

Article

Iron-Catalysed C(sp^2)-H Borylation Enabled by Carboxylate Activation

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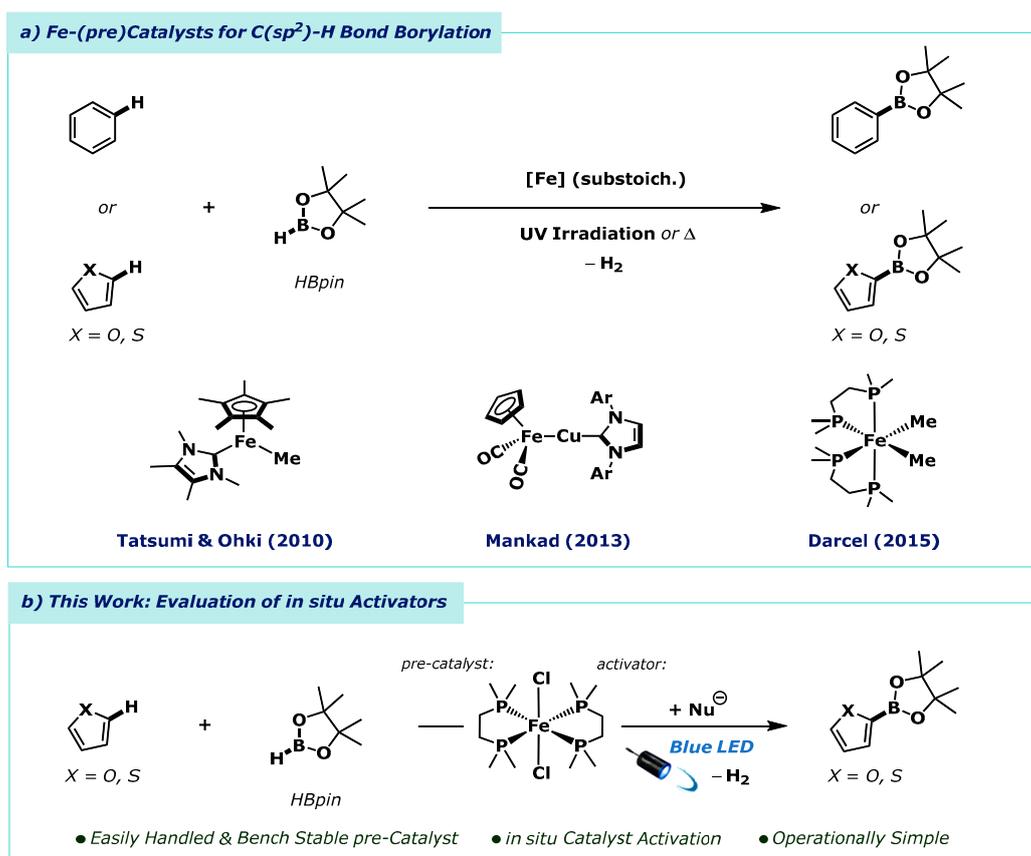
Abstract: Arene C(sp^2)-H bond borylation reactions provide rapid and efficient routes to synthetically versatile boronic esters. While iridium catalysts are well established for this reaction, the discovery and development of methods using Earth-abundant alternatives is limited to just a few examples. Applying an in situ catalyst activation method using air-stable and easily handled reagents, the iron-catalysed C(sp^2)-H borylation reactions of furans and thiophenes under blue light irradiation have been developed. Key reaction intermediates have been prepared and characterised, and suggest two mechanistic pathways are in action involving both C-H metallation and the formation of an iron boryl species.

Keywords: catalysis; borylation; Iron; C-H functionalisation; pinacolborane; photochemistry

1. Introduction

The development of sustainable methods for the selective C(sp^2)-H functionalisation of arenes is an area of intense research but is still dominated by the use of 2nd- and 3rd-row transition metals [1–7]. Earth-abundant metals offer low toxicity and inexpensive alternatives, with iron being a leading example [8–12]. Direct C(sp^2)-H borylation offers a simple and efficient route to aryl-boronic esters, which are key platforms for organic synthesis [13–15]. Iridium-based complexes have become a “go-to” for C(sp^2)-H borylation reactions [16–24], while the discovery and development of Earth-abundant alternatives remains comparatively rare [25–37].

