stoichiometric C–F bond activation of a chloro-bridged iridium(III) dimer, 2-(4,6-difluorophenyl)pyridyl (dfppy), leads to the formation of a heteroleptic cyclometalated iridium(III) complex.[17] The point of concern, however, is whether the iridium complex could be applied effectively as a chemoselective catalyst for C–F bond activation. Based on careful consideration, we believe C–F bond activation can be achieved with the help of reagents that involve Si, P, or B elements.[18] This is because the formation of the F–Si bond, F–P bond, or B–F bond is much easier than that of MF (M = metal).[19] Therefore, we have proposed a possible C–F bond activation through the release of the B–F bond (Scheme 3). The oxidative addition of fluorobenzene to the iridium catalyst formed the complex **B** species,[20] subsequently exchanging with B_2pin_2 to form **C** by releasing the B–F bond[21] to complete the C–F activation.



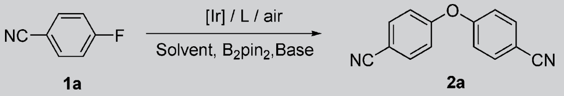
Scheme 3. The strategy of C–F bond activation by formation of the B–F bond.

Result and Discussion

On the basis of our analysis, the reaction of *para*-cyanfluorobenzene was used to test this idea by using B_2pin_2 as an additive. Interestingly, the self-coupling product was obtained, although at a low yield. Next, the screening of reaction conditions was performed to obtain a high yield. The experiments showed that the reaction could be conducted smoothly. The results are summarized in Table 1. In most cases, moderate to excellent yields were obtained when $[\{Ir(cod)Cl\}_2]$/dppe (cod = cyclooctadiene; dppe = 1,2-bis(diphenylphosphino)ethane) was used as a catalyst in dimethylformamide (DMF) to give 95 % of the product (Table 1, entry 9). A control reaction showed that the reaction could not occur without the iridium catalyst (Table 1, entry 20).

Thus, having established the optimal conditions of $[\{Ir(cod)Cl\}_2]$ (2 mol %), dppe (4.1 mol %), and Cs_2CO_3 as the base, and B_2pin_2, we explored the scope of the Ir-catalyzed etherification reaction. The results were summarized in Table 2. The reactions were carried out in DMF at 140 °C in air. Generally,

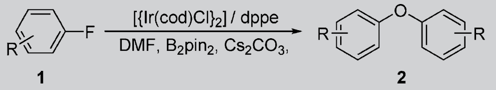
Table 1. Screening of reaction conditions.[a]

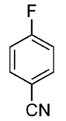
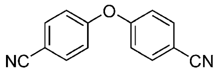
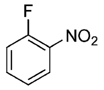
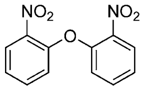
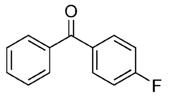
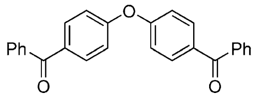
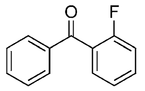
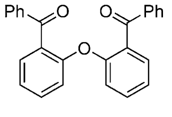
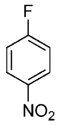
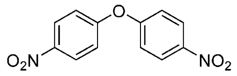
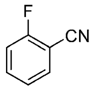
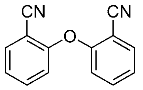


