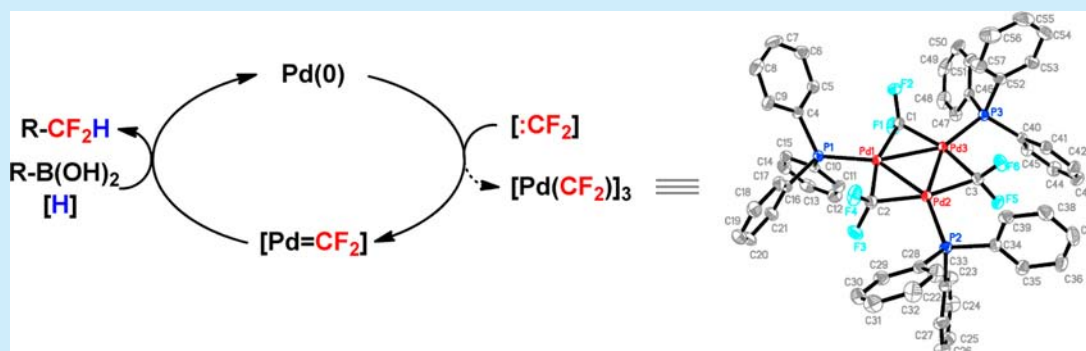


## Pd-Catalyzed Transfer of Difluorocarbene

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## S Supporting Information



**ABSTRACT:** The study of transition-metal difluorocarbene complex has long been a subject of active investigation, but the transition-metal-catalyzed transfer of difluorocarbene remains a significant challenge. The Pd-catalyzed transfer of difluorocarbene is described to realize the coupling reaction of boronic acids with difluorocarbene to give (difluoromethyl)arenes and -olefins. Mechanistic investigations reveal that the  $\text{Pd}=\text{CF}_2$  complex is an important intermediate for this transformation. This complex is prone to trimerization without the presence of starting materials.

The past decades have witnessed outstanding advances in the chemistry of difluorocarbene,<sup>1</sup> but research on the transformation of difluorocarbene is now bottlenecked by the limited reaction classes. Unlike the nonfluorinated carbene complex, metal difluorocarbene complex has seldom been used in organic reactions.<sup>2</sup> Although a number of approaches have been developed to produce the difluorocarbene complex,<sup>2–4</sup> the transfer of difluorocarbene catalyzed by metal has been found to be a very difficult task. The  $\text{metal}=\text{CF}_2$  complex, an important intermediate for the transfer reaction, may be quite sensitive to moisture, and the difluorocarbene would be easily converted into carbon monoxide (CO) by hydrolysis.<sup>2,3</sup> Some complexes are stable against moisture, but the  $\text{M}=\text{CF}_2$  bond ( $\text{M}$  = transition metal) is so strong that the  $\text{CF}_2$  moiety cannot be smoothly transferred.<sup>4</sup> Intramolecular migratory insertion of difluorocarbene would produce a new complex that cannot readily undergo demetalation, thus prohibiting further transfer of the difluorocarbene.<sup>5</sup> In addition, even if the transfer of difluorocarbene from a stoichiometric  $\text{M}=\text{CF}_2$  complex to a reaction partner can occur, it is still not easy to realize the catalytic versions. Apparently, both the facile formation of the difluorocarbene complex and the efficient cleavage of the  $\text{M}=\text{CF}_2$  bond are vital factors for the catalytic transfer of difluorocarbene.

Recently, Takahira and Morizawa reported Ru-catalyzed mild olefin cross-metathesis with tetrafluoroethylene to give *gem*-difluoroolefins.<sup>6</sup> The  $\text{Ru}=\text{CF}_2$  complex was believed to be generated and difluorocarbene in the complex was transferred, but this  $\text{CF}_2$  moiety was unwanted and released to form a side

product. Zhang et al. described the Pd-catalyzed difluoromethylation of arylboronic acids with bromodifluoroacetate to afford the difluoromethylated arenes.<sup>7</sup> They proposed that the  $\text{Pd}=\text{CF}_2$  complex was formed and the  $\text{CF}_2$  moiety was transferred to give the difluoromethylation products, whereas no strong and direct evidence was found to support the palladium–difluorocarbene process. We have been interested in the chemistry of difluorocarbene and have developed an efficient difluorocarbene reagent,  $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$  (PDFA).<sup>8</sup> Our previous observation implies that Cu might be able to transfer difluorocarbene,<sup>8k</sup> but stoichiometric copper must be used and the  $\text{Cu}=\text{CF}_2$  complex could not be identified. Herein, we report the Pd-catalyzed transfer of difluorocarbene to realize the coupling reaction of boronic acids with difluorocarbene in situ produced from PDFA to afford (difluoromethyl)arenes and -olefins.<sup>9</sup> The Pd source could react with PDFA to furnish a  $\text{Pd}-\text{CF}_2$  complex, which was confirmed by X-ray crystallography.