Tatsumi and Ohki showed that arenes would undergo thermally promoted C(sp^2)-H borylation using an *N*-heterocyclic carbene cyclopentadienyl iron(II) alkyl complex [NHC(Cp*)FeMe] as a catalyst in the presence of *tert*-butylethylene (Scheme 1a) [35]. Mankad applied heterobimetallic Fe-Cu and Fe-Zn complexes under continuous ultraviolet light irradiation to arene C(sp^2)-H borylation [36]. Similarly, Darcel and co-workers reported the use of a bis(diphosphino) iron(II) dialkyl and dihydride complexes for arene C(sp^2)-H borylation, again under continuous ultraviolet light irradiation [37]. While these landmark reports are highly significant developments, all require the prior synthesis of sensitive inorganic complexes which are synthetically challenging and difficult to handle for the non-specialist practitioner, thus limiting use by the broader synthetic community.



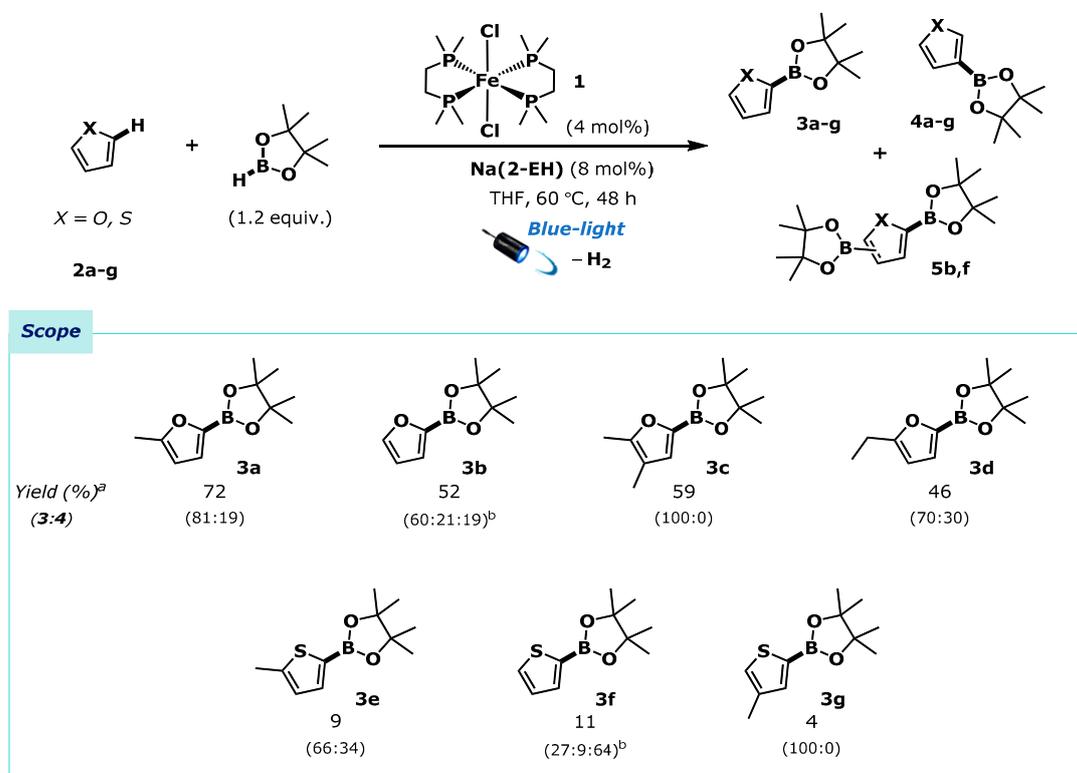
Scheme 1. Iron-catalysed C-H borylation of arenes. (a) Prior approaches to iron-catalysed C(sp²)-H-bond borylation with pinacolborane (HBpin) using organoiron and iron/copper bimetallic catalysts. (b) This work: C(sp²)-H bond borylation using dmpe₂FeCl₂ as a pre-catalyst, activated by exogenous nucleophiles, under blue light irradiation.

