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C–H and C–F bond activation of fluorinated propenes at Rh: enabling cross-coupling reactions with outer-sphere C–C coupling†‡

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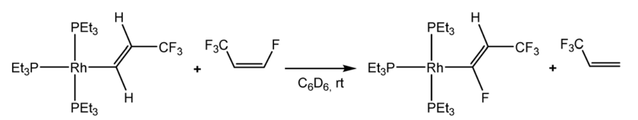
The reaction of [Rh{(*E*)-CF=CHCF$_3$}(PEt$_3$)$_3$] with Zn(CH$_3$)$_2$ results in the methylation of the alkenyl ligand to give [Rh{(*E*/*Z*)-C(CH$_3$)=CHCF$_3$}(PEt$_3$)$_3$]. Variable temperature NMR studies allowed the identification of a heterobinuclear rhodium–zinc complex as an intermediate, for which the structure [Rh(CH$_3$)(ZnCH$_3$){(*Z*)-C(CH$_3$)=CHCF$_3$}(PEt$_3$)$_2$] is proposed. Based on these stoichiometric reactions, unique Negishi-type catalytic cross-coupling reactions of fluorinated propenes by consecutive C–H and C–F bond activation steps at room temperature were developed. The C–H bond activation steps provide a fluorinated ligand at Rh and deliver the fluorinated product, whereas the C–F bond activation and C–C coupling occur *via* outer-sphere nucleophilic attack at the fluorinated alkenyl ligand.

Introduction

Fluorinated compounds are of eminent importance as they are used in a broad range of fields such as pharmaceutics, agrochemicals and materials science.[1–4] Fluorinated olefins are currently indispensable, because they have applications in automobile air-conditioning systems and as monomers for polymeric compounds such as Teflon.[5–7] While the synthesis of fluorinated olefins has been widely developed through fluorination reactions,[8,9] the activation and functionalization of olefinic or vinylic C(sp^2)–F bonds is less common,[10–13] and often it is mediated by a transition metal complex.[12,13]

A possible functionalization pathway would consist of the formation of C–C bonds by cross-coupling reactions. Such conversions have been investigated for chlorinated or brominated olefin derivatives.[14,15] For fluoroalkenes, C–C couplings have been less studied and examples include group 10 catalysts and the use of *gem*-difluoroalkenes.[16–28] The couplings proceed by an initial C–F bond oxidative addition – in some cases using lithium salts to promote the activation step – or insertion of a fluorinated olefin into a metal–carbon bond followed by β-fluorine elimination. Cao and Wu developed a Suzuki–Miyaura cross coupling arylation of *gem*-difluoroalkenes using a nickel catalyst,[21] whereas Tsui and Liu applied a palladium catalyst.[16] Xu *et al.* published the arylation of an *in situ* formed difluorovinyl ketone in the presence of a palladium catalyst and aryl boronic acids.[19] Regarding rhodium catalyzed reactions, Xia and co-workers described the formation of monofluorinated dienes from *gem*-difluorocyclopropanes, which are employed as fluoroallyl surrogates, by C–C coupling with allylboronates.[29] Negishi-type cross-coupling reactions based on vinyl C(sp^2)–F bond oxidative addition steps are rare. Saeki *et al.* functionalized the olefin CF$_2$=CH(1-naphtyl) with arylzinc derivative MeC$_6$H$_4$ZnCl in the presence of a palladium catalyst.[30] In addition, examples using Pd or Ni catalysts and lithium salts to promote the C–F bond activation have been described by Zhang *et al.* and Ogoshi and co-workers developing Negishi-type C(sp^2)–F bond alkylations of 2,3,3,3-tetrafluoropropene or tetrafluoroethylene, respectively.[31,32]

Recently, the reactivity of *Z*-1,3,3,3-tetrafluoropropene (**5a**) towards rhodium(I) complexes has been studied and it was shown that rhodium alkenyl complexes with a low fluoroorganyl content such as [Rh{(*E*)-CH=CHCF$_3$}(PEt$_3$)$_3$] can activate higher fluorinated olefins (Scheme 1). For the latter, in a C–H activation step [Rh{(*E*)-CF=CHCF$_3$}(PEt$_3$)$_3$] (**1**) and 3,3,3-trifluoropropene were produced.[33]



Scheme 1 Reaction of [Rh{(*E*)-CH=CHCF$_3$}(PEt$_3$)$_3$] with *Z*-1,3,3,3-tetrafluoropropene.[33]

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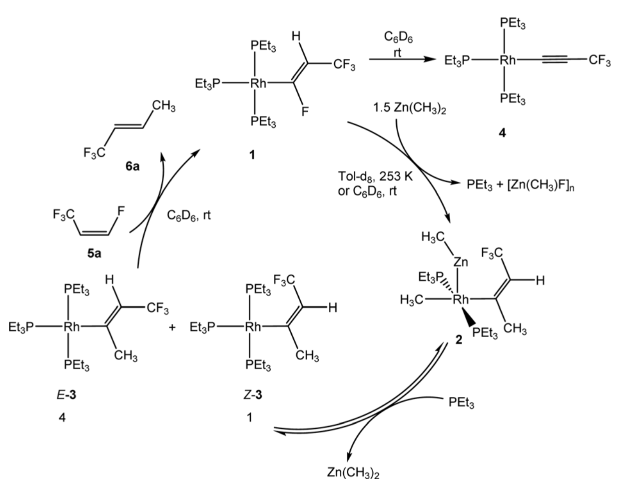
† Dedicated to Prof. Dr Helmut Werner on the occasion of his 90th birthday.