We have shown that *p*-xylene is an appropriate solvent for the dissociation of PDFA into difluorocarbene.<sup>8j</sup> Our initial attempts at the Pd-catalyzed difluorocarbene transfer in *p*-xylene at 70 °C showed that both a weak acid and a base were necessary (Table 1, entries 1–5). The weak acid was the proton source for the installation of difluoromethyl group, while the base may promote the transmetalation of boronic acid with the Pd complex.<sup>10</sup> The presence of water increased the yield

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Table 1. Screening Reaction Conditions

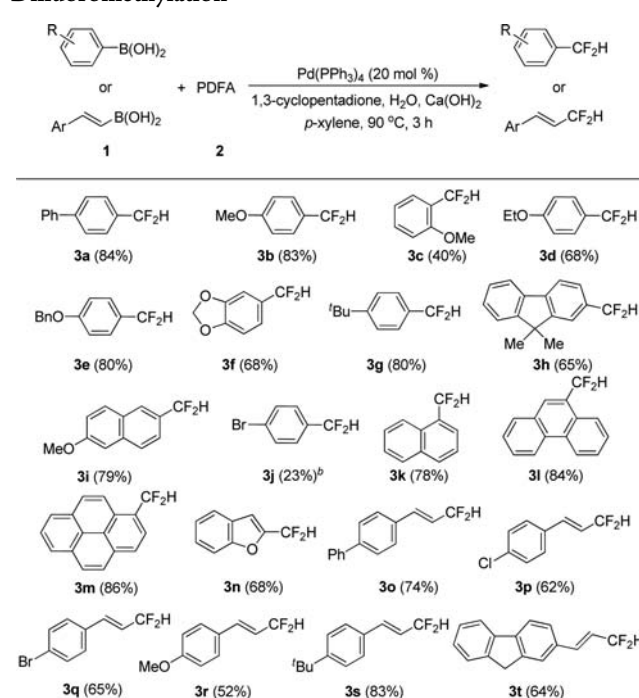
entry	[H <sup>+</sup> ]	H <sub>2</sub> O (equiv)	base (equiv)	temp (°C)	yield <sup>a</sup> (%)
1			K <sub>2</sub> CO <sub>3</sub> (2.5)	70	trace
2	H <sub>2</sub> O		K <sub>2</sub> CO <sub>3</sub> (2.5)	70	trace
3	HCO <sub>2</sub> H		K <sub>2</sub> CO <sub>3</sub> (2.5)	70	5
4	CH <sub>3</sub> COCO <sub>2</sub> H		K <sub>2</sub> CO <sub>3</sub> (2.5)	70	13
5	dione <sup>b</sup>		K <sub>2</sub> CO <sub>3</sub> (2.5)	70	27
6	dione	2.5	K <sub>2</sub> CO <sub>3</sub> (2.5)	70	42
7	dione	2.5	KOH (2.5)	70	33
8	dione	2.5	CsF (2.5)	70	14
9	dione	2.5	Ca(OH) <sub>2</sub> (2.5)	70	48
10	dione	2.5	Ca(OH) <sub>2</sub> (4.0)	70	61
11	dione	2.5	Ca(OH) <sub>2</sub> (4.0)	60	45
12	dione	2.5	Ca(OH) <sub>2</sub> (4.0)	80	67
13	dione	2.5	Ca(OH) <sub>2</sub> (4.0)	90	74
14	dione	2.5	Ca(OH) <sub>2</sub> (4.0)	100	62
15 <sup>c</sup>	dione	2.5	Ca(OH) <sub>2</sub> (4.0)	90	82
16 <sup>d</sup>	dione	2.5	Ca(OH) <sub>2</sub> (4.0)	90	90

<sup>a</sup>Determined by <sup>19</sup>F NMR using PhCF<sub>3</sub> as an internal standard.