To reduce the synthetic challenges, and need for organometallic reagents, we questioned whether the C(sp²)-H borylation chemistry reported previously could be simplified by in situ catalyst activation using only bench stable reagents. In the example reported by Darcel and co-workers the bis[1,2-bis(dimethylphosphino)ethane-*P,P'*]dimethyliron(II) pre-catalyst (dmpe₂FeMe₂) was generated by the addition of methyl lithium to the corresponding iron(II) dichloride complex (dmpe₂FeCl₂) [37]. Similarly, the catalytically active bis[1,2-bis(dimethylphosphino)ethane-*P,P'*]iron(II) dihydride (dmpe₂FeH₂) could be accessed using either LiHBET₃ or LiAlH₄ [37,38]. Given our previous work on the in situ generation of hydride donors formed by the combination of alkoxide salts and pinacolborane (HBpin) [39], we postulated that the active C(sp²)-H borylation pre-catalyst, dmpe₂FeH₂, may be accessible by the same method. Reaction of substoichiometric alkoxide salt with HBpin, the boron source used for this borylation, would generate a hydride reductant in situ to activate the dmpe₂FeCl₂ pre-catalyst to dmpe₂FeH₂, the active borylation catalyst, and thus initiate catalysis. Importantly, the dmpe₂FeCl₂ complex displays much greater air- and moisture stability compared to the dihydride and dialkyl analogues. Herein, we report the in situ activation of dmpe₂FeCl₂ and application to the C(sp²)-H borylation reaction of heteroarenes (Scheme 1b).

2. Results

Guided by the work of Darcel and co-workers, we selected 2-methylfuran **2a** as an ideal test substrate for our investigations. Darcel and co-workers showed that dmpe₂FeMe₂ could be used as a pre-catalyst for the borylation of furan **2a** (3 equiv.) using HBpin (1 equiv.) under continuous ultraviolet light irradiation to give a regioisomeric mixture of 5- and 4-borylated furans, **3a** and **4a** respectively

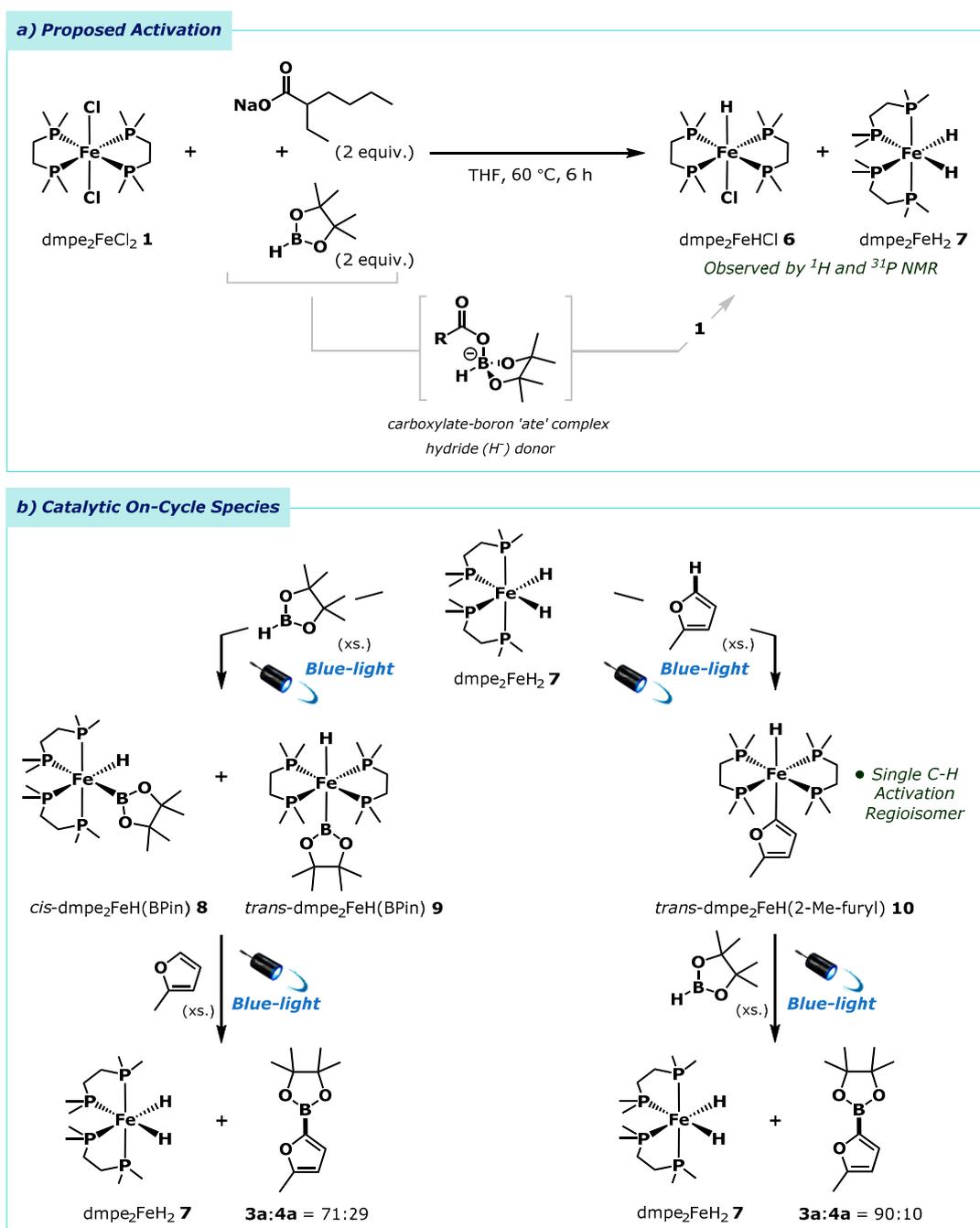
and **4d**. Unfortunately, application to thiophenes demonstrated limited reactivity under the established reaction conditions, giving only low yields of boryl-arenes **3e-g** and **4e-g**, again as a mixture of regioisomers, and bis-borylated product when the parent thiophene was used [40].



