

Iron-Catalyzed C–H Borylation of Arenes

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Supporting Information

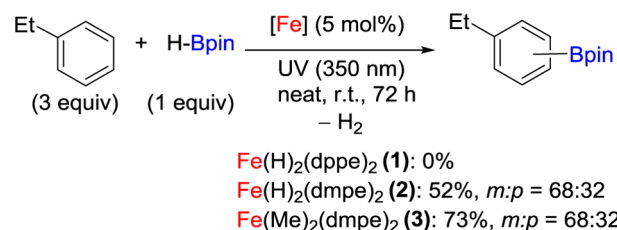
ABSTRACT: Well-defined iron bis(diphosphine) complexes are active catalysts for the dehydrogenative C–H borylation of aromatic and heteroaromatic derivatives with pinacolborane. The corresponding borylated compounds were isolated in moderate to good yields (25–73%) with a 5 mol% catalyst loading under UV irradiation (350 nm) at room temperature. Stoichiometric reactivity studies and isolation of an original *trans*-hydrido(boryl)iron complex, Fe(H)(Bpin)(dmpe)₂, allowed us to propose a mechanism showing the role of some key catalytic species.

Selective carbon–hydrogen bond activation and functionalization is highly attractive to provide more complex molecules by building C–C and C–heteroatom bonds in an eco-friendly manner.¹ Of particular interest is the borylation of arenes and heteroarenes, which represents one of the most elegant ways to obtain (hetero)-arylboronate esters, versatile synthons for Suzuki–Miyaura reactions.² Very efficient catalytic borylation processes have been developed using noble-metal-based catalysts such as iridium and rhodium complexes.² With earth-abundant transition metals as catalysts, borylation has been performed with electrophilic halide derivatives,³ and recently Chirik et al. achieved efficient catalyzed arene borylations via C–H activation using a pincer cobalt complex.⁴ In the case of iron, which has become a valuable alternative to precious transition metals in homogeneous catalysis,⁵ achieving such a transformation remains challenging. Despite early stoichiometric studies by Hartwig et al. on the ability of iron carbonyl complexes such as CpFe(Bcat)(CO)₂ to mediate borylation of arenes under photochemical conditions,^{2e,6} the main difficulty appears to be the regeneration of the active species after B–C coupling. Two catalytic iron systems, involving stoichiometric amounts either of hydrogen acceptor⁷ or base and oxidant,⁸ were reported before the recent disclosure by Mankad et al. of the activity of bimetallic complexes (Cu–Fe and Zn–Fe) under photochemical conditions (450-W Hg lamp).⁹ However, dehydrogenative C–H borylation with a mononuclear iron catalyst, without any additives, has never been reported.

To tackle this domain,¹⁰ we considered bis(diphosphine) iron dihydride complexes as promising catalyst precursors.^{11,12} Indeed, in-depth studies by Field and Perutz et al. have shown the ability of such complexes to activate C–H bonds,¹³ whereas

analogous ruthenium complexes can notably activate hydroboranes.¹⁴ Complexes of the type Fe(X)₂(L)₂ (X = H, Me; L = dppe, dmpe; complexes 1–3) have been tested as catalyst (5 mol%) for the borylation of ethylbenzene with HBpin under UV irradiation at 350 nm at room temperature for 72 h in neat conditions (Scheme 1). While complex 1, featuring diaryl-

Scheme 1. Iron-Catalyzed Borylation of Ethylbenzene^a



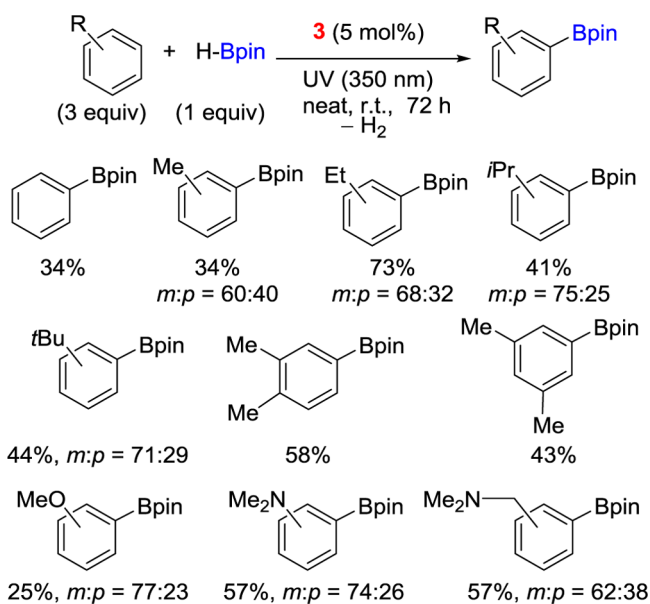
^aExperimental conditions: EtPh (1.5 mmol). Reported values are % isolated yields. Product ratios were determined by ¹H NMR. dppe = bis(diphenylphosphinoethane); dmpe = bis(dimethylphosphinoethane).