Entry	Catalyst[b]	Solvent	Yield [%][c]
1	$[(PPh_3)_3Ir(CO)H]/PPh_3$	DMF	43
2	$[(PPh_3)_3Ir(CO)H]/P(C_6H_5OCH_3)_3$	DMF	32
3	$[(PPh_3)_3Ir(CO)H]/P(C_4H_9)_3$	DMF	25
4	$[(PPh_3)_3Ir(CO)H]$/dppe	DMF	67
5	$[(PPh_3)_3Ir(CO)H]$/X-Phos	DMF	<5
6	$[\{Ir(cod)Cl\}_2]/PPh_3$	DMF	48
7	$[\{Ir(cod)Cl\}_2]/P(C_6H_5OCH_3)_3$	DMF	34
8	$[\{Ir(cod)Cl\}_2]/P(C_4H_9)_3$	DMF	<5
9	$[\{Ir(cod)Cl\}_2]$/dppe	DMF	95
10	$[\{Ir(cod)Cl\}_2]$/X-Phos	DMF	<5
11	$[\{Ir(coe)Cl\}_2]/PPh_3$	DMF	25
12	$[\{Ir(coe)Cl\}_2]/P(C_6H_5OCH_3)_3$	DMF	20
13	$[\{Ir(coe)Cl\}_2]/P(C_4H_9)_3$	DMF	<5
14	$[\{Ir(coe)Cl\}_2]$/dppe	DMF	58
15	$[\{Ir(coe)Cl\}_2]$/X-Phos	DMF	<5
16	$[\{Ir(cod)Cl\}_2]$/dppe	DMSO	47
17	$[\{Ir(cod)Cl\}_2]$/dppe	dioxane	<5
18	$[\{Ir(cod)Cl\}_2]$/dppe	toluene	<5
19	$[\{Ir(cod)Cl\}_2]$/dppe	DMA[d]	62
20[e]	none	DMF	<5

[a] Conditions: **1 a** (0.5 mmol), [Ir] (0.02 mmol, 4 mol %), ligand (0.0205 mmol, 4.1 mol %), B_2pin_2 (0.55 mmol), Cs_2CO_3 (0.55 mmol, 1.1 equiv), solvent (3 mL), 24 h, 140 °C, in air. [b] dppe = 1, 2-bis(diphenylphosphino)ethane. X-Phos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl. coe = cyclooctene. [c] Isolated yields, separated by column chromatography. [d] DMA = *N*,*N*-dimethylacetamide. [e] Catalyst was not added.

Table 2. Substrate expansion of simple fluorobenzene.[a]



Entry	Substrate	Product	Yield [%][b]
1			95 (**2a**)
2			82 (**2b**)
3			88 (**2c**)
4			trace (**2d**)
5			84 (**2e**)
6			80 (**2f**)

[a] Conditions: **1** (0.5 mmol), [{Ir(cod)Cl}$_2$] (0.01 mmol, 2 mol %), dppe (0.0205 mmol, 4.1 mol %), B$_2$pin$_2$ (0.55 mmol), Cs$_2$CO$_3$ (0.55 mmol, 1.1 equiv), DMF (3 mL), 24 h, 140 °C, in air. [b] Isolated yields based on **1**.

the substrates were converted into the desired products, and in most cases good to excellent yields were obtained (Table 2). It should be noted that substrates that contain electron-donating groups produced disappointing results. Importantly, X-ray spectrometry confirmed the structure of diaryl ether (**2a**, a known compound; see the Supporting Information).[22]

Numerous publications over the past several decades have shown that the reaction reactivity of carbon–halogen bonds is C–I > C–Br > C–Cl > C–F and that transition-metal catalysts have produced all sorts of coupling reactions. Here, however, we attempted the etherification reaction of multisubstituted, halogenated benzene. The results are summarized in Table 3. When bromo-substituted fluorobenzene was tried in this reaction, the chemoselective product of C–F bond cleavage was obtained in high yield (Table 3, entry 2). The same phenomenon was found with respect to chloro-substituted fluorobenzene (Table 3, entry 4). It is significant that the success in terms of the high selectivity of C–F > C–Br and C–F > C–Cl provides new evidence for the strategy of C–F bond activation by formation of the B–F bond, because the bond energy of B–F (613 kJ mol^{-1}) is much greater and easier to form than that of the B–Br (377 kJ mol^{-1}) and B–Cl (456 kJ mol^{-1}) bonds. Accordingly, this method provides an alternative method for C–F bond activation by using a boron reagent as an activator.

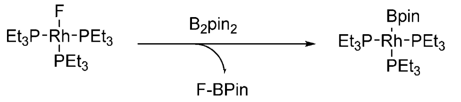
The etherification reaction of chlorobenzene was also explored. The reaction could still proceed with moderate yields obtained. For example, when nitrochlorobenzene was used in this reaction, the desired product was separated with a yield of 82 % (Scheme 4).

The diaryl ether compounds could easily be converted into the biphenyl derivative in one step on the basis of the Suzuki coupling. The reaction proceeded smoothly in toluene and gave the desired product with a nearly quantitative yield (Scheme 5).