<sup>b</sup>Dione = 1,3-cyclopentadione. <sup>c</sup>4 equiv of PDFA was used. <sup>d</sup>5 equiv of PDFA was used.

slightly (Table 1, entry 6 vs entry 5) because it is favorable for the transmetalation process by dissolving the base. A brief survey of the base (Table 1, entries 6–9) revealed that a higher yield could be obtained by using Ca(OH)<sub>2</sub> (Table 1, entry 9). Increasing the loading of Ca(OH)<sub>2</sub> further increased the yield (Table 1, entry 10 vs entry 9). The reaction temperature was also an important factor for the transfer process (Table 1, entries 10–14), where lowering the temperature led to a decrease in the yield (Table 1, entry 11 vs entry 10). Elevating the temperature to 90 °C gave a good yield of the product (Table 1, entry 13), but the yield was decreased with further temperature elevation (Table 1, entry 14). The loading of PDFA apparently affected the yield (Table 1, entries 15–16), and a 90% yield was obtained with the use of 5 equiv of PDFA (Table 1, entry 16) (For more reaction conditions, see the Supporting Information). Under these optimal conditions, *O*-difluoromethylation of dione to produce 3-(difluoromethoxy)-cyclopent-2-en-1-one was observed as a side reaction.

With the optimal reaction conditions obtained (Table 1, entry 16), we then investigated the scope of substrates for the Pd-catalyzed difluorocarbene transfer reaction. As shown in Scheme 1, the transformation can be applied not only to arylboronic acids (3a–n) but also to vinylboronic acids (3o–t). Electron-rich and -neutral arylboronic acids were adequately converted into the desired products in moderate to good yields (3a–i and 3k–m). A significantly higher yield of the *p*-MeO-substituted product (3b) was obtained compared with that of the *o*-MeO-substituted product (3c), which may be owing to steric effects. In the case of an electron-deficient aryl substrate, the desired product was produced in low yields (3j). In contrast, the difluorocarbene transfer protocol was suitable for

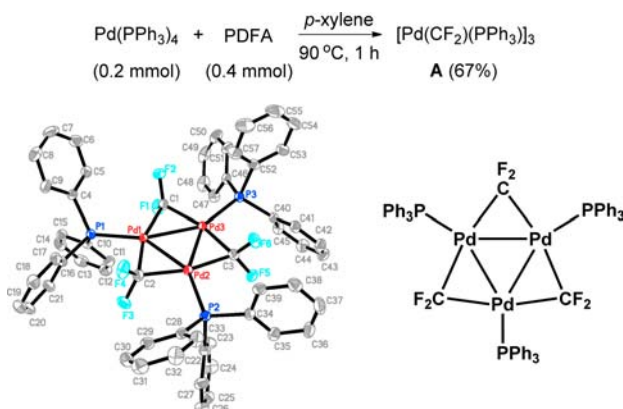
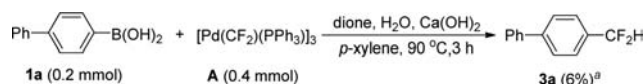
Scheme 1. Pd-Catalyzed Transfer of Difluorocarbene for Difluoromethylation<sup>a</sup>

<sup>a</sup>Reaction conditions: mixture of 1 (0.2 mmol), 2 (1.0 mmol), 1,3-cyclopentadione (0.2 mmol), Ca(OH)<sub>2</sub> (0.8 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 mmol) and H<sub>2</sub>O (0.5 mmol) in *p*-xylene (2 mL) was stirred at 90 °C for 3 h under N<sub>2</sub> atmosphere. <sup>b</sup>The yield was determined by <sup>19</sup>F NMR using PhCF<sub>3</sub> as an internal standard.

the conversion of electron-rich, -neutral, and -deficient vinylboronic acids (3o–t). It is noteworthy that only one single stereoisomer of the desired products was observed for the conversion of vinylboronic acids.