phosphine moieties, failed to catalyze the reaction,¹⁵ the dihydride complex 2, bearing more basic alkyl substituents, afforded the borylarene compound in 52% isolated yield of a 68:32 mixture of *meta* and *para* derivatives, respectively. Interestingly, when the dimethyliron analogue Fe(Me)₂(dmpe)₂ (**3**)¹⁶ was used as a catalyst precursor, the isolated yield increased to 73%, with the same *meta:para* ratio. Control experiments showed the necessity of UV irradiation, as no coupling product was detected when the reaction was performed in toluene up to 100 °C, under visible light conditions or in the dark.^{17,18}

Given the better yield obtained with complex 3, and its higher stability compared to the dihydride analogue 2, we probed the scope of the reaction with 3 as catalyst precursor (Scheme 2). Isolated yields ranging from 34 to 73% were obtained for the alkyl-substituted arenes, whereas evaluation of the crude reaction mixture by NMR spectroscopy showed higher yields.^{18a} Only in the case of toluene, trace amounts of tol(Bpin)₂ were detected by GC-MS analysis. We also probed the tolerance toward ethers and amino groups. Anisole can be

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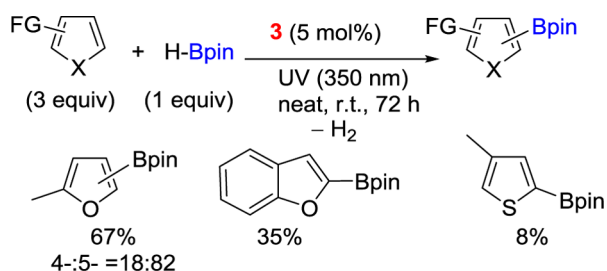
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Scheme 2. Functionalized Arene Borylation Catalyzed by $\text{Fe}(\text{Me})_2(\text{dmpe})_2$ (3**)^a**


^aReported values are % isolated yields. Product ratios were determined by ¹H NMR.

borylated in a modest isolated yield (25%), whereas dimethylamino-containing arenes, namely *N,N*-dimethylaniline and *N,N*-dimethylbenzylamine, can be efficiently borylated in 57% isolated yield (75% in the crude mixture for *N,N*-dimethylaniline). Overall, the observed regioselectivities (*meta* > *para* ≫ *ortho*) correspond to the trend commonly observed in transition metal C–H borylation.^{2c}

The catalytic performance of **3** was then evaluated with heterocyclic derivatives (Scheme 3). Starting from 2-methyl-

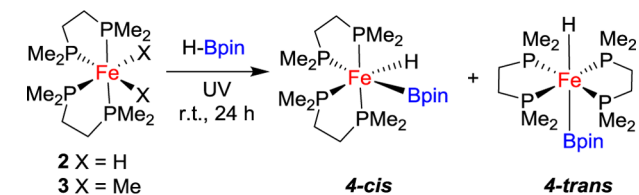
Scheme 3. Catalytic Borylation of Heterocycles Using $\text{Fe}(\text{Me})_2(\text{dmpe})_2$ (3**)^a**


^aReported values are % isolated yields. Product ratios were determined by ¹H NMR.

furan, the corresponding 4-Bpin-2-methylfuran and 5-Bpin-2-methylfuran were obtained in an overall 67% isolated yield in a ratio of 18:82. 1-Benzofuran led to the corresponding 2-Bpin-1-benzofuran in 35% yield. When starting from 3-methylthiophene, only 8% of a borylated compound was obtained, while no reaction took place with 2-methylthiophene. By contrast with iridium- and cobalt-catalyzed reactions,^{2,4} no coupling product was detected with pyridine derivatives.