Fluorine-containing polymers are new types of multifunctional materials. They have attracted considerable attention on account of their unique properties, such as low surface energy, low refractive index, oil and water repellence, and high chemical and thermal stabilities.[23] Thus, fluorinated polymers have been exploited extensively. Their applications include electronics, biomaterials, optical devices, and coatings (Scheme 6). With the aforementioned methodology, the product (**4h**) was reduced to the corresponding diamine with a 90 % yield. Finally, fluorine-containing polymers were easily obtained under the known conditions.[24]

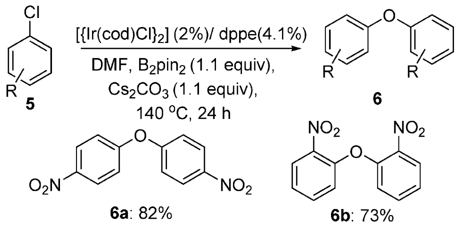
Macgregor and Braun et al., in 2010, synthesized a useful, highly reactive rhodium(I)–boryl complex through the reaction of the [Rh(PEt$_3$)$_3$F] compound with B$_2$pin$_2$, in which fluoroborane F–Bpin was formed and easily removed [Eq. (1)].[21]

We believe the reaction of an iridium compound with B$_2$pin$_2$ was also possible through formation of

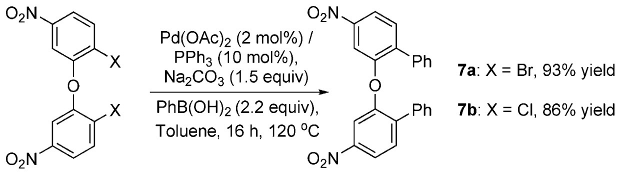


(1)

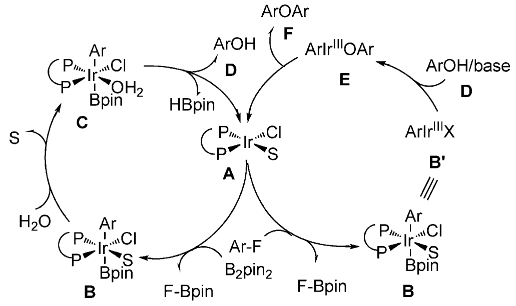
F–Bpin. Therefore, we proposed a reaction mechanism for the iridium-catalyzed C–F activation reaction (Scheme 7). Initially, we proposed the oxidative addition of the iridium catalyst



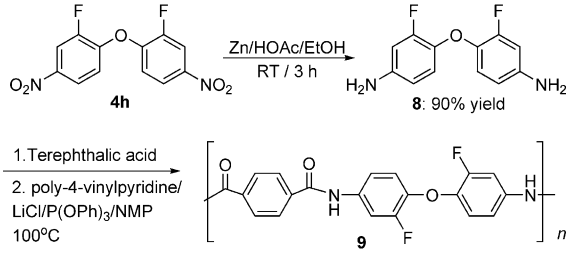
Scheme 4. The etherification reaction of chlorobenzene.



Scheme 5. The derivatization reaction of diaryl ether derivatives.



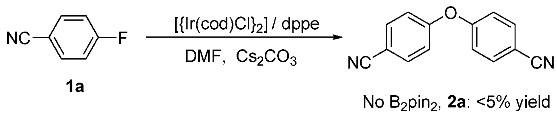
Scheme 7. The proposed possible mechanism of Ir-catalyzed C–F activation.



Scheme 6. The synthesis of fluorine-containing polymers.

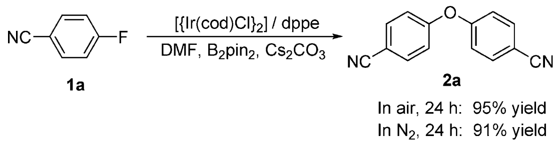
with fluorobenzene, using B_2pin_2 to generate the *cis*-*fac*-Ir^{III} complex **B** species through the release of F–Bpin[21,25] and then by exchanging organic solvent molecules with water to give the intermediate **C**. After reductive elimination, intermediate **D** (ArOH) was released (this intermediate could be detected and separated although resulted in a low yield; see the Supporting Information). Following the transmetalation of complex **B**′ species with intermediate **D** (complex **B** species is written as **B** for the sake of clarity; Scheme 7B), the complex **E** species was formed. After reductive elimination, intermediate **E** gave the product diaryl ether to complete the catalytic cycle.

