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Iron-Catalyzed Diborylation of Unactivated Aliphatic *gem*-Dihalogenoalkenes: Synthesis of 1,2-Bis(boryl)alkanes

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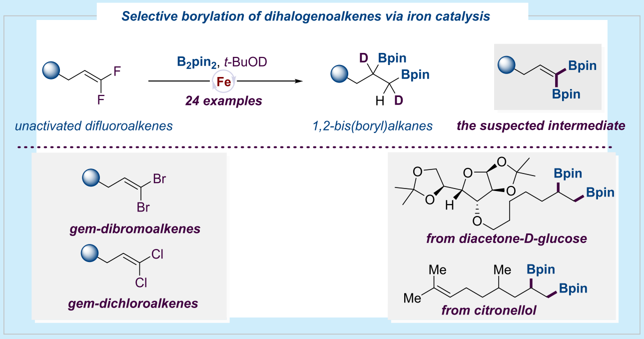
ABSTRACT: Herein, we report the first example of iron-catalyzed defluoroborylation of unactivated *gem*-difluoroalkenes, *gem*-dichloroalkenes, and *gem*-dibromoalkenes, providing the 1,2-bis(boryl)-alkanes in moderate to good yield. This transformation has high regioselectivity, wide substrate scope, and excellent functional group compatibility. Preliminary mechanistic studies indicate that double *β*-F elimination is involved in the catalytic cycle, and the 1,1-diborylated alkenes might be intermediates in this iron-catalyzed 1,2-diborylation reaction.

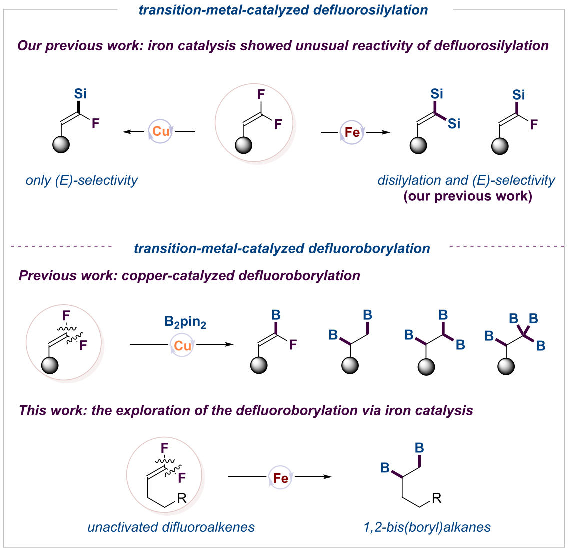


Iron catalysts have been widely employed in organic synthesis due to their advantages of nontoxicity, low cost, and abundance.[1] In addition, the different properties of iron catalysis in organic reactions make it more attractive than other transition metals.[2] For instance, palladium always exhibits a two-electron pathway in cross-coupling reactions, while iron initiates these transformations through one-electron transfer.[3] Usually, many unpredictable reactions are discovered by the one-electron transfer pathway, thus highlighting the superiority of iron catalysis.[3] In our previous work,[4] we found different reactivities of iron catalysis. Fortunately, in the recent defluorosilylation of unactivated aliphatic *gem*-difluoroalkenes,[4] iron catalysis showed different reactivity from copper, palladium, and nickel. The *gem*-disilylated alkenes were afforded via iron catalysis, while other transition metals provided the *E*-selective silylated fluoroalkenes (Scheme 1).

In 2017, borylation of *gem*-difluoroalkenes by copper was reported by the Hosoya and Cao groups, respectively, where the *E*-selective borylated compounds were delivered.[5,6] Since then, other *E*-selective borylation reactions have been reported,[7] and the main products are the monoborylated fluoroalkenes. Shi and co-workers reported an interesting work in 2018[8] in which the 1,2-diborylated, 1,1,2-triborylated, and 1,1,1,2-tetradiborylated compounds were obtained. Inspired by our recent iron-catalyzed defluorosilylation reaction,[4d] we wondered whether the defluoroborylation via iron catalysis has specific reaction properties. Therefore, as part of our continuing interest in iron catalysis,[9] we herein explore iron-catalyzed defluoroborylation of unactivated aliphatic *gem*-difluoroalkenes.[10]

With these considerations in mind, we began our investigation on the borylation of *gem*-difluoroalkenes catalyzed by iron. After evaluating iron sources, we found that 1,2-diborylated product **3a** was obtained using unactivated