Scheme 3. Na(2-EH) activated borylation of furan and thiophene derivatives using $\text{dmpe}_2\text{FeCl}_2$ **1**. ^a Yields determined by ^1H -NMR spectroscopy of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard. Product ratios were determined by ^1H -NMR spectroscopy of the crude reaction mixtures. ^b Values represent the ratio of 2-boryl:3-boryl:bis-boryl products.

2.2. Mechanistic Investigations

On the basis of successful catalysis we presumed that our in situ activation system provided access to the active iron(II) dihydride complex $\text{dmpe}_2\text{FeH}_2$ **7**, which had been shown to be catalytically active by Darcel and co-workers [37]. To support this, we combined each component in the absence of light or arene, i.e., the reaction of $\text{dmpe}_2\text{FeCl}_2$ **1**, Na(2-EH) and HBpin (Scheme 4a). This showed the formation of both the monohydride product $\text{dmpe}_2\text{FeHCl}$ **6** and the expected dihydride, $\text{dmpe}_2\text{FeH}_2$ **7**, as observed by ^{31}P -NMR spectroscopy (see Supplementary Materials, S16). Reaction of the activator, Na(2-EH), and HBpin in the absence of pre-catalyst showed ligand redistribution to a mixture of boron-containing species, including boron “ate” complexes, BH_3 and $[\text{BH}_4]^-$, as observed by ^{11}B -NMR spectroscopy (see Supplementary Materials, S3). This reactivity is in accordance with that when using other nucleophiles such as alkoxide salts [39,41]. Taken together, these observations are indicative of an in situ activation process, whereby the added carboxylate reagent Na(2-EH) triggers hydride transfer from boron to iron to form the dihydride $\text{dmpe}_2\text{FeH}_2$ **7**. Once formed, the iron dihydride $\text{dmpe}_2\text{FeH}_2$ **7** can efficiently catalyse the C(*sp*²)-H borylation reaction.



Scheme 4. (a) Pre-catalyst activation and hydride formation. (b) Mechanistic investigations of dmpe₂FeH₂ **7** produced by hydride transfer from HBpin and Na(2-EH).

As the dihydride complex dmpe₂FeH₂ **7** was readily formed using our in situ hydride transfer method, and was observable by ¹H and ³¹P-NMR spectroscopy, we next investigated the fundamental steps of this borylation reaction with the aim of identifying key reaction intermediates. Reaction of the in situ generated dmpe₂FeH₂ **7** with excess HBpin under blue light irradiation led to the formation of both *cis*-dmpe₂FeH(Bpin) **8** and *trans*-dmpe₂FeH(Bpin) **9** boryl iron complexes, as observed by ¹H, ¹¹B, and ³¹P NMR spectroscopy (see Supplementary Materials, S17-19). These complexes were previously reported by Darcel and co-workers, where they were formed from the reaction of the related dialkyl complex, dmpe₂FeMe₂, with HBpin [37]. Addition of 2-methylfuran **2a** to the mixture of *cis*-dmpe₂FeH(Bpin) **8** and *trans*-dmpe₂FeH(Bpin) **9** under blue light irradiation gave the formation

of the regioisomeric furyl boronic esters **3a** and **4a** (**3a:4a** = 71:29), notably in a different ratio to that observed during catalysis (vide supra, **3a:4a** = 81:19).