[Ph<sub>3</sub>P<sup>+</sup>CF<sub>2</sub>H X<sup>−</sup>] was observed as a side product detected by <sup>19</sup>F NMR spectroscopy in the difluorocarbene transfer process. However, no desired product was obtained using [Ph<sub>3</sub>P<sup>+</sup>CF<sub>2</sub>H Br<sup>−</sup>] instead of [Ph<sub>3</sub>P<sup>+</sup>CF<sub>2</sub>CO<sub>2</sub><sup>−</sup>] (PDFA), indicating that the conversion of PDFA into [Ph<sub>3</sub>P<sup>+</sup>CF<sub>2</sub>H X<sup>−</sup>] is not a necessary path for this transformation. We therefore reason that PDFA may readily undergo decarboxylation and subsequent dissociation to generate difluorocarbene, which then coordinates with the Pd source. Indeed, it was found that Pd(Ph<sub>3</sub>P)<sub>4</sub> can react with PDFA to give a Pd–CF<sub>2</sub> complex A, [Pd(CF<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>], which may be produced from the Pd=CF<sub>2</sub> monomer through trimerization (Scheme 2). The structure of this complex was confirmed by X-ray crystallography.<sup>11</sup> Interestingly, the bond lengths [2.051(3)–2.090(3) Å] of the six Pd–CF<sub>2</sub> bonds are slightly different, as are the lengths of the three Pd–Pd bonds [2.5891(3)–2.5916(3) Å] (see the Supporting Information). The length of any Pd–CF<sub>2</sub> bond is shorter than the sum (2.15 Å) of the covalent radii between the Pd (1.39 Å) and C (0.76 Å) atom, implying that a strong interaction between Pd and CF<sub>2</sub> exists.

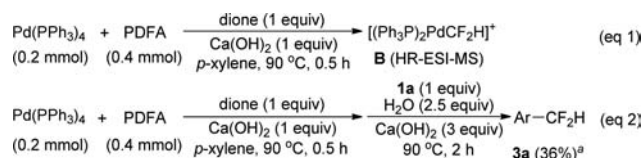
The Pd–CF<sub>2</sub> complex A was detected by <sup>19</sup>F NMR spectroscopy (<5%) in the difluorocarbene transfer reaction, and the use of complex A instead of the Pd/PDFA system could also produce the expected coupling product albeit at a low yield (6%) (Scheme 3). It is reasonable to speculate that the real active intermediate for the transfer reaction is not the trimer A but a palladium–difluorocarbene monomer. The

Scheme 2. Formation of the Pd–CF<sub>2</sub> ComplexScheme 3. Difluoromethylation with Pd–CF<sub>2</sub> Trimer

<sup>a</sup>Determined by <sup>19</sup>F NMR using PhCF<sub>3</sub> as an internal standard.

monomer would readily undergo trimerization to produce **A** without the presence of starting materials. The low yield obtained by using trimer (**Scheme 3**) might be because the detrimerization of **A** to generate the monomer was not easy or the trimer may undergo decomposition to give other unknown species instead of monomer.

Because the Pd=CF<sub>2</sub> monomer may be the active species, we then collected more experimental data to determine how this species is converted. Stirring the Pd/PDFA system with the mixture of dione/Ca(OH)<sub>2</sub> (dione = 1,3-cyclopentadione) produced a Pd–CF<sub>2</sub>H complex **B**, which was confirmed by <sup>19</sup>F NMR and HR ESI-MS (**Scheme 4**, eq 1) (see the [Supporting](#)

Scheme 4. Conversion of Pd=CF<sub>2</sub> monomer to Pd–CF<sub>2</sub>H

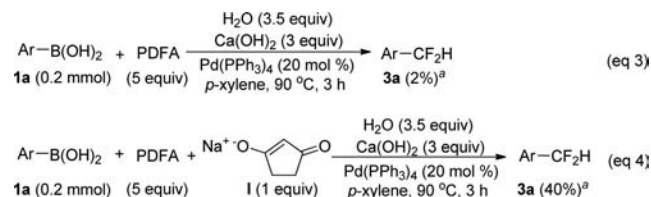
<sup>a</sup>Determined by <sup>19</sup>F NMR using PhCF<sub>3</sub> as an internal standard.

**Information**). After complex **B** was generated and the PDFA was completely consumed, the addition of substrate **1a** and water into the reaction mixture furnished the expected product (**Scheme 4**, eq 2). It seems that the Pd=CF<sub>2</sub> monomer can be easily protonated by the dione/Ca(OH)<sub>2</sub> system to give Pd–CF<sub>2</sub>H **B**, which should be an important intermediate for this difluorocarbene transfer reaction. How the protonation process proceeds remains elusive. The proton may directly attack at the CF<sub>2</sub> moiety, but it may also first attack at Pd to afford HPd<sup>+</sup>=CF<sub>2</sub>, which was followed by intramolecular proton migration to produce **B**.