Scheme 1. Transition-Metal-Catalyzed the Transformation of *gem*-Difluoroalkenes



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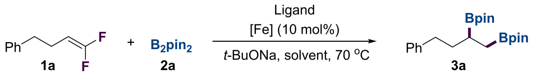
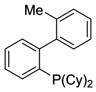
aliphatic *gem*-difluoroalkene **1a** as the substrate. In addition, this reaction could not provide the triborylated and tetraborylated compounds, which were produced via copper catalysis reported by the Shi group.[8] 1,2-Bis(boryl)alkanes are an important class of synthons that have attracted much attention due to their versatile transformation. Several important methods for the synthesis of 1,2-bis(boryl)alkanes from alkenes or alkynes have been reported.[11] Although significant progress has been developed, the iron-catalyzed synthesis of 1,2-bis(boryl)alkanes is still attractive.

Encouraged by these results, other iron salts were tested in the presence of dppp (Table 1, entries 1−4; for details, see the Supporting Information). Fe(OAc)$_2$ exhibited good efficiency, providing the desired product **3a** in 50% yield (Table 1, entry 2). Poor yields were obtained using high-valent iron salts, such as Fe(acac)$_3$ or Fe(OTf)$_3$ (Table 1, entry 1 and entry 3). Subsequently, when Fe(OAc)$_2$ was used as the catalyst, other ligands were carefully screened. The bidentate or monodentate phosphine ligands and nitrogen-based ligands could promote this transformation smoothly (Table 1, entries 5−8; for details, see the Supporting Information). The moderate yield was obtained using tri(*o*-tolyl)phosphine as the ligand (Table 1, entry 8). By slightly increasing the loading of bis(pinacolato)diboron **2a**, a 63% yield was provided (Table 1, entry 9). Other solvents were also investigated, and this reaction proceeded well in ether solvents (for details, see the Supporting Information). Dioxane could provide the desired product in 47% yield, and THF was the best choice (Table 1, entries 9 and 10). Some additives as proton resources were added to improve the efficiency of this conversion (Table 1, entries 11−13; for details, see the Supporting Information). When methanol was used as the additive, 68% yield was obtained using JohnPhos as the ligand (Table 1, entry 12). Gratifyingly, the best result (85% yield upon ^{1}H NMR) was provided when *tert*-butyl alcohol was used (Table 1, entry 13), and only 64% of the isolated yield was obtained due to the instability of alkyl 1,2-bis(boronates) **3a** in our catalytic system. Control experiments demonstrated the importance of additive, and only 53% yield was obtained in the absence of *tert*-butyl alcohol (Table 1, entry 14). Only the moderate yield was provided without ligands, and no desired product was observed in the absence of the iron catalyst, which demonstrated the necessity of iron catalysts (Table 1, entries 15 and 16). Some transition metals, such as copper, palladium, and nickel sources, were also tested, but no desired product was observed (for details, see the Supporting Information).

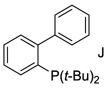
Table 1. Representative Results for the Optimization of the Iron-Catalyzed Defluoroborylation of 1a[a]



entry	[Fe]	ligand	solvent	additive	yield[b] (%)
1	Fe(acac)$_3$	dppp	THF		28
2	Fe(OAc)$_2$	dppp	THF		50
3	Fe(OTO$_3$	dppp	THF		12
4	FeBr$_2$	dppp	THF		46
5	Fe(OAc)$_2$	Xantphos	THF		36
6	Fe(OAc)$_2$	Mephos	THF		50
7	Fe(OAc)$_2$	TMEDA	THF		40
8	Fe(OAc)$_2$	P(*o*-tol)$_3$	THF		60
9[c]	Fe(OAc)$_2$	P(*o*-tol)$_3$	THF		63
10[c]	Fe(OAc)$_2$	P(*o*-tol)$_3$	dioxane		47
11[c]	Fe(OAc)$_2$	P(*o*-tol)$_3$	THF	MeOH (2.0 equiv)	61
12[c]	Fe(OAc)$_2$	JohnPhos	THF	MeOH (2.0 equiv)	68
13[d]	Fe(OAc)$_2$	JohnPhos	THF	*t*-BuOH (5.0 equiv)	85 (64)
14[d]	Fe(OAc)$_2$	JohnPhos	THF		53
15[d]	Fe(OAc)$_2$		THF	*t*-BuOH (5.0 equiv)	63
16[d]		JohnPhos	THF	*t*-BuOH (5.0 equiv)	0



Mephos



Johnphos

[a] Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), bis(pinacolato)diboron **2a** (0.5 mmol, 2.5 equiv), [Fe] (0.02 mmol, 0.1 equiv), ligand (0.1−0.2 equiv), *t*-BuONa (0.55 mmol, 2.75 equiv), solvent (1.5 mL), 70 °C, 12 h. [b] Determined by ^{1}H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses. [c] bis(pinacolato)diboron **2a** (0.6 mmol, 3.0 equiv), *t*-BuONa (0.7 mmol, 3.5 equiv). [d] bis(pinacolato)diboron **2a** (0.8 mmol, 4.0 equiv), *t*-BuONa (0.6 mmol, 3.0 equiv).