B_2pin_2 was tested in this reaction [Eq. (2)] to verify the proposed reaction mechanism. It could not occur in the absence of B_2pin_2.



(2)

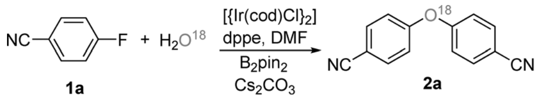
Another key point here is the origin of the oxygen atom. Possible sources include dioxygen, water, the boron reagent, and the solvent itself. First, the control experiments for air were conducted. The results showed that the desired product still could be separated with nearly the same yield even under a nitrogen atmosphere [Eq. (3)].



(3)

Next, the control experiments for water were set up. Nothing of the product was detected with dry DMF as a solvent. Subsequent experiments focused on the various ratios of DMF with water. It was found that excessive or insufficient water worsened the reaction. Thus we determined that the optimal ratio of DMF with water for this reaction is 300:1 (Table 4, entry 4).

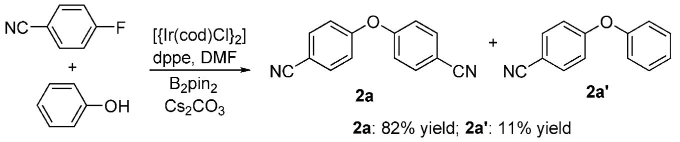
An isotopic labeling experiment was also conducted to support the hypothesis that water is the source of the oxygen atom. The reaction of *para*-cyanofluorobenzene with $H_2{}^{18}O$ was conducted under optimal conditions [Eq. (4)]. Upon completion of the reaction, the separated product was analyzed by mass spectrometry and the ^{18}O isotopic-labeled product was found (see the Supporting Information). On the basis of these experiments, we suggest that the oxygen of diaryl ether comes from water.



(4)

Finally, we propose that the reaction can proceed by means of a phenol intermediate. Fortunately, the intermediate signal was tracked in this reaction by means of mass spectrometry. Importantly, the key intermediate (ArOH) could be separated by column chromatography on silica gel with a very low yield, which was characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry (see the Supporting Information). Therefore, this is very important proof that is sufficient to support the proposed idea.

A reaction of *para*-cyanofluorobenzene with phenol was conducted under optimal conditions [Eq. (5)] to affirm the proposed intermediate. The results showed that the mixture of two products was obtained and compound **2a** was the major product, which is very important proof of the phenol intermediate (**D**) proposed.

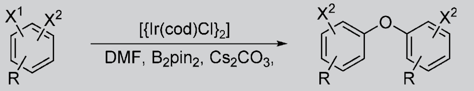


(5)

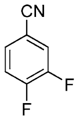
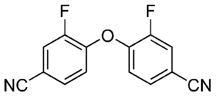
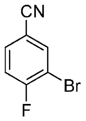
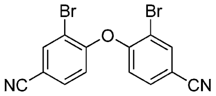
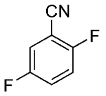
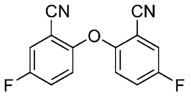
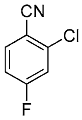
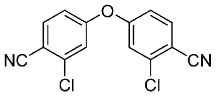
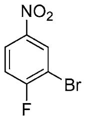
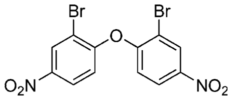
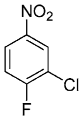
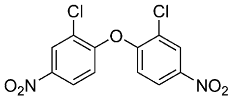
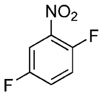
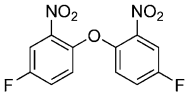
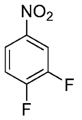
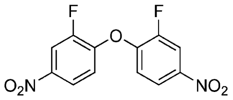
Conclusion

In conclusion, the iridium-catalyzed C–F activation was achieved with the help of B_2pin_2. This strategy has provided a convenient method for the conversion of fluoride aromatic compounds into symmetrical diaryl ether compounds. Additionally, some natural diaryl ether compounds and valuable polymers could be obtained through this methodology. Moreover, the chemoselective products of C–F bond cleavage were obtained with high yields with the C–Br and C–Cl bonds remaining.

