

Palladium-Catalyzed Base-Free Suzuki–Miyaura Coupling Reactions of Fluorinated Alkenes and Arenes via a Palladium Fluoride Key Intermediate

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A new strategy for C–C bond formation with organoboronates through C–F activation of fluorinated alkenes and arenes was developed. In this Pd-catalyzed Suzuki–Miyauratype cross-coupling reaction, neither a base for enhancing the reactivity of the organoboron reagents nor a Lewis acid

Introduction

Over the past few decades, the transition-metal-mediated activation of carbon-fluorine bonds has attracted much attention because this bond is thermally and chemically robust and because this bond can undergo a number of unique functionalization reactions for the preparation of intricate compounds that are otherwise difficult to prepare.^[1] We have recently demonstrated the palladium-catalyzed coupling reaction of tetrafluoroethylene (TFE) with arylzinc compounds to yield (α,β,β-trifluoro)styrene derivatives.^[2] Our next concern is to apply the C(sp²)-F bond activation methodology to Suzuki-Miyaura-type C-C bondforming reactions, which generally tolerate a broad range of functional groups.^[3] So far, most of the reported Suzuki-Miyaura-type reactions that occur through C-F bond activation, which are performed with either highly electron-deficient organofluorine compounds or compounds bearing a directing group, have been conducted in the presence of a base (Scheme 1a),^[4] whereas the fluoride anion itself is regarded as a good activator for neutral organoboron compounds.^[5,6] In fact, Widdowson noted the possibility that the use of an extraneous base should be, in principle, catalytic:^[4a] however, such a reaction has not been developed. We speculated that if the transition-metal fluorides (R-TM-F) generated by direct oxidative addition of a C-F bond would have reactivity that was high enough to act as a fluoride donor, the development of base-free C-C couplings with organoboron reagents would be a significant development to Suzuki-Miyaura couplings with organofluorine

Homepage: http://www.chem.eng.osaka-u.ac.jp/~ogoshi-lab/ english/indexEN.html for promoting C–F bond activation was required. A fluoropalladium intermediate played an essential role in this reaction. In addition, a Ni(NHC) catalyst was efficient for C–C coupling through C–F bond activation of fluoroarenes.

compounds (Scheme 1b). Herein, we report the first basefree C–C bond-forming reactions of perfluoroalkenes with arylboronates in the presence of a Pd^0 catalyst. This reaction was successfully expanded to other fluorinated alkenes as well as fluorinated arenes.



Scheme 1. Possible path for the Suzuki–Miyaura coupling reaction based on C–F bond activation reactions: (a) The previously reported reactions conducted in the presence of a base, (b) the key role of metal fluoride in novel base-free Suzuki–Miyaura-type reactions, (c) C–F bond cleavage assisted by Lewis acids following C– C bond formation in the presence of base.

Results and Discussion

We first began by seeking an active species that could cleave the C–F bond of TFE without additives, because our original protocol involving the use of Lewis acid additives (MX) inevitably lost the chance to generate the transitionmetal fluoride intermediate in return for efficient C–F bond cleavage, and the extraneous addition of base was thereby required (Scheme 1c).^[2,7,8] As a result, the thermolysis of $[(\eta^2-CF_2=CF_2)Pd(PCy_3)_2]$ (1a)^[9,10] in THF at 100 °C under a N₂ atmosphere underwent C–F bond activation of TFE to yield expected trifluorovinylpalladium(II) fluoride 2 in 45% yield (Scheme 2). Analysis by NMR spectroscopy revealed the concomitant formation of palladium 2-per-

