Ligand Effects

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Regioselective C–F Bond Activation of Hexafluoropropylene on Palladium(0): Formation of a Cationic η^2-Perfluoroallylpalladium Complex**

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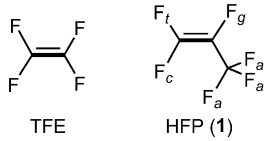
Abstract: *A chemoselective C(sp^2)–F or C(sp^3)–F bond activation of hexafluoropropylene (HFP) was achieved by adopting the proper combination of a Lewis acid co-additive with a ligand which coordinates Pd^0. The treatment of [(η^2-HFP)Pd(PCy_3)$_2$] with $B(C_6F_5)_3$ allowed a chemoselective C(sp^3)–F bond cleavage of HFP to give a unique cationic perfluoroallypalladium complex. In this complex, the coordination mode of the perfluoroallyl ligand was considered to be of the unique η^2-fashion.*

The selective C–F bond activation of perfluoro organic compounds by transition-metal complexes has been a crucial subject in the fields of organic and organometallic chemistry because it provides novel synthetic routes to fluorinated organic molecules which are difficult to access by conventional procedures.[1] Although striking developments have been made in recent years on the intermolecular C–F bond activation of fluorinated olefins,[2] the alkenyl C(sp^2)–F bond activation of perfluoroalkenes remains a great challenge. We have developed the first coupling reaction of tetrafluoroethylene (TFE) with aryl zinc compounds to yield (α,β,β-trifluoro)styrene derivatives, in which an efficient C–F bond cleavage with palladium was achieved by using lithium iodide as a co-additive.[3] Recently, we also demonstrated that the C–F bond cleavage of TFE using a group 10 metal was accelerated by the addition of not only metal halides such as lithium iodide but also boron Lewis acids, such as BF_3 and $B(C_6F_5)_3$.[4] Our next concern was to develop a novel strategy for the regioselective C–F bond activation of perfluoroolefins. Hexafluoropropylene (HFP; **1**) is the simplest perfluoroalkene, second only to TFE, and **1** contains four different types of fluorine atoms whereas TFE consists of chemically equivalent ones (Scheme 1). Although a limited number of transition metal mediated or catalyzed C–F bond-activation reactions of **1** have been reported,[5,6] no active species capable of recognizing different types of fluorines and cleaving them chemoselectively, has been developed. In addition, the product that would be generated from the C(sp^3)–F bond cleavage of **1** on palladium is expected to be a perfluoroallylpalladium complex,[7,8] and the coordination mode as well as the fluxional behavior of the perfluoroallyl ligand on palladium is of great interest especially as a comparison to the well-known allylpalladium species.[9] Herein, we report the novel regioselective C–F bond-cleavage reactions of **1** with zero-valent palladium in the presence of co-additives. Our novel methodology achieves the chemoselective C(sp^2)–F or C(sp^3)–F bond activation of **1** by adopting the proper combination of a Lewis acid as a co-additive with a ligand that will coordinate to palladium(0). In addition, the employment of $B(C_6F_5)_3$ and a palladium(0) species supported by PCy_3 ligands allowed regioselective C(sp^3)–F bond activation of **1** to give a unique cationic perfluoroallylpalladium complex.



Scheme 1. Tetrafluoroethylene (TFE) and hexafluoropropylene (**1**; HFP). The difference in regiochemistry of the fluorine atoms is indicated by a subscript.