Table 3. Substrate expansion of multisubstituted halogenated benzene.[a]

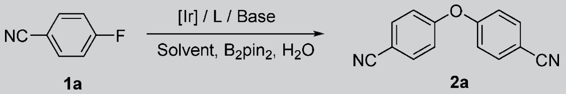


3 X^1 = F; X^2 = F, Cl, Br **4**

Entry	Substrate	Product	Yield [%][b]
1			86 (**4a**)
2			90 (**4b**)
3			76 (**4c**)
4			92 (**4d**)
5			82 (**4e**)
6			81 (**4f**)
7			75 (**4g**)
8			80 (**4h**)

[a] Conditions: **3** (0.5 mmol), [{Ir(cod)Cl}$_2$] (0.01 mmol, 2 mol%), dppe (0.0205 mmol, 4.1 mol%), B$_2$pin$_2$ (0.55 mmol), Cs_2CO_3 (0.55 mmol, 1.1 equiv), DMF (3 mL), 24 h, 140 °C, in air. [b] Isolated yields based on **3**.

Table 4. The control experiments of DMF with water.[a]



1a **2a**

Entry	DMF/H_2O (v/v)	Yield [%][b]
1	dry	<5
2	1000:1	26
3	500:1	58
4	300:1	92
5	100:1	40
6	10:1	13

[a] Conditions: **1a** (0.5 mmol), [{Ir(cod)Cl}$_2$] (0.01 mmol, 2 mol%), dppe (0.0205 mmol, 4.1 mol%), B$_2$pin$_2$ (0.55 mmol), Cs_2CO_3 (0.55 mmol, 1.1 equiv), DMF (3 mL), 24 h, 140 °C, in air. [b] Isolated yields, separated by column chromatography.

Experimental Section

General Procedure for the Reaction of Fluorobenzene

[{Ir(cod)Cl}$_2$], dppe, Cs_2CO_3, and B$_2$pin$_2$ were added into a 50 mL Schlenk tube in air. Then a solution of fluorobenzene in DMF (3 mL) was added in air. The mixture was stirred for 24 h at 140 °C. Upon completion, the reaction mixture was dissolved in water, then extracted with ethyl acetate (3×15 mL), dried with ($MgSO_4$), and evaporated to give the residue. The residue was then purified by column chromatography on silica gel (dichloromethane/*n*-hexane 1:1–1:2) to provide the corresponding product.

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Keywords: arenes · C–F activation · chemoselectivity · homogeneous catalysis · iridium

[1] For selected reviews, see: a) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293–1314; b) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147–1169; c) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879–5918; d) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931.

[2] For selected reviews, see: a) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119–2183; b) M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3328–3348; *Angew. Chem.* **2013**, *125*, 3412–3433; c) A. D. Sun, J. A. Love, *Dalton Trans.* **2010**, *39*, 10362–10374; d) D. O'Hagan, *Chem. Soc. Rev.* **2008**, *37*, 308–319.

[3] For selected examples, see: a) K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama, *Angew. Chem. Int. Ed.* **2009**, *48*, 8070–8073; *Angew. Chem.* **2009**, *121*, 8214–8217; b) X. Pigeon, M. Bergeron, F. Barabé, P. Dubé, H. N. Frost, J.-F. Paquin, *Angew. Chem. Int. Ed.* **2010**, *49*, 1123–1127; *Angew. Chem.* **2010**, *122*, 1141–1145; c) M. F. Kühnel, D. Lentz, *Angew. Chem. Int. Ed.* **2010**, *49*, 2933–2936; *Angew. Chem.* **2010**, *122*, 2995–2998; d) G. Haufe, S. Suzuki, H. Yasui, C. Terada, T. Kitayama, M. Shiro, N. Shibata, *Angew. Chem. Int. Ed.* **2012**, *51*, 12275–12279; *Angew. Chem.* **2012**, *124*, 12441–12445; e) S. Yow, S. J. Gates, A. J. P. White, M. R. Crimmin, *Angew. Chem. Int. Ed.* **2012**, *51*, 12559–12563; *Angew. Chem.* **2012**, *124*, 12727–12731; f) G. Podolan, D. Lentz, H.-U. Reissig, *Angew. Chem. Int. Ed.* **2013**, *52*, 9491–9494; *Angew. Chem.* **2013**, *125*, 9669–9672.