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fluorobutenyl species $3^{[11]}$ The recovery of $[Pd(PCy_3)_2]$ (26%) indicated the existence of a coordination-dissociation equilibrium of TFE to palladium under the reaction conditions. Thus, this reaction was carried out under a TFE atmosphere (1 atm), and this resulted in an improved yield of 2. By contrast, C-F bond activation did not proceed at all by heating the PPh₃ analogue, $[(\eta^2-CF_2=CF_2)Pd (PPh_3)_2$] (1b); instead, the decomposition of 1b along with the liberation of a molecule of TFE and the precipitation of Pd black was observed.^[2] In addition, the nickel analogue, $[(\eta^2-CF_2=CF_2)Ni(PCy_3)_2]$ (4), was found to cleave the C-F bond of TFE at 100 °C under a N2 atmosphere to give corresponding trifluorovinylnickel fluoride 5 in 70% yield (Scheme 2).^[9] However, conducting this reaction under a TFE atmosphere (1.0 atm) resulted in the formation of difluorophosphorane, F₂PCy₃, and desired complex 5 was not obtained at all. Characteristic upfield-shifted resonance attributable to a fluorine adjacent to a group 10 metal appeared at $\delta = -317.9$ and -385.7 ppm in the ¹⁹F NMR spectrum of 2 and 5, respectively. The structures of palladium and nickel fluorides 2 (Figure 1) and 5, respectively, were unambiguously determined by X-ray diffraction analysis.^[12,13] To the best of our knowledge, examples of fluoropalladium complexes generated by oxidative addition of a C-F bond are very rare.^[4i,14] In addition, complexes 2 and 5 are the first examples of structurally well-defined oxidative addition products of TFE on transition metals without the use of Lewis acid additives.



Scheme 2. Generation of trifluorovinylpalladium(II) and trifluorovinylnickel(II) fluorides by direct oxidative addition of TFE.

We next examined the reaction of **2** with a stoichiometric amount of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**6a**) to evaluate the degree of reactivity of **2** towards organoborane reagents. Treatment of **2** with **6a** (4 equiv.) in THF at 100 °C for 2 h gave desired coupling product (α , β , β -trifluoro)styrene (**7a**) in 75% yield (Scheme 3). In contrast, no C–C bond formation occurred, even after a prolonged reaction time when **6a** was treated with corresponding palladium iodide **8a**, which reacts with ZnPh₂.^[9] In addition, neither palladium bromide **8b** nor palladium chloride **8c** underwent the coupling reaction with **6a**.^[9] Furthermore, trifluorovinylnickel fluoride **5** also reacted with **6a** to afford **7a** in 61% yield, whereas corresponding nickel iodide **9a** did not give **7a** at all. These observations clearly show that C–C bond formation with organoboron compounds is



Figure 1. ORTEP drawing of 2 with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

unique to metal fluorides **2** and **5** among all the other corresponding metal halides.^[4e] In fact, the Pd⁰-catalyzed coupling reaction of chlorotrifluoroethylene with **6a** in the absence of base did not give any coupling product, probably as a result of the generation of an unreactive trifluorovinyl-palladium chloride intermediate.^[15]



Scheme 3. Reactivity of group 10 trifluorovinyl halides towards 6a.

It seemed logical to use this reaction scheme to conduct a palladium- or nickel-catalyzed cross-coupling reaction of TFE with **6a**. In the presence of Pd(dba)₂ (10 mol-%) and PCy₃ (20 mol-%), the coupling reaction of TFE with **6a** took place at 100 °C in the absence of any additive to give desired product **7a** in 66% yield.^[16] This result pointed out that the reaction proceeds even in the absence of a base, whereas the use of a base is generally indispensable for the Suzuki–Miyaura coupling reaction to enhance the reactivity of the organoboron reagents. The addition of cesium carbonate did not affect the yield of **7a**. In contrast, in the absence of any additive, the use of $[Ni(cod)_2/PCy_3]$ (10/20 mol-%) gave only a small amount of **7a** (5%). This is probably rationalized by the fact that potential η^2 -TFE nickel precursor **4** gradually decomposes under the TFE atmosphere (Scheme 2). Further optimization of the cross-coupling reaction of TFE with arylboronates was conducted by using a Pd⁰ species.^[16] As a result, the reaction of TFE with **6a** at 100 °C in the presence of [Pd(dba)₂/P*i*Pr₃] in THF led to the formation of desired product **7a** in 87% yield.^[17]

