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Palladium-Catalyzed Coupling Reactions of Tetrafluoroethylene with Arylzinc Compounds

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Supporting Information

ABSTRACT: Organofluorine compounds are widely used in all aspects of the chemical industry. Although tetrafluoroethylene (TFE) is an example of an economical bulk organofluorine feedstock, the use of TFE is mostly limited to the production of poly(tetrafluoroethylene) and copolymers with other alkenes. Furthermore, no catalytic transformation of TFE that involves carbon−fluorine bond activation has been reported to date. We herein report the first example of a palladium-catalyzed coupling reaction of TFE with arylzinc reagents in the presence of lithium iodide, giving α,*β*,*β*-trifluorostyrene derivatives in excellent yields.

Organofluorine compounds are important components of a variety of commercial products.[1] Therefore, an economical, bulk organofluorine feedstock is needed as the starting material for the synthesis of commercial products. Tetrafluoroethylene (TFE) is an ideal starting material because it is industrially an economical bulk organofluorine feedstock for the production of poly(tetrafluoroethylene) and copolymers with other alkenes.[2] However, only a few reactions that substitute carbon nucleophiles for a fluorine on TFE to form a new C−C bond have been reported.[3] Moreover, the previously described reactions suffer from undesired side reactions, even at low reaction temperatures.[3a,3b] Recently, homogeneous catalytic reactions involving C−F bond activation have received increasing attention.[4−9] However, to the best of our knowledge, no catalytic reactions that involve TFE have been reported.[10] Therefore, the development of a selective transition-metal-catalyzed transformation of TFE via C−F bond activation would be a remarkable breakthrough that would greatly increase the potential of TFE as a useful starting material for a variety of organofluorine compounds. To date, C−F bond activation in TFE has been achieved only in a few stoichiometric reactions.[11] In a groundbreaking study of C−F bond activation in TFE, Hacker, Littlecott, and Kemmitt[11a] reported that LiI promotes the oxidative addition of TFE to Pt(0). This observation inspired us to develop a transition-metal-catalyzed cross-coupling reaction of TFE with organometallic compounds. Herein we report the formation, structure, and reactivity of a trifluorovinylpalladium complex obtained by oxidative addition of the C−F bond of TFE to Pd(0) promoted by LiI. Moreover, a novel Pd-catalyzed coupling reaction of TFE with arylzinc compounds is also discussed.

Reaction of (η^2-$CH_2{=}CH_2$)$Pd(PPh_3)_2$[12] with TFE (**1**; 1 atm) in toluene for 1 h resulted in substitution of the coordinated ethylene, giving (η^2-$CF_2{=}CF_2$)$Pd(PPh_3)_2$ (**2**) in 96% isolated yield.[13] In contrast, treatment of $Pd_2(dba)_3$ with **1** in the presence of PPh_3 (2 equiv relative to Pd) gave an equilibrium mixture of **2** and (η^2-dba)$Pd(PPh_3)_2$[14] even under high-pressure (3.5 atm) conditions. X-ray diffraction study of **2** clearly demonstrated that a TFE molecule is coordinated to the Pd atom with a trigonal-planar coordination geometry (Figure 1).

Addition of LiI to a solution of **2** in THF promoted the oxidative addition of a C−F bond, which proceeded smoothly to afford a trifluorovinylpalladium(II) iodide species (**3**) in nearly quantitative yield (Scheme 1). In contrast to the known Pt analogue,[11a] the C−F bond cleavage on Pd took place without heating of the reaction mixture. An attempt to cleave the C−F bond in **2** at 100 °C without LiI resulted in decomposition of **2** along with the liberation of a TFE molecule and the precipitation of Pd black. Thus, cleavage of the C−F bond to generate trifluorovinylpalladium complex **3** requires LiI. Lithium iodide would act as a Lewis acid to enhance the elimination ability of fluorine. Formation of a strong Li−F bond might also be important for the occurrence of the oxidative addition at room temperature. The ORTEP drawing of **3** (Figure 2) unambiguously shows that the Pd in **3** adopts a square-planar coordination geometry and is coordinated to two PPh_3 ligands in a trans manner. Complex **3** is the first example of a mononuclear trifluorovinyl complex generated by C−F bond cleavage of **1** and having a well-defined structure.[15]