The reaction of [Pd(PCy_3)$_2$] with **1** at room temperature led to the clean formation of [(η^2-CF_2=$CFCF_3$)Pd(PCy_3)$_2$] (**2a**; Scheme 2). Other η^2-HFP complexes with various monodentate phosphine ligands, [(η^2-CF_2=$CFCF_3$)Pd(PR_3)$_2$] (**2b**: R = *i*Pr, **2c**: R = Ph), as well as a dppf analogue, [(η^2-CF_2=$CFCF_3$)Pd(dppf)] (**2d**; dppf = 1,1′-bis(diphenylphosphino)ferrocene), could be isolated in good to excellent yields. An attempt at the preparation of the nickel analogue of **2a** by treating [Ni(cod)$_2$] with **1** in the presence of PCy_3 was unsuccessful. Instead, a vinylphosphorane, $Cy_3P(F)((Z)$-CF=$CFCF_3)$, was obtained in a quantitative yield.[10,11] The coordinating HFP molecule to the palladium in **2a** showed signals at $\delta_F = -68.3$ (3F), −105.9 (1F), −115.4 (1F), and −204.4 ppm (1F), which are assignable to the allyl, *trans*, *cis*, and *gem* fluorines, respectively. Unlike [(η^2-CF_2=CF_2)Pd(PCy_3)$_2$], the unequal resonances of two phosphorus atoms

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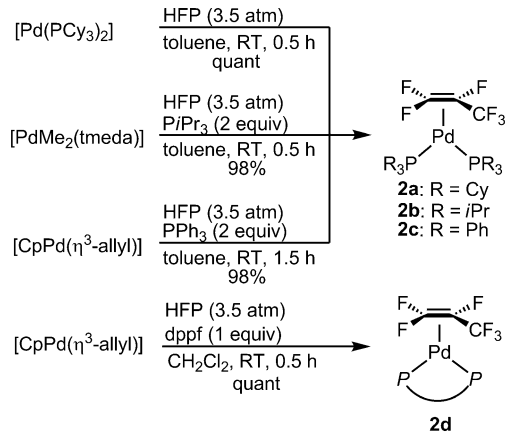
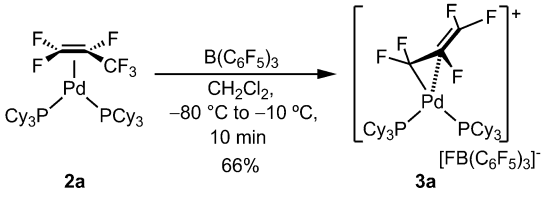


Scheme 2. Generation of η^2-HFP palladium complexes.

appeared at $\delta_P = 29.9$ (ddm, $J_{PF} = 52.5$, 52.5 Hz) and 33.7 ppm (m). An X-ray diffraction study of **2a** demonstrated a significant difference in the bond lengths of the two Pd–C bonds [Pd-C1: 2.018(3), Pd-C2: 2.105(3) Å], probably resulting from the steric hindrance of the trifluoromethyl group bound to C2.[12] Both the elongation of the C1–C2 bond (1.435(4) Å) and the pyramidal angle value [the normal angles between the F1-C1-F2 and F3-C2-C3 planes: 100.76(21)°][13] strongly support the large contribution of a back-donation from palladium to the π* antibonding orbital of the C=C bond. Geometrical features similar to those of **2a** were observed in the molecular structure of **2d**.[12]

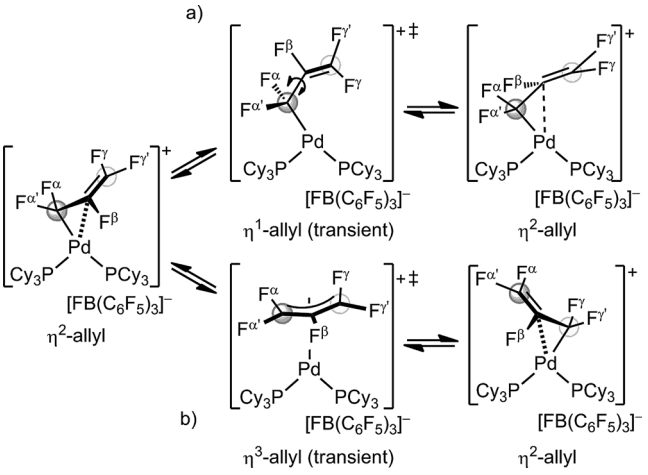
We next investigated which additives can regioselectively cleave the C–F bond of **1**, since thermolysis of **2a** at 100 °C for 24 h gave a mixture of palladium fluorides as a result of the occurrence of an uncontrollable C–F bond cleavage.[14] Treatment of **2a** with $B(C_6F_5)_3$ underwent an allylic $C(sp^3)$–F bond cleavage to give a cationic perfluoroallylpalladium complex (**3a**; Scheme 3). Monitoring of the reaction in CD_2Cl_2 at 0 °C demonstrated an immediate conversion of **2a** and $B(C_6F_5)_3$