Blue light irradiation of the dihydride complex $\text{dmpe}_2\text{FeH}_2$ **7** in the presence of excess 2-methylfuran **2a** led to exclusive $\text{C}(sp^2)\text{-H}$ bond metallation at the 5-position to give *trans*- $\text{dmpe}_2\text{FeH}(2\text{-Me-furyl})$ **10**, as observed by ^1H and ^{31}P NMR spectroscopy (see Supplementary Materials, S22-24). Addition of HBpin to *trans*- $\text{dmpe}_2\text{FeH}(2\text{-Me-furyl})$ **10** and irradiation with blue light induced formation of the furyl boronic esters **3a** and **4a** (**3a:4a** = 90:10). Again, in a different ratio to that observed under catalysis. As the ratio of regioisomers observed under catalytic conditions (**3a:4a** = 81:19) appears to be a combination of the ratios observed in the stoichiometric studies (**3a:4a** = 71:29, and 90:10 respectively), it is suggestive that both the C-H metallation and iron boryl pathways are operative. Specifically, the reaction can precede by $\text{C}(sp^2)\text{-H}$ bond metallation to give $\text{dmpe}_2\text{FeH}(2\text{-Me-Furyl})$ **10**, followed by $\text{C}(sp^2)\text{-B}$ bond formation, or by direct reaction of arene with the iron boryl species *cis*- $\text{dmpe}_2\text{FeH}(\text{Bpin})$ **8** and *trans*- $\text{dmpe}_2\text{FeH}(\text{Bpin})$ **9**. The relative ratios of the furyl boronic ester regioisomers indicate both pathways are equally accessible for the activated catalyst. (53% by C-H metallation, 47% by the iron boryl species).

3. Conclusions

In summary, we have investigated the applicability of several alkoxide, carboxylate and other, common bench stable reagents towards the in situ activation of an iron(II) pre-catalyst for $\text{C}(sp^2)\text{-H}$ bond borylation. We found a sodium carboxylate salt Na(2-EH) in combination with HBpin to be a potent pre-catalysts activator generating the iron dihydride $\text{dmpe}_2\text{FeH}_2$ **7** in situ. The validity of this method was demonstrated by the generation of catalytically relevant species that were used as mechanistic probes. These suggest two C-H borylation pathways are operating to give the aryl boronic ester products; C-H metallation followed by borylation, and formation of an iron boryl species followed by arylation.

4. Materials and Methods

4.1. General Information

All compounds reported in the manuscript are commercially available or have been previously described in the literature unless indicated otherwise. All experiments involving iron were performed using standard Schlenk techniques under argon or nitrogen atmosphere. All yields refer to yields determined by ^1H -NMR spectroscopy of crude reaction mixtures using an internal standard. All product ratios refer to product ratios determined by ^1H -NMR spectroscopy of the crude reaction mixtures. ^1H -NMR and ^{13}C -NMR data are given for all compounds when possible in the experimental section for characterisation purposes. Spectroscopic data matched those reported previously.

4.2. Activator Synthesis

Tetra-*n*-butylammonium 2-ethylhexanoate TBA(2-EH)

A suspension of KH (80 mg, 2 mmol) in anhydrous THF (20 mL) was prepared under an N_2 atmosphere, 2-ethylhexanoic acid (0.32 mL, 2 mmol) was added dropwise whilst stirring. *n.b.* gas evolution (H_2). The solution was stirred for 3 h at room temperature, and the THF removed in vacuo to give an amorphous colourless solid. The solid was re-dissolved in MeOH (20 mL) and tetra-*n*-butylammonium chloride (556 mg, 2 mmol) was added, the solution was stirred for 16 h, filtered through a glass frit and dried in vacuo without further purification to give tetra-*n*-butylammonium 2-ethylhexanoate (0.72 g, 1.86 mmol, 93%) as an amorphous white solid.