[4] O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574.

[5] a) Y. Xiong, J. Wu, S. Xiao, J. Xiao, S. Cao, *J. Org. Chem.* **2013**, *78*, 4599–4603; b) K. Mikami, Y. Tomita, Y. Itoh, *Angew. Chem. Int. Ed.* **2010**, *49*, 3819–3822; *Angew. Chem.* **2010**, *122*, 3907–3910; c) M. Takachi, Y. Kita, M. Tobisu, Y. Fukumoto, N. Chatani, *Angew. Chem. Int. Ed.* **2010**, *49*, 8717–8720; *Angew. Chem.* **2010**, *122*, 8899–8902; d) M. Bergeron, T. Johnson, J.-F. Paquin, *Angew. Chem. Int. Ed.* **2011**, *50*, 11112–11116; *Angew. Chem.* **2011**, *123*, 11308–11312; e) T. Iida, R. Hashimoto, K. Aikawa, S. Ito, K. Mikami, *Angew. Chem. Int. Ed.* **2012**, *51*, 9535–9538;

Angew. Chem. **2012**, *124*, 9673 – 9676; f) K. Fuchibe, M. Takahashi, J. Ichikawa, *Angew. Chem. Int. Ed.* **2012**, *51*, 12059 – 12062; *Angew. Chem.* **2012**, *124*, 12225 – 12228; g) J. Terao, M. Nakamurab, N. Kambe, *Chem. Commun.* **2009**, 6011 – 6013; h) M. Janjetovic, A. M. Träff, T. Ankner, J. Wettergren, G. Hilmersson, *Chem. Commun.* **2013**, *49*, 1826 – 1828.

[6] a) Z. Chen, C.-Y. He, Z. Yin, L. Chen, Y. He, X. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 5813 – 5817; *Angew. Chem.* **2013**, *125*, 5925 – 5929; b) D. Yu, L. Lu, Q. Shen, *Org. Lett.* **2013**, *15*, 940 – 943; c) J.-H. Zhan, H. Lv, Y. Yu, J.-L. Zhang, *Adv. Synth. Catal.* **2012**, *354*, 1529 – 1541.

[7] Y. P. Yan, P. Feng, Q.-Z. Zheng, Y.-F. Liang, J.-F. Lu, Y. X. Cui, N. Jiao, *Angew. Chem. Int. Ed.* **2013**, *52*, 5827 – 5831; *Angew. Chem.* **2013**, *125*, 5939 – 5943.

[8] a) J. Yang, M. Brookhart, *J. Am. Chem. Soc.* **2007**, *129*, 12656 – 12657; b) N. Yoshikai, H. Mashima, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 17978 – 17979.

[9] J.-C. Chen, K. Rajendran, Y.-H. Chang, S.-W. Huang, Y.-T. Chern, *J. Appl. Polym. Sci.* **2011**, *120*, 3159 – 3170.

[10] For selected examples, see: a) J. Zhang, J. Wu, Y. Xiong, S. Cao, *Chem. Commun.* **2012**, *48*, 8553 – 8555; b) T. Saitoh, J. Ichikawa, *J. Am. Chem. Soc.* **2005**, *127*, 9696 – 9697; c) E. Buck, Z. J. Song, D. Tschaen, P. G. Dormer, R. P. Volante, P. J. Reider, *Org. Lett.* **2002**, *4*, 1623 – 1626; d) B. H. Lipshutz, J. B. Unger, B. R. Taft, *Org. Lett.* **2007**, *9*, 1089 – 1092; e) A. D. Sagar, R. H. Tale, R. N. Adude, *Tetrahedron Lett.* **2003**, *44*, 7061 – 7063; f) Z. Liu, R. C. Larock, *Org. Lett.* **2004**, *6*, 99 – 102; g) N. Xia, M. Taillefer, *Chem. Eur. J.* **2008**, *14*, 6037 – 6039; h) K. Swapna, S. N. Murthy, M. T. Jyothi, Y. V. D. Nageswar, *Org. Biomol. Chem.* **2011**, *9*, 5978 – 5988; i) I. Fukawa, T. Tanabe, T. Dozono, *J. Chem. Soc. Perkin Trans. 2* **1992**, 377 – 382.

