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## C<sub>sp</sub><sup>2</sup>–H/F bond activation and borylation with iron†

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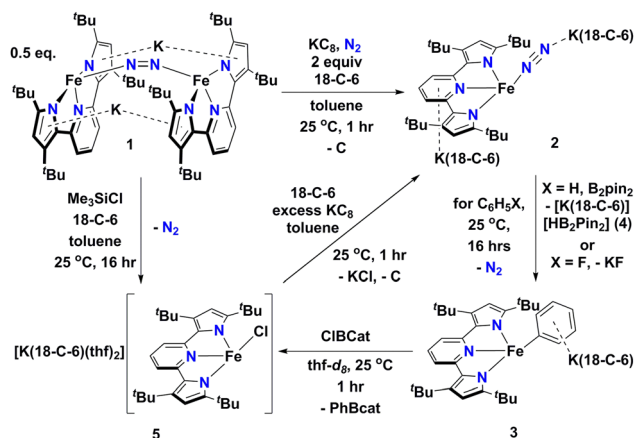
**Reduction of [K<sub>2</sub>{(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe}<sub>2</sub>(μ-N<sub>2</sub>)] (1) with two equiv. of KC<sub>8</sub> in the presence of crown-ether 18-C-6 yields the N<sub>2</sub> adduct [{K(18-C-6)}<sub>2</sub>(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe(N<sub>2</sub>)] (2). Complex 2 heterolytically splits the C<sub>sp</sub><sup>2</sup>–H bond of benzene to form [{K(18-C-6)}(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe(C<sub>6</sub>H<sub>5</sub>)] (3), whereby usage of a diboron B<sub>2</sub>pin<sub>2</sub> promotes hydride elimination to form the salt [K(18-C-6)HB<sub>2</sub>pin<sub>2</sub>] (4). Similarly, 3 can also be formed by cleavage of the C–F bond of fluorobenzene. Reaction of 3 with ClBcat yields [K(18-C-6)(thf)<sub>2</sub>](<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)FeCl (5) and PhBcat and the former can be reduced to 2 to complete a synthetic cycle for heterolytic benzene C–H activation and borylation.**

The activation and functionalization of C–H bonds is a crucial step toward converting an unreactive and abundant substrate into more reactive or synthetically versatile functionalities.<sup>1</sup> Much of the early literature on C–H activation focuses on the oxidative addition of C–H bonds at low valent precious metals.<sup>2</sup> This research was performed in the context of cross-coupling reactions which typically go through catalytic cycles consisting of oxidative addition, transmetalation, and reductive elimination.<sup>3</sup> A particularly useful target for C–H functionalization would be the generation of C–B bonds due to their prevalence in Suzuki–Miyaura cross coupling reactions.<sup>4</sup> While C–H activation is usually accomplished with precious metals, there is precedent for this reaction at iron,<sup>5</sup> which is the most abundant metal in Earth's crust.<sup>6</sup> To this end, borylation of aryl C<sub>sp</sub><sup>2</sup>–H bonds by photolysis of an iron boryl species has been reported,<sup>7</sup> with more recent studies expanding this work to catalytic processes for C–H borylation.<sup>8</sup> While mechanistic studies for arene C–H borylation reactions have been studied in detail with first row transition metals such as Co,<sup>9</sup> similar studies clearly showing the bond

forming and breaking processes at the Fe center have been exceptionally rare.<sup>5e,7b,7c,8a,8j,10</sup>

In this contribution, we show how a formally Fe<sup>0</sup> and mononuclear Fe dinitrogen complex [{K(18-C-6)}<sub>2</sub>(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe(N<sub>2</sub>)] (2) (<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr<sup>2-</sup> = 3,5-<sup>t</sup>Bu<sub>2</sub>-bis(pyrr<sub>2</sub>)pyridine; 18-C-6 = 18-crown-6) can activate the C<sub>sp</sub><sup>2</sup>–H bond of benzene (and the C–F bond of fluorobenzene) at room temperature to yield the ferrous phenyl complex [{K(18-C-6)}(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe(C<sub>6</sub>H<sub>5</sub>)] (3). We propose the C–H activation process to be heterolytic in nature by trapping KH with B<sub>2</sub>pin<sub>2</sub> (pin = pinacolato) to form the adduct [K(18-C-6)HB<sub>2</sub>pin<sub>2</sub>] (4). The aryl ligand from 3 can be transmetalated using ClBcat (cat = catecholato) to yield the discrete salt [{K(18-C-6)(thf)<sub>2</sub>}(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)FeCl] (5) along with the borane PhBcat (6). Finally, we show how 5 can be reduced to 2 to close a synthetic cycle for room temperature C<sub>sp</sub><sup>2</sup>–X bond activation and borylation (Scheme 1).

We have previously shown that reduction of the ferrous precursor [(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe(OEt<sub>2</sub>)]<sup>11</sup> with one equiv. of KC<sub>8</sub> yields the formally Fe<sup>I</sup> end-on and bridging N<sub>2</sub> complex [K<sub>2</sub>{(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe}<sub>2</sub>(μ-N<sub>2</sub>)] (1) in which the N<sub>2</sub> ligand bridging the two Fe centers is



**Scheme 1** Reaction scheme outlining formation and reactions of [{K(18-C-6)}<sub>2</sub>(<sup>t</sup>Bu<sub>2</sub>pyrr<sub>2</sub>pyr)Fe(N<sub>2</sub>)] (2).

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## Data availability

Data for this article including full synthetic procedures and characterization are available in the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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