The 1,3-cyclopentadione is a weak acid and Ca(OH)<sub>2</sub> is a strong base, meaning that the dione/Ca(OH)<sub>2</sub> system might undergo full neutralization to produce 1 equiv of water (**Scheme 4**, eq 1). However, the addition of 1 equiv of water instead of dione/Ca(OH)<sub>2</sub> to the Pd/PDFA system did not result in the desired protonation to afford the Pd–CF<sub>2</sub>H

complex, suggesting that the dione is necessary for the formation of complex **B**. Indeed, under the optimal reaction conditions, except that the additional 1 equiv of water was used instead of dione (1 equiv)/Ca(OH)<sub>2</sub> (1 equiv), only trace amounts of the desired product (2%) was observed (**Scheme 5**,

Scheme 5. Effects of Dione

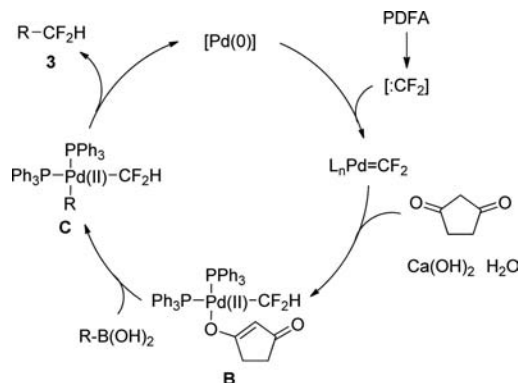


<sup>a</sup>Determined by <sup>19</sup>F NMR using PhCF<sub>3</sub> as an internal standard.

eq 3). However, although the presence of the basic form of 1,3-cyclopentadione (compound **I**) can significantly increase the yield (40% vs 2%), the yield was still quite low (**Scheme 5**, eq 4). Apparently, 1,3-cyclopentadione played two important roles in this difluorocarbene transfer reaction. First, after its neutralization with Ca(OH)<sub>2</sub>, the basic form can act as a ligand to coordinate with the Pd complex, which aids the formation of the Pd–CF<sub>2</sub>H complex. Second, compared with water, 1,3-cyclopentadione is also a superior hydrogen source to directly protonate the Pd=CF<sub>2</sub> monomer. Though a strong base can easily neutralize 1,3-cyclopentadione, the low solubility of Ca(OH)<sub>2</sub> may lead to a rather slow neutralization process. Therefore, both water and 1,3-cyclopentadione are proton sources for the conversion of Pd=CF<sub>2</sub> to Pd–CF<sub>2</sub>H.

On the basis of the above results, we propose the reaction mechanism shown in **Scheme 6**. Decarboxylation and further

Scheme 6. Proposed Reaction Mechanism



dissociation of PDFA generate difluorocarbene.<sup>8a,j</sup> Difluorocarbene then coordinates with the Pd source to produce the Pd=CF<sub>2</sub> complex, whose protonation gives the intermediate **B**. In the protonation process, both dione and water may be the possible proton sources, but dione should be the superior one. The proton may attack at two different sites in the monomer, Pd or CF<sub>2</sub>.<sup>4c</sup> If it attacks at Pd, the intramolecular proton migration would then occur to produce the complex **B**. The coordination of the basic form of dione with Pd is very important for the formation of complex **B**. Transmetalation of boronic acid with **B** affords the intermediate **C**, whose reductive elimination affords the final product and regenerates the catalyst.



In summary, we have developed an efficient Pd-catalyzed difluorocarbene transfer reaction for the coupling reaction of boronic acids with difluorocarbene to furnish (difluoromethyl)-arenes and -olefins. This work represents the first example providing valuable experimental evidence to elucidate the mechanism for the palladium-catalyzed difluorocarbene transfer reaction. The mechanism investigations revealed the formation of the palladium–difluorocarbene complex, which was prone to trimerization. This convenient strategy may find widespread applications in other transition-metal-catalyzed difluorocarbene transfer reactions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02141.

Experimental procedures, analytical data for products, X-ray data, and NMR spectra of products (PDF)

X-ray data for the Pd–CF<sub>2</sub> complex (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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