Having established that **2** and **3** serve as catalyst precursors, we sought mechanistic information. We first examined the reactivity of the iron complexes with pinacolborane. To our delight, both the dihydride and dimethyl complexes reacted

with HBpin, under irradiation, to afford the new hydrido-(boryl)iron complex $\text{Fe}(\text{H})(\text{Bpin})(\text{dmpe})_2$ (**4**), as evidenced by spectroscopic and X-ray diffraction studies. In solution, two isomers in a 1:1 ratio, 4-*trans* and 4-*cis*, were identified by NMR spectroscopy (Scheme 4). Complex 4-*trans* is characterized by

Scheme 4. Synthesis of the Hydrido(boryl)iron Complex **4**


a hydride signal in ¹H NMR at –12.75 ppm (q, $J_{\text{HP}} = 42$ Hz) and a sharp doublet in ³¹P NMR (77.7 ppm, $J_{\text{HP}} = 40$ Hz). Variable-temperature ¹H and ³¹P NMR analyses indicate that complex 4-*cis* is highly fluxional, showing at 213 K a multiplet at –13.6 ppm in ¹H NMR and four signals at 77.3, 76.2, 59.9, and 58.4 ppm in ³¹P{¹H} NMR, interpreted as an AA'MN second-order system by NMR data simulation.^{18a} These features are similar to those of the ruthenium analogues *cis*- and *trans*- $\text{Ru}(\text{H})(\text{Bpin})(\text{dmpe})_2$, which were also obtained under UV irradiation.^{14a} The solution IR spectrum displays two bands at 1684 and 1797 cm^{-1} , assigned to the Fe–H stretching frequencies of 4-*trans* and 4-*cis*, respectively, by comparison with DFT calculations conducted on both isomers ($\nu_{\text{calc,Fe-Htrans}} = 1718$ cm^{-1} ; $\nu_{\text{calc,Fe-Hcis}} = 1856$ cm^{-1}).^{18a} When the 4-*trans* and 4-*cis* solution was evaporated to dryness, the resulting solid was identified as solely 4-*trans* ($\nu_{\text{Fe-H}} = 1671$ cm^{-1} ; ¹H and ³¹P solid-state NMR resonances at –13 and 78 ppm, respectively). When complex 4-*trans* was redissolved, signals for 4-*cis* and 4-*trans* were observed in an identical equimolar ratio as a result of fast isomerization in solution.

We were able to obtain crystals of 4-*trans* suitable for X-ray diffraction analysis (Figure 1, left). The iron center adopts an

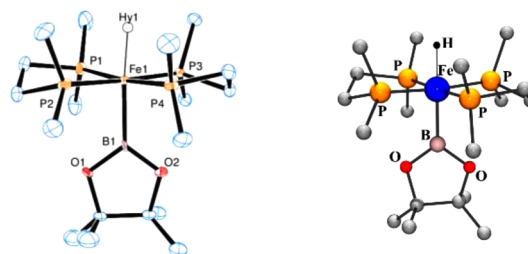


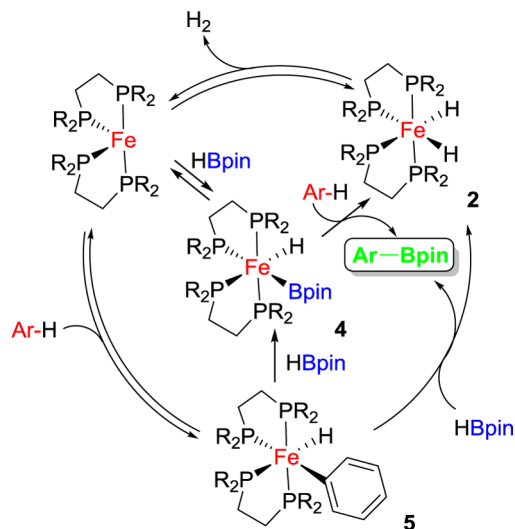
Figure 1. X-ray diffraction structure of 4-*trans* (left), and DFT/B3PW91-D3BJ calculated geometry (right). Hydrogen atoms, except the hydride, were omitted for clarity.

octahedral geometry, with the four phosphorus atoms located in the equatorial plane. The Fe–B distance of 2.024(4) Å is in the range of iron–boryl bonds,¹⁹ slightly shorter than the Fe–Bpin distance (2.065(3) Å) recently reported for the iron(I) boryl complex $\text{Fe}(\text{Bpin})(\text{dpbz})_2$,^{3c} and slightly longer than in the series of $\text{CpFe}(\text{Bpin})(\text{PR}_3)_2$ complexes (1.996(3)–2.002(10) Å).²⁰ The hydride has been localized by Fourier difference map analysis with a Fe–H distance of 1.63(8) Å, and DFT calculation ascertained the hydrogen location, with $d_{\text{calc}}(\text{Fe-H}) = 1.561$ Å (Figure 1, right).