Trifluorovinylpalladium complex **3** seemed to be a promising reaction intermediate for the preparation of various trifluorovinyl derivatives via cross-coupling reactions of TFE with organometallic reagents. In particular, each reaction step in the cross-coupling of TFE with arylmetal reagents to give trifluorovinylarenes must occur at a relatively low temperature, since undesired side reactions of the resulting trifluorovinylarenes give a complex mixture. In fact, [2 + 2] cyclodimerization of α,*β*,*β*-trifluorostyrene occurs in a head-to-head manner at 80 °C to give a mixture of cis and trans isomers.[16] Therefore, **3** was reacted with a stoichiometric amount of $ZnPh_2$ (**4a**) to determine whether the expected reaction to give α,*β*,*β*-trifluorostyrene (**5a**) would occur at room temperature. Although the reaction of **3** with 0.5 equiv of **4a** in THF resulted in a complicated mixture that contained a small amount of the expected compound **5a**, the reaction of **3** with **4a** in the presence of LiI and *trans,trans*-dibenzylideneacetone (DBA) proceeded smoothly to give **5a** in 87% yield (Scheme 1). Both LiI and DBA are potential additives

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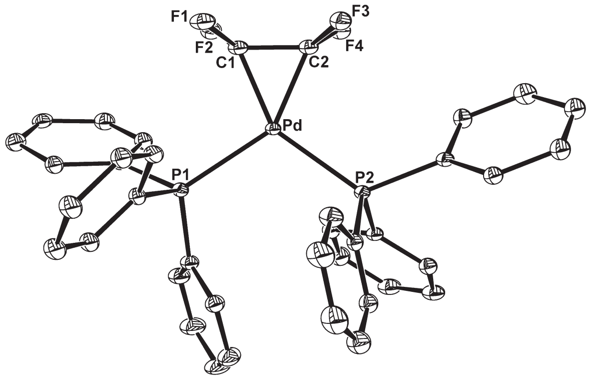


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. H atoms and solvated molecules (toluene) have been omitted for clarity.

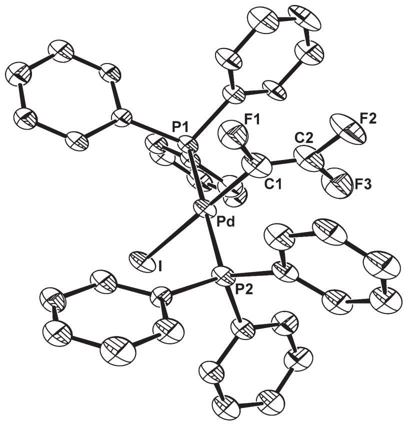
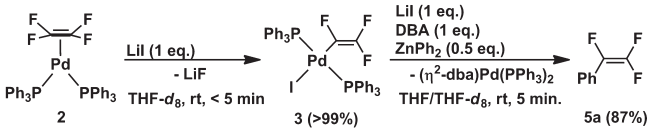


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

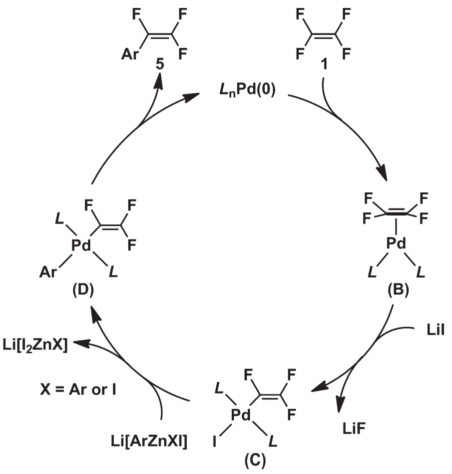
Scheme 1. Transformation of TFE to α,β,β-Trifluorostyrene via C−F Bond Cleavage on Palladium



in the cross-coupling reaction, since the reaction of TFE with $Pd_2(dba)_3$ and PPh_3 in the presence of LiI to give **3** simultaneously yields uncoordinated DBA. The role of LiI in this reaction is the formation of reactive zincates such as Li[ArZnXI] (X = Ar, I; see below).[17] In contrast, Pt is unlikely as a catalyst for the cross-coupling reaction because the oxidative addition of TFE to Pt(0) requires both a much higher temperature and a longer reaction time (95 °C for 24 h).[11a]

It was a logical extension of this reaction scheme to conduct a Pd-catalyzed coupling reaction of **1** with **4a** in the presence of LiI, and the results are summarized in Table 1. In the presence of 5 mol % $Pd_2(dba)_3$ and 20 mol % PPh_3, the coupling reaction of **1** with **4a** (which was prepared in situ by treating $ZnCl_2$ with 2 equiv of PhMgBr) took place at room temperature. The desired product **5a** was obtained in 55% yield (entry 1). As expected from the stoichiometric reactions, the addition of LiI was essential for the Pd-catalyzed coupling reaction (entry 2).