With the optimized reaction conditions, the scope of the cross-coupling reaction was investigated with respect to the arylboronates (Table 1). Reactions with naphthylboronates (6b, Ar = 1-naphthyl; 6c, Ar = 2-naphthyl) gave 7b and 7c in 88 and 73% yield, respectively, and furthermore, the reaction with 1-pyrenylboronate (6d) gave 7d in moderate yield. In addition, the reactions with 4-trifluoromethylphenyl-, 4-anisyl-, and 4-vinylphenylboronates (i.e., 6e-g) also afforded the corresponding trifluorostyrene derivatives (i.e., 7e-g) in good to moderate yields. Of the 4-halogenophenylboronates employed, 4-fluorophenyl- and 4-chlorophenylboronates gave *p*-fluoro- and *p*-chloro-substituted $(\alpha,\beta,\beta$ -trifluoro)styrenes **7h** and **7i** in 74 and 76% yield, respectively, whereas no coupling product was obtained with 4-bromophenylboronate, probably because of the occurrence of undesired oxidative addition of the C-Br bond. The reaction with 2-benzofulylboronate (6i) yielded corresponding product 7j in moderate yield. In some cases, relatively lower isolated yields were obtained relative to the yields calculated by NMR spectroscopy because of the high volatility of the compounds at room temperature.

Although this catalytic reaction leaves much to be desired with regard to the catalyst loading and the product yield, it is of great significance in preparing trifluorostyrene derivatives substituted with nitro, aldehyde, ester, and cyano groups (i.e., 7k-n). These functional groups can easily react with Grignard reagents that are required for the in situ preparation of organozinc reagents, and therefore, products 7k-n are difficult to synthesize from a coupling reaction with organozinc reagents. In addition, bis(boronate) reagents such as 4,4'-biphenyldiboronate (**60**) can be used to prepare monotrifluorovinyl compounds, and the unreacted boronate moiety can be used in further cross-coupling reactions to synthesize highly functionalized derivatives.^[18]

This base-free coupling reaction with arylboronates can be expanded to other organofluorine molecules. The reaction of vinylidene fluoride with **6b** proceeded in the presence of Pd⁰/PiPr₃ to give 1-(1-fluorovinyl)naphthalene (**11**) in 86% yield (Scheme 4a). In addition, the corresponding reaction with hexafluoropropylene gave a mixture of regioisomers **12** (Scheme 4b).^[19] Although the Pd⁰ catalyst was ineffective,^[20] [{Ni(*i*Pr₂Im)₂}₂(cod)] {*i*Pr₂Im = 1,3-bis-(isopropyl)imidazolin-2-ylidene}^[21] showed catalytic activity towards the base-free coupling reaction of fluoroarenes (Scheme 4c). That is, the reaction of octafluorotoluene with **6f** in THF at 100 °C for 10 h gave desired product



Table 1. Substrate scope.^[a]



[a] General conditions: **6** (1.00 mmol), solvent (10.0 mL), TFE (3.5 atm). Yields were determined by analysis of the crude product by ¹⁹F NMR spectroscopy with α,α,α -trifluorotoluene as an internal standard. The values in square brackets are the isolated yields. [b] Using PnBu₃ instead of P*i*Pr₃. [c] Reaction conditions: **60** (0.30 mmol), solvent (1.5 mL), TFE (30 mg, 0.30 mmol). Analysis by NMR spectroscopy revealed that 29% of **60** remained and that the bistrifluorovinyl compound was generated in 7% yield. [d] Reaction conditions: **60** (0.95 mmol), solvent (10.0 mL), TFE (100 mg, 1.00 mmol). After the isolation procedure, 130 mg (36%) of **60** was recovered and the bistrifluorovinyl compound was isolated in 10% yield.

13 in excellent yield. The use of hexafluorobenzene allowed the formation of corresponding biphenyl 14. Moreover, this base-free coupling protocol can be applied to fluorobenzene, which needed to be used as a solvent, to give 4-methoxybiphenyl (15). Unlike the catalytic reaction with TFE, the usefulness of the nickel species in the base-free coupling

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Scheme 4. Group 10 metal catalyzed base-free cross-coupling reaction of fluorinated compounds with arylboronate **6**. Yields were determined by analysis of the crude product by ¹⁹F NMR spectroscopy with α,α,α -trifluorotoluene as an internal standard. Isolated yields are given in square brackets. Note that in the preparation of **15**, C₆H₅F was used as the reaction solvent (1 mL).