[11] a) H. J. Cristau, P. P. Cellier, S. Hamada, J. F. Spindler, M. Taillefer, *Org. Lett.* **2004**, *6*, 913 – 916; b) A. Ouali, J.-F. Spindler, H. J. Cristau, M. Taillefer, *Adv. Synth. Catal.* **2006**, *348*, 499 – 505; c) F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.* **2008**, *47*, 3096 – 3099; *Angew. Chem.* **2008**, *120*, 3140 – 3143; d) F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.* **2009**, *48*, 6954 – 6971; *Angew. Chem.* **2009**, *121*, 7088 – 7105; e) A. Tlili, N. Xia, F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.* **2009**, *48*, 8725 – 8728; *Angew. Chem.* **2009**, *121*, 8881 – 8884; f) A. Tlili, F. Monnier, M. Taillefer, *Chem. Eur. J.* **2010**, *16*, 12299 – 12302; g) S. Benyahya, F. Monnier, M. Taillefer, M. W. C. Man, C. Bied, F. Ouazzani, *Adv. Synth. Catal.* **2008**, *350*, 2205 – 2208.

[12] a) S. Yang, W. Xie, H. Zhou, C. Wu, Y. Yang, J. Niu, W. Yang, J. Xu, *Tetrahedron* **2013**, *69*, 3415 – 3418; b) S. Yang, C. Wu, M. Ruan, Y. Yang, Y. Zhao, J. Niu, W. Yang, J. Xu, *Tetrahedron Lett.* **2012**, *53*, 4288 – 4292; c) S. Yang, C. Wu, H. Zhou, Y. Yang, Y. Zhao, C. Wang, W. Yang, J. Xu, *Adv. Synth. Catal.* **2013**, *355*, 53 – 58.

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

[14] a) J.-F. Marcoux, S. Doye, S. L. Buchwald, *J. Am. Chem. Soc.* **1997**, *119*, 10539 – 10540; b) C. H. Burgos, T. E. Barder, X. Huang, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2006**, *45*, 4321 – 4326; *Angew. Chem.* **2006**, *118*, 4427 – 4432; c) L. Salvi, N. R. Davis, S. Z. Ali, S. L. Buchwald, *Org. Lett.* **2012**, *14*, 170 – 173; d) R. Zhu, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2013**, *52*, 12655 – 12658; *Angew. Chem.* **2013**, *125*, 12887 – 12890; e) A. Correa, O. García Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108 – 1117; f) Y. Yuan, I. Thomé, S. H. Kim, D. Chen, A. Beyer, J. Bonnamour, E. Zuidema, S. Chang, C. Bolm, *Adv. Synth. Catal.* **2010**, *352*, 2892 – 2898; g) S. L. Buchwald, C. Bolm, *Angew. Chem. Int. Ed.* **2009**, *48*, 5586 – 5587; *Angew. Chem.* **2009**, *121*, 5694 – 5695.

[15] R. Arundhathi, D. Damodara, Pravin. R. Likhar, *Adv. Synth. Catal.* **2011**, *353*, 1591 – 1600.

[16] For selected examples, see: a) Y. Isomura, T. Narushima, H. Kawasaki, T. Yonezawab, Y. Obora, *Chem. Commun.* **2012**, *48*, 3784 – 3786; b) N. Jalalian, T. B. Petersen, B. Olofsson, *Chem. Eur. J.* **2012**, *18*, 14140 – 14149; c) M. A. Zolfigol, V. Khakyzadeh, A. R. Moosavi-Zare, A. Rostami, A. Zare, N. Iranpoor, M. H. Beyzavi, R. Luque, *Green Chem.* **2013**, *15*, 2132 – 2140; d) N. Jalalian, E. E. Ishikawa, L. F. Silva, Jr., B. Olofsson, *Org. Lett.* **2011**, *13*, 1552 – 1555; e) H. Joshi, K. N. Sharma, A. K. Sharma, O. Prakash, A. K. Singh, *Chem. Commun.* **2013**, *49*, 7483 – 7485.