After establishing the optimized reaction conditions, we set out to evaluate the scope of the iron-catalyzed diborylation of *gem*-difluoroalkenes. As shown in Table 2, various unactivated aliphatic *gem*-difluoroalkenes could undergo this transformation smoothly, and the corresponding products were afforded in moderate isolated yields. Substrates containing an aromatic ring at the carbon chain performed this diborylation well, affording the desired products in moderate yields. Gratifyingly, this reaction showed excellent functional group tolerance. For instance, CF$_3$, F, Cl, Br, OBn, carboxylate, TIPS, and carbamate were well-tolerated in this catalytic system (**3d**, **3e**, **3i**, **3j**, **3n**, **3o**, **3r**, **3s**, and **3t**). *gem*-Difluoroalkenes with a fluoro or chloro group on the aromatic ring reacted well, and 58% yield was delivered (**3i**, **3j**). In addition, substrates bearing a chloro or bromo group underwent this transformation smoothly, and the diborylated products were obtained in moderate yields (**3n**, **3o**). The saturated linear substrate could also perform this diborylation, and 56% yield was obtained (**3u**). The heteroaromatic ring could be tolerated as well, and the desired product was produced in 60% yield (**3m**). Substrates with a substituted alkyl group near the *gem*-difluoroalkenyl group performed this conversion well, and the diborylated products were generated in moderate yields (**3k**, **3l**). The excellent value of this iron-catalyzed 1,2-diborylation reaction was further exhibited in its application in biomolecules. Citronellol, myrac aldehyde, and diacetone-D-glucose-derived *gem*-difluoroalkenes performed this transformation smoothly, as shown in Table 2, and the alkenyl group could be well-tolerated, affording the desired 1,2-diborylated products in moderate yields (**3v**, **3w**, **3x**).

In the previous work,[8] the unactivated *gem*-dibromoalkenes were not suitable for copper-catalyzed borylation. Encouraged by the results of the iron-catalyzed 1,2-diborylation of unactivated *gem*-difluoroalkenes, we wondered whether the fluorine group was necessary for our developed protocol. Therefore, according to the literature, the unactivated *gem*-dibromoalkene **1a′** and *gem*-dichloroalkene **1a′′** were synthesized to perform this conversion. As shown in Scheme 2, the excellent yields determined by ^{1}H NMR were observed, but moderate isolated yields were obtained due to the instability of