Scheme 3. $B(C_6F_5)_3$-promoted $C(sp^3)$–F bond activation of HFP (**1**) using palladium having PCy_3 ligands.

into the cationic **3a** and the $[FB(C_6F_5)_3]^-$ anion, respectively. Among the η^2-HFP monophosphine-ligated palladium complexes prepared, only **2a** yielded the isolable perfluoroallylpalladium species while the corresponding reaction with **2b** afforded a very unstable product.[15] The reaction of **2c** with $B(C_6F_5)_3$ gave a complicated mixture. The isolation of **3a** was achieved by mixing **2a** with $B(C_6F_5)_3$ in CH_2Cl_2 at low temperature, thus delivering **3a** in 66 % yield as a pale yellow powder. Combustion analysis of **3a** agreed with the results of theoretical studies (see below) which showed the chemical composition of **3a** to be $[(CF_2\text{-}CF{=}CF_2)Pd(PCy_3)_2][FB(C_6F_5)_3]$, for which the coordination mode of the perfluoroallyl ligand is regarded to be η^2-fashion. The $^{13}C\{^{19}F\}$ resonances assignable to the β-carbon atom and the γ-carbon atom in the perfluoroallyl ligand in **3a**, measured in CD_2Cl_2 at −90 °C, were observed at $\delta_C = 122.0$ and 147.0 ppm, respectively, whereas the α-carbon atom could not be detected because of its fluxionality to be hereinafter described. In the ^{19}F NMR spectrum at −90 °C, five independent resonances of the perfluoroallyl ligand appeared at $\delta_F = -29.0$ (br, F^{α}), −58.0 (br, $F^{\alpha'}$), −94.1 (dd, 69.7, 52.3 Hz, F^{γ}), −104.8 (m, $F^{\gamma'}$), and −167.0 ppm (dm, 113.7 Hz, F^{β}), wherein their ^{13}C–^{19}F correlations were confirmed by the ^{13}C–^{19}F HSQC spectrum.[16]

VT-NMR analyses of **3a** in CD_2Cl_2 revealed the existence of two independent fluxionalities of the perfluoroallyl ligand (Scheme 4): a) the rotation about the C^{α}–C^{β} bond in the



Scheme 4. Fluxional behavior of the perfluoroallyl ligand in **3a**. a) Rotation about the C^{α}–C^{β} bond via an η^2-η^1-η^2 mechanism. b) C^{α}–C^{γ} exchange by an η^2-η^3-η^2 mechanism.

transient η^1-perfluoroallyl form and b) the exchange between the α-carbon atom and the γ-carbon atom via the transient η^3-perfluoroallyl intermediate. The crosspeak between the two α-fluorine atoms observed in the ^{19}F–^{19}F EXSY spectrum at −80 °C provided clear evidence for the occurrence of the rotation depicted in Scheme 4 a.[16,17] In addition, the two α-F resonances coalesced ahead of the rest upon elevating the temperature to −50 °C,[16] and thus also supported the rotation. Furthermore, as the temperature further increased at 0 °C, the β-fluorine resonance was observed as a sharp quintet with a coupling constant of 29.6 Hz, whereas the remaining ^{19}F signals, attributable to the perfluoroallyl group in **3a**, were extensively broadened. The $^{31}P\{^1H\}$ NMR spectrum of **3a** measured at 0 °C displayed an apparent quintet at $\delta_P = 25.5$ ppm ($J_{PF} = 21.9$ Hz), although it was observed as a broad signal with a linewidth at half the height of 291.6 Hz at −90 °C. These observations clearly indicated that four terminal fluorines are averaged on the NMR timescale, and it

was unexplainable on the basis of a sole fluxionality depicted in Scheme 4a. In other words, another fluxionality involving the C^{α}–C^{γ} exchange (Scheme 4b) simultaneously existed.