We then conducted a series of experiments to gain more information on the role of **2**, **3**, and **4** using multinuclear ^1H , ^2H , ^{31}P , and ^{11}B NMR spectroscopy: (i) Monitoring the catalytic borylation reaction using **2** or **3** as catalyst precursors, in C_7D_8 or C_6D_6 , respectively, showed the formation of the corresponding borylated product and the coexistence of **2**, **4** (major species), and unknown organometallic species together with evolution of H_2 and HD (Figures S17–S19). (ii) When HBpin was added to a C_6D_6 solution of **3**, monitoring the reaction without irradiation at room temperature for 3 days led to the detection of the hydrido(boryl) complex **4** in 15% conversion. In the absence of any arene, addition of neat HBpin to **3** and irradiation resulted in the formation of complex **4** together with Me-Bpin, as detected by the ^{11}B NMR signal at +33.9 ppm.²¹ (iii) We checked that isolated complex **4** catalyzes the borylation of ethylbenzene in the standard conditions (isolated yield of $\text{EtC}_6\text{H}_4\text{Bpin}$, 45% with a m/p ratio of 68/32). (iv) At the stoichiometric level, complex **4**, which is stable in C_6D_6 without irradiation, undergoes B–C coupling upon irradiation, and the deuterated complexes $\text{FeH(D)}(\text{dmpe})_2$ (**2_D**) and $\text{FeD}(\text{C}_6\text{D}_5)(\text{dmpe})_2$ (**5_D**) as well as evolution of HD and H_2 were detected (Figures S20, S21). When **4** was dissolved in 30 equiv of DBpin, upon irradiation, scrambling resulted in the formation of $\text{FeD}(\text{Bpin})(\text{dmpe})_2$ (**4_D**) and HBpin (Figures S22, S23). (v) Finally, the hydrido(aryl)iron complex $\text{FeH}(\text{C}_6\text{H}_5)(\text{dmpe})_2$ (**5**), in situ generated by the reaction of **2** with benzene at room temperature under irradiation,^{13a} reacted with HBpin in the absence of irradiation, and a mixture of **2** and **4** was characterized (Figures S24–S27; a small amount of the B–C product was detected by GC). This is in agreement with the reported reversibility of C–H arene activation at $[\text{Fe}(\text{dmpe})_2]$.¹³

On the basis of all these data, we propose a mechanism for the iron-catalyzed borylation of arenes under irradiation, which is illustrated in Scheme 5. The dihydride complex **2** affords the related Fe(0) compound under irradiation.^{13c} This highly reactive species can react with HBpin to generate the hydrido(boryl) complex **4** (the observed H/D scrambling experiments indicate that oxidative addition of HBpin to the iron(0) species $\text{Fe}(\text{dmpe})_2$ is reversible under irradiation) or

Scheme 5. Proposed Mechanism for the Iron-Catalyzed Borylation of Arenes under UV Irradiation



with the arene to afford the aryl hydride intermediate **5**, which can react with HBpin to produce **4**. The hydrido(boryl) complex **4** can then react with an incoming arene to afford ultimately B–C coupling and restore the dihydride complex **2**. At this stage, direct formation of Ar–Bpin by the reaction of the hydrido(aryl) complex **5** with HBpin under irradiation cannot be ruled out.²² When the dimethyl complex **3** was used,¹⁷ its reaction with HBpin under irradiation afforded the hydrido(boryl) complex **4**, which can lead to the coupling product or to the transient Fe(0) species.

In summary, we report the first dehydrogenative borylation of (hetero)arenes catalyzed by iron without the need for any additives, although this method led to lower yields in comparison to previously described Ir-, Rh-, and Co-catalyzed borylations. Our system operates at ambient temperature under UV irradiation (350 nm) with an electron-rich iron catalyst. We could isolate and characterize the first hydrido(boryl)iron complex and prove its involvement in the catalytic process. Studies of the scope of these findings are currently underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, NMR and IR data, DFT calculations, and crystallographic data for **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(17) When **3** was irradiated in C_6D_6 but without any pinacolborane, only *cis/trans* isomerization was observed. Apart from ca. 5% MeBpin which was detected consistently in all our experiments when starting from **3** (5 mol%), we never observed any aliphatic C–H borylation, neither of the alkyl arene substituents nor when performing the reaction in pentane.

(18) (a) See Supporting Information for details. (b) It is also worth noting that no coupling occurred when replacing HBpin by B_2pin_2 (bis(pinacolato)diboron) with precatalysts **2** and **3** under our standard conditions.

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