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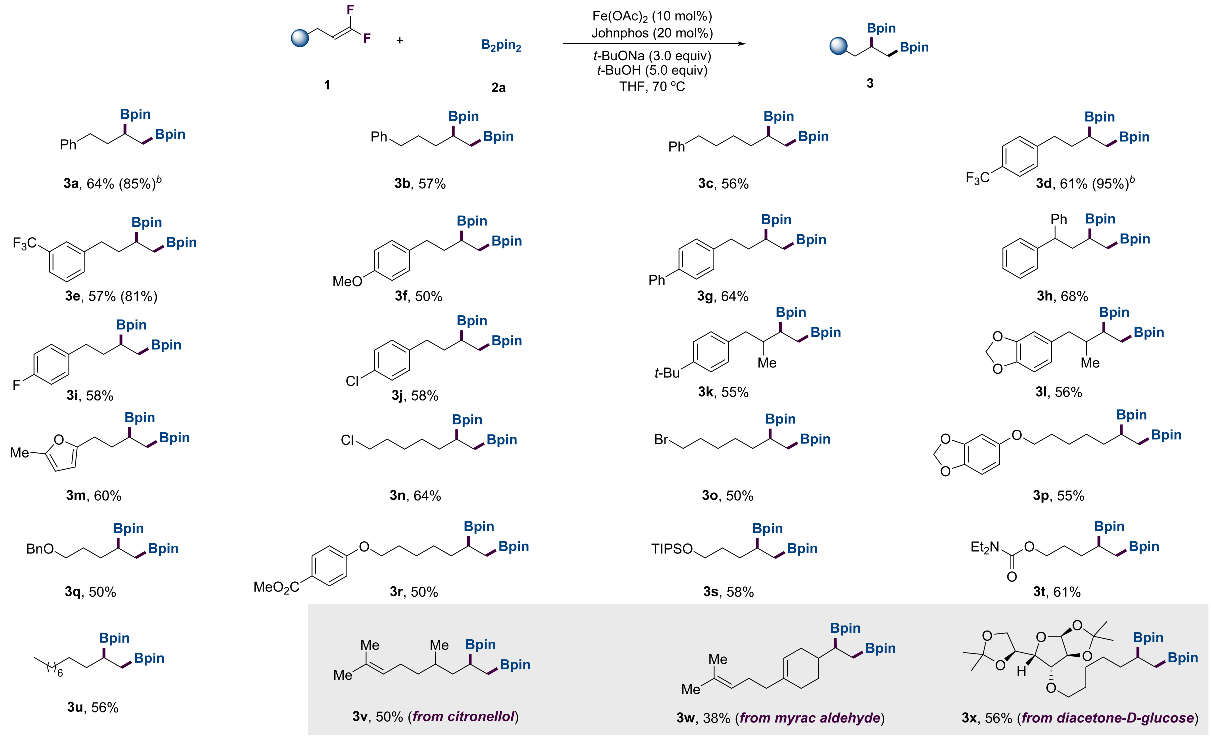
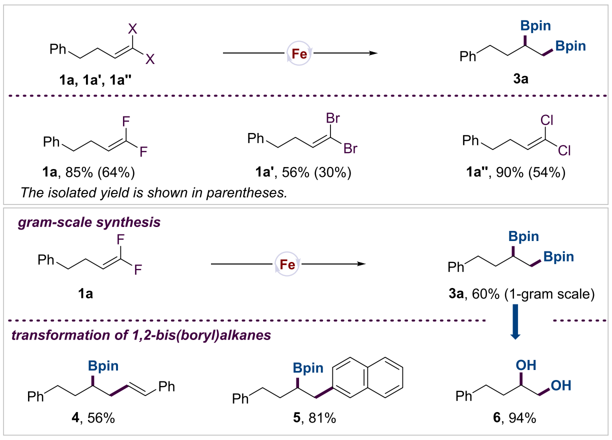
Table 2. Scope of the Iron-Catalyzed Diborylation of Unactivated *gem*-Difluoroalkenes[a]



[a] Reaction conditions (unless otherwise specified): *gem*-difluoroalkenes (0.2 mmol, 1.0 equiv), bis(pinacolato)diboron **2a** (0.8 mmol, 4.0 equiv), *t*-BuONa (0.6 mmol, 3.0 equiv), Fe(OAc)$_2$ (0.02 mmol, 0.1 equiv), JohnPhos (0.04 mmol, 0.2 equiv), THF (1.5 mL), 70 °C, 12 h. [b] The yield determined by ^{1}H NMR using mesitylene as an internal standard is shown in parentheses.

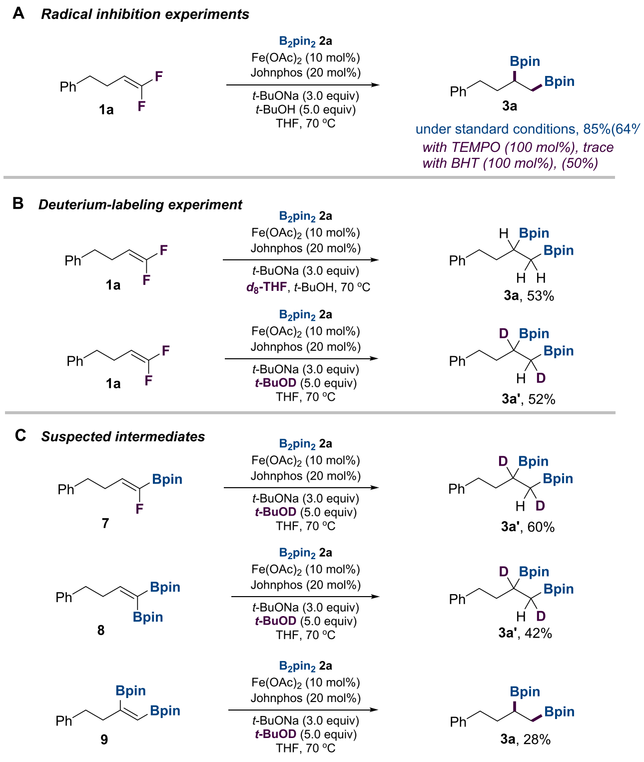
Scheme 2. Iron-Catalyzed Diborylation of Unactivated *gem*-Dibromoalkenes and *gem*-Dichloroalkenes and Transformation of 1,2-Bis(boryl)alkane 3a