^1H -NMR (500 MHz, CDCl_3) δ 3.51–3.35 (m, 8H), 2.09 (tt, J = 8.4, 5.4 Hz, 1H), 1.66 (m, 8H), 1.62–1.54 (m, 2H), 1.48–1.39 (m, 8H), 1.39–1.23 (m, 6H), 0.98 (t, J = 7.3 Hz, H), 0.91 (t, J = 7.4 Hz, 3H), 0.88–0.82 (m, 3H). ^{13}C -NMR (126 MHz, CDCl_3) δ 181.2, 59.0, 51.1, 33.1, 30.5, 26.4, 24.3, 23.2, 19.8, 14.2, 13.7, 12.7.

4.3. Pre-catalyst Synthesis

dmpe₂FeCl₂ **1** [42]

Anhydrous iron dichloride (0.21 g, 1.67 mmol) was charged to a Schlenk flask and dissolved in anhydrous THF (10 mL), dmpe [(bis(dimethylphosphino)ethane); 0.50 g, 3.33 mmol] were added to the flask under an Ar atmosphere and the solution left to stir for 48 h at room temperature. The solvent was removed in vacuo, and in an argon-filled glove box, the residue was re-dissolved in dichloromethane (5 mL) and filtered through glass wool. The filtrate was reduced in vacuo to produce a green amorphous solid (0.549 g, 1.29 mmol, 77%).

¹H-NMR (400 Hz, d⁸-THF) δ 2.18 (s, 8H), 1.42 (s, 24H). ³¹P-NMR (202 MHz, CDCl₃) δ 59.0.

4.4. General Borylation Procedure

In an argon-filled glovebox, dmpe₂FeCl₂ **1** (8.6 mg, 0.02 mmol), sodium 2-ethylhexanoate (6.6 mg, 0.04 mmol), HBpin (87 μL, 0.6 mmol), substrate (0.5 mmol), and THF (1 mL) were added to a 1.7 mL sample vial and shaken to ensure full dissolution. The vial was placed under blue light radiation for 48 h and then allowed to cool to room temperature. Yields determined by ¹H-NMR spectroscopy of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard [0.5 mL; standard solution = 1,3,5-trimethoxybenzene (0.336 g, 2.0 mmol) in diethyl ether (10 mL)]. Product ratios were determined by ¹H-NMR spectroscopy of the crude reaction mixtures.

4.5. Characterisation of Borylated Products

4.5.1. 2-Methylfuran Derivatives

4,4,5,5-Tetramethyl-2-(5-methylfuran-2-yl)-1,3,2-dioxaborolane **3a** [37], 4,4,5,5-tetramethyl-2-(5-methylfuran-3-yl)-1,3,2-dioxaborolane **4a** [37]

Following the general procedure; 2-methylfuran **2a** (41 mg, 44 μL, 0.5 mmol). Yield = 72%. **3a:4a** = 81:19. ¹H-NMR (500 MHz, CDCl₃) **3a**: δ 6.99 (d, *J* = 3.2 Hz, 1H), 6.06–6.01 (m, 1H), 2.36 (s, 3H), 1.34 (s, 12H). **4a**: δ 7.62 (d, *J* = 0.9 Hz, 1H), 6.15 (t, *J* = 1.0 Hz, 1H), 2.29 (d, *J* = 1.1 Hz, 3H), 1.31 (s, 12H). ¹³C-NMR (126 MHz, CDCl₃) **3a**: δ 157.8, 124.8, 106.9, 84.0, 24.7, 13.9. **4a**: δ 152.7, 149.7, 108.8, 83.3, 24.9, 13.1. ¹¹B-NMR (160 MHz, CDCl₃) **3a**: δ 27.1. **4a**: δ 29.8.

4.5.2. Furan Derivatives

4,4,5,5-Tetramethyl-2-(furan-2-yl)-1,3,2-dioxaborolane **3b** [43], 4,4,5,5-tetramethyl-2-(furan-3-yl)-1,3,2-dioxaborolane **4b** [44], 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan **5ba** [45], 2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan **5bb** [45]