DFT calculations on the $B(C_6F_5)_3$-mediated C–F bond-activation reaction of **1** on $[Pd(PCy_3)_2]$ were carried out to gain deeper insight into the regioselectivity. The calculation was conducted with a real molecule system, because the choice of phosphine ligands affected the regioselectivity of the C–F bond activation of HFP (see below). The complex **2a** is 0.6 kcal mol^{-1} beneath $[Pd(PCy_3)_2]+\mathbf{1}$ (Figure 1).[18] The transition state for the $B(C_6F_5)_3$-mediated allylic C–F bond

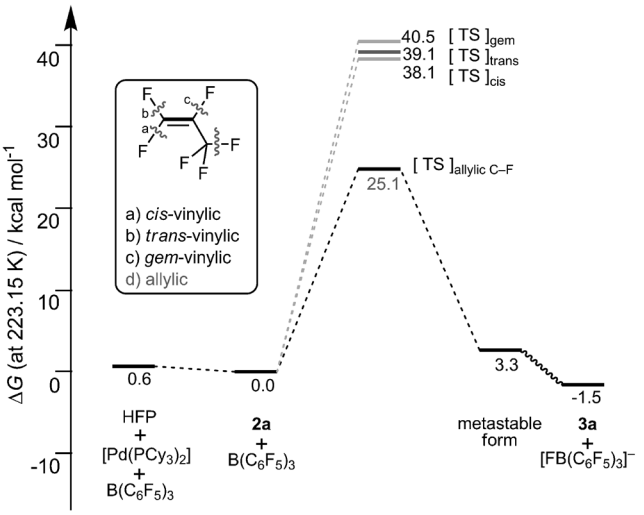
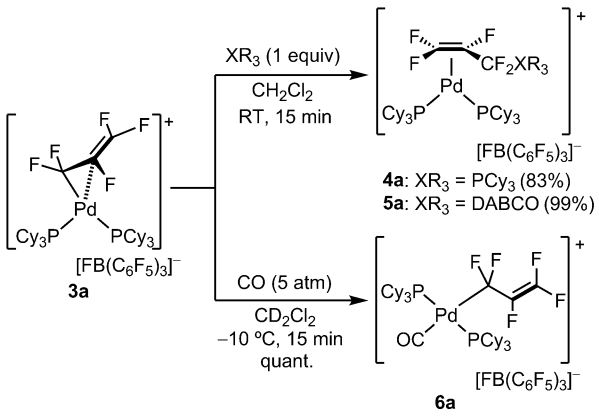


Figure 1. Energy profile for the $B(C_6F_5)_3$-promoted C–F bond activation of HFP (**1**) on $[Pd(PCy)_2]$. Relative Gibbs energies at 223.15 K (in CH_2Cl_2, relative to **2a**) are given in kcal mol^{-1}.