products, 1,2-bis(boryl)alkanes in our catalytic system. These results indicate that our iron-catalyzed diborylation reaction exhibits more general reactivity, not only for *gem*-difluoroalkenes but also for *gem*-dichloroalkenes and *gem*-dibromoalkenes. This 1,2-diborylation reaction could be carried out on a 1 g scale, providing the corresponding product **3a** in 60% yield (Scheme 2). Subsequently, the 1,2-bis(boryl)alkane **3a** could undergo Suzuki cross-coupling reactions with organoboronic esters and afforded the secondary alkylboronic esters (**4**, **5**) instead of primary alkylboronic esters in moderate to good yields (Scheme 2).[12] It is worth noting that the resulted alkylboronic esters **4** and **5** could also undergo the downstream transformation through the functionalization of C−B bond. Thus, this protocol could offer an excellent synthetic route for the diversification of *gem*-difluoroalkenes. Additionally, **3a** could be directly converted into 1,2-diol derivative **6** in excellent yield (Scheme 2).[13]

Next, radical inhibition experiments were conducted to understand the mechanism of this iron-catalyzed 1,2-diborylation reaction (Scheme 3A). This transformation was almost completely suppressed when the radical scavenger TEMPO (100 mol %) was used as an additive. The addition of radical inhibitor BHT (100 mol %) under the standard reaction conditions provided the desired product in 50% yield. On the basis of these results, the free-radical pathway could not be excluded in this catalytic system. During our evaluation of reaction conditions, we found that this reaction could also proceed smoothly without *t*-BuOH as a proton source, and a moderate yield (53% yield upon ^{1}H NMR) was obtained. In order to determine the source of protons in the 1,2-diborylated products, deuterium-labeling experiments were carried out (Scheme 3B). When d_8-THF was used as the solvent, this 1,2-diborylation reaction proceeded well in the presence of *t*-BuOH, and no deuterated desired product was obtained. Interestingly, when *t*-BuOD was employed as an additive under standard reaction conditions, the deuterated 1,2-diborylated product **3a′** was afforded in 42% yield. The structure of the deuterated product **3a′** was inconsistent with the copper-catalyzed 1,2-diborylation,[8] which suggested that iron-catalyzed defluoroborylation proceeded in a different pathway. Furthermore, other suspected intermediates were synthesized to perform this transformation under standard reaction conditions. To our delight, both monoborylated fluoroalkene **7** and the 1,1-diborylated alkene **8** could undergo this 1,2-

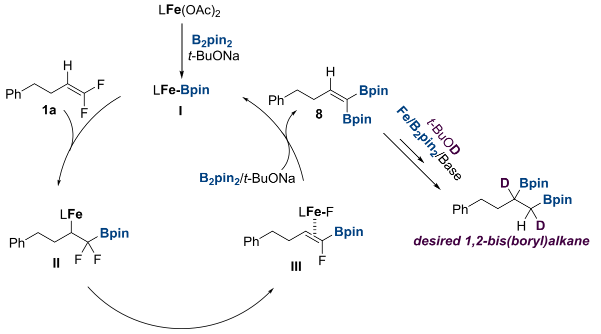
Scheme 3. Mechanistic Studies



diborylation, providing the corresponding deuterated product in comparable yield (Scheme 3C). The 1,2-diborylated alkene **9** could also perform this transformation,[14] but no deuterated product **3a′** was observed. These results indicated that compounds **7** and **8** might be the intermediates of this reaction.

According to these mechanistic studies, a proposed pathway for the iron-catalyzed 1,2-diborylation was provided, as shown in Scheme 4. First, the iron−borane complex **I** was generated

Scheme 4. Proposed Mechanism



and then inserted into the *gem*-difluoroalkene **1a**. Subsequently, the monoborylated fluoroalkene **7** was formed through β-F elimination,[4d] which performed the second borylation reaction to afford the 1,1-diborylated alkene **8**. Finally, the critical compounds **7** and **8** underwent further transformations to obtain the desired 1,2-diborylated product, but the mechanism of this process is still unclear.

In conclusion, we have developed an efficient iron-catalyzed protocol for the 1,2-diborylation of unactivated *gem*-difluoroalkenes. This reaction exhibits a wide range of substrates and excellent functional group tolerance. Moreover, the products 1,2-diborylated alkanes could be further converted into other functional molecules, thus providing excellent opportunities for the diversification of *gem*-difluoroalkenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01967.

Experimental data and copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds (PDF)

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#S.Z. and Y.P. contributed equally.

Notes

The authors declare no competing financial interest.

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