Following the general procedure; furan **2b** (34 mg, 36 μL, 0.5 mmol). Yield = 52%. **3b:4b:5ba:5bb** 60:21:4:5. ¹H-NMR (600 MHz, CDCl₃) **3b**: δ 7.65 (d, *J* = 1.7 Hz, 1H), 7.07 (d, *J* = 3.4 Hz, 1H), 6.44 (dd, *J* = 3.4, 1.6 Hz, 1H), 1.35 (s, 12H). **4b**: δ 7.78 (s, 1H), 7.46 (m, *J* = 1.6 Hz, 1H), 6.59 (d, *J* = 1.7 Hz, 1H), 1.32 (s, 1H). **5ba**: δ 7.06 (s, 2H), 1.33 (s, 24H). **5bb**: δ 7.78 (s, 1H), 7.28 (s, 1H), 1.30 (s, 24H). ¹³C-NMR (126 MHz, CDCl₃) **3b**: δ 147.3, 123.2, 110.3, 84.2, 24.8. **4b**: δ 151.2, 142.9, 113.1, 83.5, 24.9. **5ba**: δ 123.2, 83.5, 24.8. **5bb**: δ 151.2, 83.2, 75.1, 24.6. ¹¹B-NMR (160 MHz, CDCl₃) **3b**: δ 27.2. **4b**: δ 29.8.

4.5.3. 2,3-Dimethylfuran Derivatives

4,4,5,5-Tetramethyl-2-(4,5-dimethylfuran-2-yl)-1,3,2-dioxaborolane **3c** [46]

Following the general procedure; 2,3-dimethylfuran **2c** (48 mg, 53 μ L, 0.5 mmol). Yield = 46%. **3c:4c** = 100:0. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 6.87 (s, 1H), 2.26 (s, 3H), 1.94 (s, 3H), 1.33 (s, 12H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ 153.4, 127.1, 115.2, 83.9, 24.7, 11.8, 9.7. $^{11}\text{B-NMR}$ (160 MHz, CDCl_3) δ 27.2.

4.5.4. 2-Ethylfuran Derivatives

4,4,5,5-Tetramethyl-2-(5-ethylfuran-2-yl)-1,3,2-dioxaborolane **3d** [47], 4,4,5,5-tetramethyl-2-(5-methylfuran-3-yl)-1,3,2-dioxaborolane **4d** [47]

Following the general procedure; 2-ethylfuran **2d** (48 mg, 53 μ L, 0.5 mmol). Yield = 59%. **3d:3d** = 70:30. $^1\text{H-NMR}$ (500 MHz, CDCl_3) **3d**: δ 7.01 (d, J = 3.3 Hz, 1H), 6.05 (d, J = 3.1, 1H), 2.72 (q, J = 7.6 Hz, 2H), 1.34 (s, 12H), 1.25 (m, 3H). **4d**: δ 7.64 (d, J = 0.8 Hz, 1H), 6.18 (d, J = 1.1 Hz, 1H), 2.6 (q, J = 7.5, 2H), 1.31 (s, 12H), 1.25 (m, 3H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) **3d**: δ 163.6, 124.7, 105.2, 84.0, 24.7, 21.6, 12.2. **4d**: δ 163.6, 149.6, 107.2, 83.3, 24.9, 21.1, 12.1. $^{11}\text{B-NMR}$ (160 MHz, CDCl_3) **3d**: δ 27.2. **4d**: δ 29.9.

4.5.5. 2-Methylthiophene Derivatives

4,4,5,5-Tetramethyl-2-(5-methylthiophen-2-yl)-1,3,2-dioxaborolane **3e** [47], 4,4,5,5-tetramethyl-2-(5-methylthiophen-3-yl)-1,3,2-dioxaborolane **4e** [47]

Following the general procedure; 2-methylthiophene **2e** (49 mg, 48 μ L, 0.5 mmol). Yield = 9%. **3e:4e** = 66:34. $^1\text{H-NMR}$ (500 MHz, CDCl_3) **3e**: δ 7.45 (d, J = 3.4 Hz, 1H), 6.84 (d, J = 3.4, 1H), 2.53 (s, 3H), 1.33 (s, 12H). **4e**: δ 7.67 (d, J = 1.2 Hz, 1H), 7.04 (s, 1H), 2.49 (d, J = 1.1 Hz, 3H), 1.32 (s, 12H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) **3e**: δ 147.5, 137.6, 127.0, 83.9, 24.9, 15.4. **4e**: not observed. $^{11}\text{B-NMR}$ (160 MHz, CDCl_3) δ 28.7.