[17] For selected papers in our group, see: a) L. Liang, F. Wu, S. L. Zhang, D. W. Wang, Y. Q. Ding, Z. Z. Zhu, *Dalton Trans.* **2013**, *42*, 4539 – 4543; b) W. Yang, D. Wang, Q. Song, S. Zhang, Q. Wang, Y. Ding, *Organometallics* **2013**, *32*, 4130 – 4135; c) W. Yang, S. Zhang, Y. Ding, L. Shi, Q. Song, *Chem. Commun.* **2011**, *47*, 5310 – 5312; d) W. Yang, H. Fu, Q. Song, M. Zhang, Y. Ding, *Organometallics* **2011**, *30*, 77 – 83.

[18] a) G. Meier, T. Braun, *Angew. Chem. Int. Ed.* **2009**, *48*, 1546 – 1548; *Angew. Chem.* **2009**, *121*, 1575 – 1577; b) M. Teltewskoi, J. A. Panetier, S. A. Macgregor, T. Braun, *Angew. Chem. Int. Ed.* **2010**, *49*, 3947 – 3951; *Angew. Chem.* **2010**, *122*, 4039 – 4043; c) M. Ahrens, G. Scholz, T. Braun, E. Kemnitz, *Angew. Chem. Int. Ed.* **2013**, *52*, 5328 – 5332; *Angew. Chem.* **2013**, *125*, 5436 – 5440; d) G. Ung, G. Bertrand, *Chem. Eur. J.* **2012**, *18*, 12955 – 12957.

[19] a) H. Lv, Y. B. Cai, J.-L. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3203 – 3207; *Angew. Chem.* **2013**, *125*, 3285 – 3289; b) T. Stahl, H. F. T. Klare, M. Oestreich, *ACS Catal.* **2013**, *3*, 1578 – 1587.

[20] a) T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 390 – 391; b) T. A. Boebel, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 7534 – 7535; c) C. W. Liskey, J. F. Hartwig, *J. Am. Chem. Soc.* **2012**, *134*, 12422 – 12425.

[21] For the Rh–F exchanges with B_2pin_2 by release of the B–F bond, see Ref. 18b.

[22] A. Dey, G. R. Desiraju, *Chem. Commun.* **2005**, 2486 – 2488.

[23] a) W. Yang, Y. Chen, D. Han, L. Zhu, *J. Fluorine Chem.* **2013**, *149*, 8 – 12; b) W. Xu, Q. An, L. Hao, Z. Sun, W. Zhao, *Fibers Polym.* **2013**, *14*, 895 – 903.

[24] R. Simonutti, A. Mariani, P. Sozzani, S. Bracco, M. Piacentini, S. Russo, *Macromolecules* **2002**, *35*, 3563 – 3568.

[25] For a Pd-catalyzed F/Cl exchange example, see Ref. 6a.

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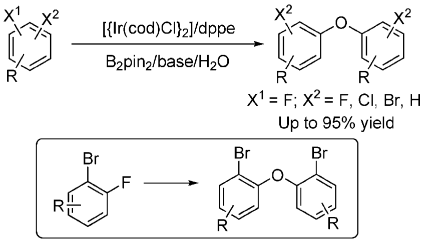
FULL PAPER

Perfect partners: The iridium-catalyzed C–F activation of fluorarenes was achieved through the use of bis(pinacolato)diboron with the formation of the B–F bond and self-coupling. This strategy provides a convenient method with which to convert fluoride aromatic compounds into symmetrical diaryl ether compounds (see scheme).



C–F Activation

Jianping Chen, Keyan Zhao, Bingyang Ge, Chongying Xu, Dawei Wang, Yuqiang Ding**

■■ – ■■

Iridium-Catalyzed Synthesis of Diaryl Ethers by Means of Chemoselective C–F Bond Activation and the Formation of B–F Bonds