activation had a Gibbs energy of 25.1 kcal mol^{-1} relative to $\mathbf{2a}+B(C_6F_5)_3$. In the optimized structure of the transition state, one of the allylic C–F bonds was elongated to 1.670 Å, and a migrating fluorine atom was located at 1.729 Å from the B atom (see Figure S10 in the Supporting Information). This transition state was about 13 kcal mol^{-1} lower than other transition states for vinylic C–F bond activation ($\Delta G^{\ddagger}=$ 38.1 kcal mol^{-1} for *cis*-vinylic C–F bond, $\Delta G^{\ddagger}=39.1$ kcal mol^{-1} for *trans*-vinylic C–F bond, and $\Delta G^{\ddagger}=40.5$ kcal mol^{-1} for *gem*-vinylic C–F bond), and this result rationalized the occurrence of the selective allylic C–F bond cleavage of HFP. Such a specific regioselectivity may have been due to the steric repulsion between the bulkier PCy_3 ligand and $B(C_6F_5)_3$. An IRC calculation supported the theory that the migration of the fluorine to $B(C_6F_5)_3$ led to the generation of **3a** with a cationic palladium(II) center which possessed a tricoordinated planar geometry (see Figure S11 in the Supporting Information). In the optimized structure of **3a**, the Pd–C1 bond length of 2.013 Å corresponded to that of a typical Pd–C single bond. The Pd-C1-C2 bond angle of 90.7° was much more acute than the ideal tetrahedral angle, and the interatomic distance between Pd and C2 approximated 2.518 Å. The C1–C2 bond length of 1.488 Å was comparable to the typical value of a C–C bond, whereas the C2–C3 bond length of 1.349 Å was typical of a C=C bond. Therefore, the allyl ligand was considered to be localized. The unoccupied π* orbital between the C2–C3 bond weakly interacted with the palladium, and this intricately hybridized molecular orbital consisted of the HOMO of the cationic portion of **3a**.[16] Such a feeble coordination might have a stabilizing influence on **3a**, though the cationic trifluorovinyl analogue, $[(PCy_3)_2Pd(CF{=}CF_2)][FB(C_6F_5)_3]$, generated by the reaction of $[(\eta^2\text{-}CF_2{=}CF_2)Pd(PCy_3)_2]$ with $B(C_6F_5)_3$ was too unstable to be isolated.[4]

The perfluoroallyl ligand in **3a** showed reactivities toward nucleophiles. When **3a** was treated with an equimolar amount of either PCy_3 or 1,4-diazabicyclo[2.2.2]octane (DABCO) in CH_2Cl_2 at room temperature, $[(\eta^2\text{-}CF_2{=}CFCF_2XR_3)Pd(PCy_3)_2][FB(C_6F_5)_3]$ (**4a**; $XR_3=PCy_3$, **5a**; $XR_3=$ DABCO) was generated in quantitative yield (Scheme 5). In the

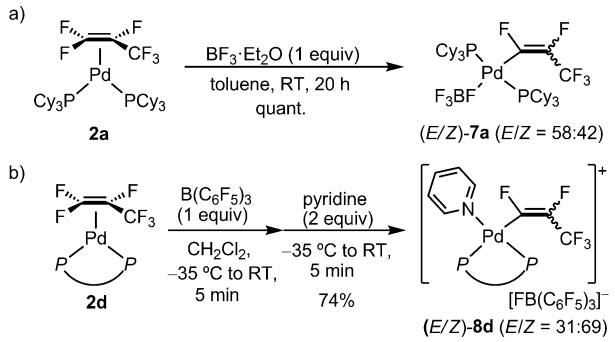


Scheme 5. Reactivity of **3a**.

^{31}P NMR spectrum of **4a**, three resonances with the same intensity appeared at $\delta=29.8$ (ddm, $J_{PF}=45.4$, 45.4 Hz), 33.5 (dddm, $J_{PF}=38.9$, 26.5, 26.5 Hz), and 47.4 ppm (ddd, $J_{PF}=$ 121.0, 84.8, 25.2 Hz), the last of which was characteristic of phosphonium. The fluorine atoms bound to the allylic carbon atom in **4a** were chemically inequivalent and regarded as resonance set at $\delta_F=-65.6$ and -97.0 ppm with a $^2J_{FF}$ coupling constant of 312.5 Hz. In addition, the ^{19}F NMR spectrum of **4a** displayed three resonances at $\delta_F=-103.3$, -108.4, and -195.7 ppm, which were attributable to the CF_2= CF- moiety. Although stoichiometric, these reactions were the first substitution reaction of the allylic fluorine in **1** with a nonhydrogen atom.[5h,i,19,20]