4.5.6. Thiophene Derivatives

4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane **3f** [48], 4,4,5,5-tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane **4f** [49], 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene **5f** [48]

Following the general procedure; thiophene **2f** (42 mg, 40 μ L, 0.5 mmol). Yield = 11%. **3f:4f:5f** = 27:9:64. $^1\text{H-NMR}$ (500 MHz, CDCl_3) **3f**: δ 7.64 (m, 1H), 7.63 (d, J = 4.8 Hz, 1H), 7.19 (d, J = 4.8 Hz, 1H), 1.35 (s, 12H). **4f**: δ 7.92 (d, J = 2.6 Hz, 1H), 7.41 (d, J = 4.9 Hz, 1H), 7.34 (dd, J = 4.8, 2.7 Hz, 1H), 1.35 (s, 12H). **5f**: δ 7.66 (s, 2H), 1.34 (s, 24H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) **3f**: δ 137.2, 132.4, 128.2, 83.2, 24.9. **4f**: δ 136.5, 129.0, 125.3, 83.2, 24.8. **5f**: δ 137.7, 84.1, 24.8. $^{11}\text{B-NMR}$ (160 MHz, CDCl_3) δ 29.2.

4.5.7. 3-Methylthiophene Derivatives

4,4,5,5-Tetramethyl-2-(4-methylthiophen-2-yl)-1,3,2-dioxaborolane **3g** [17]

Following the general procedure; 3-methylthiophene **2g** (49 mg, 48 μ L, 0.5 mmol). Yield = 4%. **3g:4g** = 100:0. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.44 (d, J = 1.2 Hz, 1H), 7.19 (t, J = 1.1 Hz, 1H), 2.29 (d, J = 0.9 Hz, 3H), 1.34 (s, 12H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ 139.5, 139.0, 128.2, 84.0, 24.9, 15.1. $^{11}\text{B-NMR}$ (160 MHz, CDCl_3) δ 29.1.

4.6. Mechanistic Investigations

$\text{dmpe}_2\text{FeH}_2$ **7** [37]

$\text{dmpe}_2\text{FeCl}_2$ **1** (10 mg, 0.023 mmol), sodium 2-ethylhexanoate (7.6 mg, 0.046 mmol), and HBpin (7 μ L, 0.046 mmol) were added to a Young's NMR tube under an Ar atmosphere and heated at 60 $^\circ\text{C}$ for 3 days. $^1\text{H-NMR}$ (600 MHz, THF) δ -14.38 (m). $^{31}\text{P-NMR}$ (500 MHz, THF) δ 76.9 (t, J = 28 Hz), 67.7 (t, J = 28 Hz).

cis- $\text{dmpe}_2\text{FeH}(\text{Bpin})$ **8** and *trans*- $\text{dmpe}_2\text{FeH}(\text{Bpin})$ **9** [37]

dmpe₂FeCl₂ **1** (4.3 mg, 0.001 mmol), sodium 2-ethylhexanoate (3.3 mg, 0.002 mmol), and HBpin (87 µL, 0.6 mmol) were added to a Young's NMR tube under an Ar atmosphere and irradiated with blue light for 16 h. ¹H-NMR (500 MHz, THF) δ -13.1 (p, J = 43.2 Hz), -14.0 (m). ³¹P-NMR (500 MHz, THF) δ 77.6(m), 77.2 (m), 59.7 (m), 58.9 (m).

dmpe₂FeH(2-Me-furyl) **10**

dmpe₂FeCl₂ **1** (10 mg, 0.023 mmol), sodium 2-ethylhexanoate (30.4 mg, 0.184 mmol), and HBpin (7 µL, 0.046 mmol) were added to a Young's NMR tube under an Ar atmosphere and warmed at 60 °C for 24 h. 2-methylfuran (8 µL, 0.092 mmol) was added under an Ar atmosphere and the sample irradiated with blue light for 3 h. This complex was observed *in situ*. ¹H-NMR (500 MHz, THF) δ -18.93 (q, J = 45.8 Hz). ³¹P-NMR (500 MHz, THF) δ 77.1 (d, J = 38.1 Hz). MS: (HRMS – EI⁺) Found 438.12041 (C₁₇H₃₈O₁⁵⁶Fe₁P₄), requires 438.12171.

Supplementary Materials: The following are available online.

Author Contributions: L.B. and J.H.D. carried out the experimental work. J.H.D., A.P.D. and S.P.T. conceived and supervised the project. L.B., J.H.D., and S.P.T. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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Sample Availability: Samples of the pre-catalyst **1** are available from the authors.



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