On the basis of the results described above, the additivefree, Pd-catalyzed monoaryl substitution of TFE might proceed as follows (Scheme 5). Coordination of a molecule of TFE to Pd⁰ takes place to generate η^2 -TFE species **A**. Then, the combination of Pd⁰ and the trialkylphosphane, which is a strong σ -donor, enables the oxidative addition of a C–F bond to Pd⁰ with no additives, and this generates trifluorovinylpalladium(II) fluoride intermediate **B**. Transmetalation of **B** with the arylboronate^[23] gives **C**. Reductive elimination then affords **7** along with regeneration of the

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Scheme 5. A plausible reaction mechanism.

Pd⁰ species and the boron fluorides.^[24] It should be emphasized that no extraneous base was required at all in this reaction, although extraneous base is generally a requisite for the Suzuki–Miyaura cross-coupling reaction to promote the transmetalation step with the organoboron reagent.

Conclusions

In summary, we demonstrated the Pd^0/PR_3 -catalyzed cross-coupling reaction of fluoroalkenes with arylboronates, in which neither an extraneous base to enhance the reactivity of the organoboronates nor a Lewis acid additive to promote the oxidative addition of the C–F bond was required. The key palladium(II) fluoride intermediate that showed unique reactivity towards the organoboron compounds was isolated. We also successfully expanded this novel coupling reaction with arylboronates to fluoroarenes by using a Ni⁰/NHC catalyst. These results may open new avenues for the development of a base-free Suzuki–Miyaura coupling reaction, including the in situ generation of a metal fluoride intermediate through C–F bond activation.

Experimental Section

General Procedure for the Pd⁰-Catalyzed Coupling Reaction of TFE with 5,5-Dimethyl-2-aryl-1,3,2-dioxaborinane (6): All catalytic reactions were conducted in a pressure-tight NMR tube (Wilmad-LabGlass, 524-PV-7) and monitored by ¹¹B NMR and ¹⁹F NMR spectroscopy. A mixture of **6** (0.10 mmol), Pd(dba)₂ (5.6 mg, 0.01 mmol), P*i*Pr₃ (3.2 mg, 0.02 mmol), and α,α,α -trifluorotoluene (12.0 µL, 0.097 mmol; as an internal standard for ¹⁹F NMR spectroscopy) was dissolved in THF/[D₈]THF (4:1 v/v, 0.5 mL). The resulting solution was transferred into the NMR tube, which was then charged with TFE (3.5 atm, >0.30 mmol). The reaction mixture was thermostatted at 100 °C until the reaction was terminated. Monitoring the reaction and determination of the yield of **7** were performed by ¹⁹F NMR spectroscopy.

Isolation of 7: A mixture of 6 (1.00 mmol), Pd(dba)₂ (56.5 mg, 0.10 mmol), and PiPr₃ (32.0 mg, 0.20 mmol) was dissolved in THF (10.0 mL). The resulting solution was transferred into an autoclave reactor, and then TFE (3.5 atm) was charged into the reactor. The reaction mixture was thermostatted at 105 °C (in most cases, the reaction bath temperature was set higher than that of the tube experiment in view of the thermal gradient in the autoclave reactor) for the given reaction time. After the unreacted TFE was purged from the reactor (Caution! The reaction mixture must be handled in a well-ventilated fume hood), the reaction mixture was concentrated in vacuo. Pentane was added to the residue, and the resulting suspension was filtered through a short silica column. The filtrate was concentrated in vacuo and purified by HPLC (CHCl₃). The desired compounds were isolated as a CHCl₃ solution because of their high vapor pressure and/or the occurrence of cyclodimerization at higher concentrations. Yields were determined by ¹⁹F NMR spectroscopy with α, α, α -trifluorotoluene as an internal standard.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures and analytical and spectroscopic data for all new compounds.

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