Treating **3a** with carbon monoxide resulted in a clean formation of *trans*-$[(PCy_3)_2Pd(CO)(\eta^1\text{-}CF_2CF{=}CF_2)][FB(C_6F_5)_3]$ (**6a**; Scheme 5). A reversible dissociation of the carbonyl ligand in **6a** to regenerate **3a** was observed when a CD_2Cl_2 solution of **6a** was concentrated under reduced pressure. In the ^{19}F NMR spectrum of **6a**, an η^1-perfluoroallyl ligand appeared at $\delta_F=-61.9$ (br, 2F), -94.9 (dd, 53.8, 32.0 Hz, 1F), -105.5 (ddt, 112.6, 53.8, 14.5 Hz, 1F), and -167.3 ppm (br d, 112.6 Hz, 1F). The observation of the ^{31}P resonance (t, $J_{PF}=21.6$ Hz) confirmed the *trans* geometry around the palladium center in **6a**.

It should be emphasized that the choice of both the Lewis acid additives and the phosphine ligands also affected the regioselectivity of the C–F bond activation of **1**. Treatment of **2a** with $BF_3{\cdot}Et_2O$ at room temperature promoted the $C(sp^2)$–F bond cleavage of **1** with palladium to afford *trans*-$[(PCy_3)_2Pd(BF_4)(CF{=}CFCF_3)]$ (**7a**) as a mixture of *E*/*Z* geometric isomers (Scheme 6a). Unlike the reaction of **2a** with



Scheme 6. $C(sp^2)$–F bond activation of HFP (**1**) using palladium: a) $BF_3{\cdot}Et_2O$-promoted reaction using Pd^0/PCy_3 system. b) $B(C_6F_5)_3$-promoted reaction using Pd^0/dppf system.

$B(C_6F_5)_3$, the allylic $C(sp^3)$–F bond cleavage of **1** did not proceed at all. Recrystallization from toluene/hexane at room temperature gave a microcrystalline of the major *E* isomer [(*E*)-**7a**], and its molecular structure was unambiguously determined by X-ray diffraction study (Figure 2). Significant structural features of (*E*)-**7a** included cleavage of the *cis* $C(sp^2)$–F bond with respect to the CF_3 group of **1** along with one of the fluorine atoms in the tetrafluoroborate bridges between the palladium and boron atoms. In the ^{19}F NMR spectrum of (*E*)-**7a**, resonances that were assignable to the (*E*)-perfluoro-prop-1-en-1-yl group appeared at $\delta_F = -65.2$ (br, 3F), −76.4 (br, 1F), and −145.5 ppm (m, 1F), whereas a characteristic $^3J(trans)$ coupling constant of 119 Hz was observed in the minor isomer (*Z*)-**7a**.

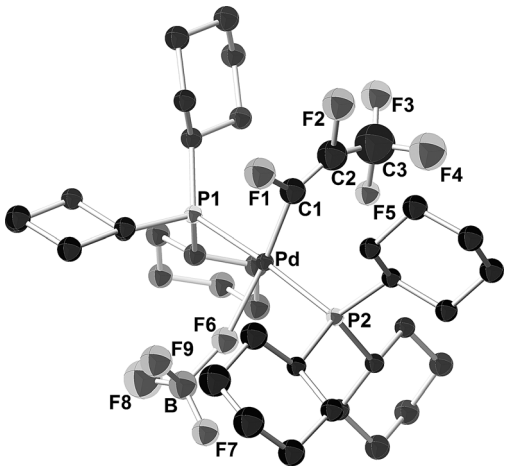


Figure 2. ORTEP drawings of (*E*)-**7a** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