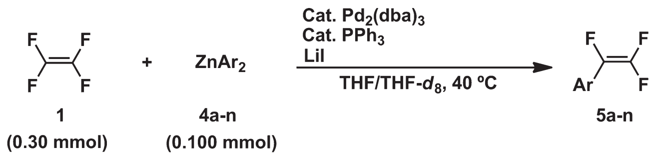
Scheme 2. Plausible Reaction Mechanism



Although either elongation of the reaction time or elevation of the reaction temperature was required, reduced catalyst loading increased the yield of **5a** (entries 3 and 4). Even in the presence of 0.01 mol % $Pd_2(dba)_3$, the catalytic reaction proceeded smoothly at 40 °C to give **5a** in 72% yield (entry 4). The rate of the coupling reaction was remarkably enhanced by omission of PPh_3 from the catalytic system, and **5a** was obtained in 73% yield (entry 5). Under the same reaction conditions, the reaction with isolated $ZnPh_2$ occurred somewhat slowly relative to that with $ZnPh_2$ prepared in situ (entry 6). In contrast, in the absence of Pd(0), the reaction of **1** with $ZnPh_2$ was negligible. This result clearly indicates that Pd(0) catalyzes the coupling reaction with or without LiI (entries 7 and 8).

With the optimized reaction conditions, the scope of the diarylzinc reagent was investigated. Treatment of **1** with **4a** prepared by the reaction of $ZnCl_2$ with PhMgCl gave **5a** in 81% yield, which was the highest reactivity among the arylzinc reagents (turnover number = 8100; entry 9). It should be mentioned that in comparison with PhMgBr (entry 5), the use of PhMgCl for the preparation of **4a** resulted in a higher yield of **5a**. In addition, the reactions with $Zn(4\text{-}MeC_6H_4)_2$ (**4b**) and $Zn(3\text{-}MeC_6H_4)_2$ (**4c**) gave the monoaryl-substituted products **5b** and **5c** in yields of 75 and 72%, respectively (entries 10 and 11), while the reaction with $Zn(2\text{-}MeC_6H_4)_2$ (**4d**) gave only a 57% yield of **5d** (entry 12). Reactions with fluoro-substituted arylzinc reagents (**4e** and **4f**) yielded the corresponding products (**5e** and **5f**) in 53 and 55% yield, respectively (entries 13 and 14). Reactions with para-substituted arylzinc reagents such as $Zn(4\text{-}MeOC_6H_4)_2$ (**4g**) and $Zn(4\text{-styryl})_2$ (**4h**) also afforded the corresponding products (**5g** and **5h**) in good yields (entries 15 and 16). In contrast, $Zn(4\text{-}CF_3C_6H_4)_2$ (**4i**), $Zn(4\text{-}MeSC_6H_4)_2$ (**4j**), and $Zn(4\text{-}ClC_6H_4)_2$ (**4k**) required prolonged reaction times to yield the corresponding monoaryl-substituted products (**5i**−**k**) in moderate yields (entries 17−19). In addition, the reaction with $Zn(4\text{-}Me_2NC_6H_4)_2$ (**4l**) was terminated within 2 h, and consequently, the yield of the desired product (**5l**) remained at 30% (entry 20). This catalytic system was also successfully applied to $Zn(2\text{-naphthyl})_2$ (**4m**), which gave the corresponding product (**5m**) in 61% yield (entry 21). Use of $Zn(2\text{-thienyl})_2$ (**4n**) allowed the reaction with **1** to proceed to give **5n**, although a much longer reaction time was required and the product yield was low (entry 22). Reaction products were isolated in THF solution to avoid the occurrence of cyclodimerization to give

Table 1. Pd(0)-Catalyzed Coupling Reaction of TFE (1) with $ZnAr_2$ (4)[a]



				ZnAr₂			product	
entry	$Pd_2(dba)_3$ (mol %)	PPh_3 (mol %)	LiI (mmol)	4	Ar	time (h)	5	yield (%)[b]
1[c]	5.0	20.0	0.240	**4a**	Ph	20.0	**5a**	55
2[c]	5.0	20.0	–	**4a**	Ph	50.0	**5a**	22
3[c]	1.0	4.0	0.240	**4a**	Ph	46.0	**5a**	58
4	0.01	0.04	0.240	**4a**	Ph	24.0	**5a**	72
5	0.01	–	0.240	**4a**	Ph	4.0	**5a**	73 (52)
6[d]	0.01	–	0.240	**4a**	Ph	9.0	**5a**	60
7	–	–	0.240	**4a**	Ph	24.0	**5a**	3
8	–	–	–	**4a**	Ph	24.0	**5a**	9
9[e]	0.01	–	0.240	**4a**	Ph	2.0	**5a**	81 (62)
10	0.01	–	0.240	**4b**	4-Tol	6.0	**5b**	75 (34)
11[e]	0.01	–	0.240	**4c**	3-Tol	4.0	**5c**	72 (45)
12[e]	0.01	–	0.240	**4d**	2-Tol	8.0	**5d**	57 (30)
13	0.01	–	0.240	**4e**	$3\text{-}FC_6H_4$	8.0	**5e**	53 (45)
14	0.01	–	0.240	**4f**	$4\text{-}FC_6H_4$	4.0	**5f**	55 (51)
15	0.01	–	0.240	**4g**	4-anisyl	2.5	**5g**	63 (39)
16	0.01	–	0.240	**4h**	4-styryl	4.0	**5h**	65 (71)
17	0.01	–	0.240	**4i**	$4\text{-}CF_3C_6H_4$	18.0	**5i**	31 (14)
18	0.01	–	0.240	**4j**	$4\text{-}MeSC_6H_4$	21.0	**5j**	41 (37)
19	0.01	–	0.240	**4k**	$4\text{-}ClC_6H_4$	28.0	**5k**	37 (10)
20	0.01	–	0.240	**4l**	$4\text{-}Me_2NC_6H_4$	2.0	**5l**	30 (25)
21	0.01	–	0.240	**4m**	2-naphthyl	4.0	**5m**	61 (37)
22	0.01	–	0.240	**4n**	2-thienyl	75.0	**5n**	34 (14)

[a] General conditions: **1** (3.5 atm, >0.30 mmol as estimated from an equation of state), **4** (0.100 mmol, prepared in situ by treating $ZnCl_2$ with 2 equiv of ArMgBr) and solvent (0.5 mL). All of the reactions were conducted in a pressure-tight NMR tube. [b] Yields are based on the aryl group and were determined by ^{19}F NMR analysis of the crude product using α,α,α-trifluorotoluene as an internal standard. The values in parentheses are isolated yields. Detailed procedures for the isolation experiments are provided in the Supporting Information. [c] Run at room temperature. [d] Run with isolated **4a** (0.100 mmol, purchased from Strem) [e] Run with ArMgCl instead of ArMgBr (0.200 mmol).

hexafluorocyclobutane derivatives at higher concentrations.[18] The relatively lower isolated yields were caused either by the high volatility even at room temperature or by the cyclodimerization.

On the basis of the results described above, the Pd-catalyzed monoaryl substitution reaction of TFE might proceed via the mechanism depicted in Scheme 2. Coordination of a TFE molecule to Pd(0) takes place, generating an η^2-TFE species (**B**). Next, oxidative addition of a C−F bond to Pd(0) is promoted by LiI, generating a trifluorovinylpalladium(II) intermediate (**C**). Transmetalation of **C** with Li[ArZnXI] yields a transient arylpalladium intermediate (**D**), which undergoes reductive elimination to afford α,β,β-trifluorostyrene derivative **5** along with regeneration of the Pd(0) species. Addition of LiI is essential not only for accelerating the cleavage of the C−F bond but also for enhancing the reactivity of the arylzinc reagent via the formation of a zincate such as Li[ArZnXI].

In summary, we have demonstrated the first Pd-catalyzed monoarylation of TFE by employing in situ-prepared diarylzinc reagents to yield α,β,β-trifluorostyrene derivatives in excellent yields with high selectivity. C−F bond activation of TFE was achieved by the synergetic effects of the Pd(0) species and LiI and generated a trifluorovinyl palladium(II) intermediate whose structure was unambiguously determined by X-ray diffraction. Further studies of the application of the C−F bond activation of TFE to other catalytic transformations are in progress in our group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) ***Caution!*** Tetrafluoroethylene is suspected to be carcinogenic. The reaction mixture must be handled in a well-ventilated fume hood.

(14) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Oefele, K.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *461*, 51–60.

(15) A sole example of a well-defined dinuclear trifluorovinyl complex generated by C−F bond cleavage of **1** has been reported.[11c]

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(17) Achonduh, G. T.; Hadei, N.; Valente, C.; Avola, S.; O'Brien, C. J.; Organ, M. G. *Chem. Commun.* **2010**, *46*, 4109–4111.

(18) Heinze and Burton claimed that some α,β,β-trifluorostyrene derivatives (especially in pure form) are prone to cyclodimerize under higher-concentration conditions even at room temperature or below. See: Heinze, P. L.; Burton, D. J. *J. Org. Chem.* **1988**, *53*, 2714–2720.

■ NOTE ADDED AFTER ASAP PUBLICATION

The new bond identified in the fourth sentence of the first paragraph was corrected February 18, 2011.