Furthermore, when **2d**, bearing the dppf instead of PCy_3 as an auxiliary ligand, was treated with $B(C_6F_5)_3$ in toluene at room temperature, the desired $C(sp^3)$–F bond cleavage of **1** with palladium did not proceed at all. Instead, a smooth $C(sp^2)$–F bond cleavage took place to give a cationic perfluoro-1-propenyl palladium complex, and the product was isolated as the stable pyridine-capped adduct *cis*-$[(CF{=}CFCF_3)(py)Pd(dppf)][FB(C_6F_5)_3]$ (**8d**; Scheme 6b). Similar to the generation of the *E*/*Z* mixture of **7a**, *E*/*Z* selectivity cannot be controlled in this reaction, and therefore, **8d** was also obtained as a mixture of *E*/*Z*-geometric isomers. Thus, these results clearly demonstrate the usefulness of our methodology for chemo- and regioselective C–F bond cleavage because the selectivity could be controlled by altering the phosphine ligands and Lewis acid additives that were used.

In conclusion, we have developed the regioselective C–F bond activation of **1** with zero-valent palladium. Altering either the phosphine ligands which coordinate to palladium or Lewis acid co-additives which promote C–F bond activation enabled the control of the chemo- and regioselectivity of the C–F bond activation reaction. In addition, by employing a combination of $[Pd(PCy_3)_2]$ and $B(C_6F_5)_3$, the unprecedented $C(sp^3)$–F bond cleavage of **1** occurred to give the unique η^2-perfluoroallyl palladium complex **3a**. The stoichiometric systems demonstrated here will be developed extensively with the goal of constructing catalytic systems for the preparation of functionalized organofluorine compounds.

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[10] The formation of $n\mathrm{Bu_3P(F)((}Z\mathrm{)\text{-}CF{=}CFCF_3)}$ analogue generated by the reaction of **1** with $n\mathrm{Bu_3P}$ had been reported by Burton et al. See also: D. J. Burton, S. Shinya, R. D. Howells, *J. Am. Chem. Soc.* **1979**, *101*, 3689 – 3690.

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[14] The major product was *trans*-$[(PCy_3)_2Pd(F)((E)\text{-}CF{=}CFCF_3)]$ (50%), and its *Z* isomer (6%) and other unidentified palladium fluorides were detected by NMR analysis of the crude product (see the Supporting Information for details). The regioselectivity did not conflict with that observed in the palladium(0)-catalyzed coupling reaction product of **1** with 1-naphthylboronate. See also Ref. [6].

[15] Observation of a similar quintet ($\delta_P = 39.0$ ppm, $J = 21.2$ Hz) in the ^{31}P NMR spectrum measured at −50 °C may indicate a formation of the corresponding perfluoroallylpalladium species.

[16] See the Supporting Information for details.

[17] At the same time, crosspeaks corresponding to the F^{α}–F^{γ} exchange were observed in the EXSY spectrum, which also supported the fluxionality depicted in Scheme 4.

[18] IRC calculation indicated an existence of a zwitterionic metastable state, which was about 5 kcal mol^{-1} higher in energy than than the ion-separated form of **3a**. See the Supporting Information (Figure S12) for details.

[19] Hughes and Davis reported that the reaction of a 1,2,3,6-η-octafluorocycloocta-2,4,7-triene-1,6-diyl iron(II) complex with PMe_3 resulted in an nucleophilic attack of PMe_3 on the internal perfluoroallylic carbon atom. See also: R. T. Carl, R. P. Hughes, J. A. Johnson, R. E. Davis, R. P. Kashyap, *J. Am. Chem. Soc.* **1987**, *109*, 6875 – 6876.

[20] A net insertion reaction of SO_3 into an allylic C–F bond in **1** is known to give perfluoroallyl fluorosulfate, $CF_2{=}CFCF_2OSO_2F$. This product can be employed in a wide variety of nucleophilic reactions, thus yielding perfluoroallylic derivatives. See also: a) C. G. Krespan, D. C. England, *J. Am. Chem. Soc.* **1981**, *103*, 5598 – 5599; b) I. Wlassics, V. Tortelli, S. Carella, C. Monzani, G. Marchionni, *Molecules* **2011**, *16*, 6512 – 6540.