‡ Electronic supplementary information (ESI) available: Synthesis and analytics of all compounds and details of the DFT calculations. See DOI: https://doi.org/10.1039/d4sc00951g

Herein studies on catalytic C–C coupling reactions at fluorinated alkenyl ligands are described. Stoichiometric model reactions give an insight into a possible reaction mechanism. Unprecedented rhodium catalyzed Negishi-type cross-coupling reactions of fluorinated olefins have been developed, based on both C(sp^2)–F and C(sp^2)–H bond activation and, remarkably, involving a C–C coupling step in the outer coordination sphere.

Results and discussion

Treatment of complex [Rh{(*E*)-CF=CHCF$_3$}(PEt$_3$)$_3$] (**1**) with one equivalent of Zn(CH$_3$)$_2$ in C$_6$D$_6$ yielded after 20 min at room temperature a mixture of complexes, which included a heterobimetallic compound, for which the structure [Rh(CH$_3$)(ZnCH$_3$){(*Z*)-C(CH$_3$)=CHCF$_3$}(PEt$_3$)$_2$] (**2**) is suggested, as well as the isomers [Rh{(*E*)-C(CH$_3$)=CHCF$_3$}(PEt$_3$)$_3$] (*E*-**3**), [Rh{(*Z*)-C(CH$_3$)=CHCF$_3$}(PEt$_3$)$_3$] (*Z*-**3**), the alkynyl complex [Rh(C≡CCF$_3$)(PEt$_3$)$_3$] (**4**) and an unknown product in a ratio of 3 : 0.7 : 2.5 : 1, respectively. When the reaction was run in the presence of one equivalent of PEt$_3$, a mixture of complexes **2** and *Z*-**3** in a 1 : 17 ratio was observed after 10 minutes. The preferential formation of the *Z*-**3** isomer might indicate a diminished role of **2** for the reaction mechanism in this case. When the reaction was monitored at 253 K by NMR spectroscopy, after 4 h 75% conversion of complex **1** was observed to give complex **2** and a second complex (ratio 9 : 1), which is possibly an isomer of **2**, together with the release of triethylphosphine (Scheme 2). The rhodium-zinc heterobimetallic complex **2** is not stable at low temperatures, and after one day, reductive elimination of Zn(CH$_3$)$_2$ took place followed by coordination of phosphine to rhodium leading to the *Z*/*E*-**3** isomers in a 1 : 4 ratio. Treatment of the product mixture with *Z*-1,3,3,3-tetrafluoropropene (**5a**) led then to the regeneration of complex **1** and release of *E*-1,1,1-trifluorobut-2-ene (**6a**) by C–H bond activation and formation (Scheme 2). This step comprises the replacement of a lower fluorinated ligand by a higher fluorinated ligand by C–H bond activation as a higher degree of fluorination often leads to stronger bonds.[34] As previously reported, complex **1** is not stable and after a dehydrofluorination step complex **4** is obtained.[33]



Scheme 2 Reactivity of complex **1** towards Zn(CH$_3$)$_2$.

In an alternative approach in which complex **1** was treated with LiCH$_3$ instead of Zn(CH$_3$)$_2$, a mixture of complexes (*Z*/*E*)-**3** and **4** was also obtained. However, in this case a heterobinuclear intermediate similar to **2** was not observed. Note that Rh–Zn bimetallic complexes have been described before.[35–39]

The formation of **2** followed by the generation of *E*/*Z*-**3** from complex **1** can be considered as a case for a rare outer-sphere reaction where a nucleophile attacks the fluorinated ligand bonded at rhodium. Note that the attack of a fluorosilicate at the carbon atom of a fluorinated pyridyl ligand has been proposed at rhodium.[40] The attack of PEt$_3$ at the β-carbon atom of a perfluorovinyl ligand at nickel was also described.[41] In addition, outer-sphere electrophilic fluorination was reported by Lynam, Slattery and co-workers.[42,43] The rearrangements of the alkenyl ligands for the conversion of **2** into *E*-**3**, **1** into **2** and *E*-**3** into **6a** comprise an isomerization at the double bond. This might involve an intermediate vinylidene complex that can be formed by a reversible migration of a methyl group from the alpha carbon to the metal center. Intermediate metallacyclopropene-like species have also been discussed for such rearrangements.[44–46] In addition, a negative hyperconjugation of the π-electron density into antibonding orbitals at the CF$_3$ group might weaken the C=C double bond and allow for an isomerization of the alkenyl ligands. Note that Ojima *et al.* proposed a zwitterionic carbene–rhodium complex as an intermediate for such a *cis*/*trans* rearrangement.[47] However, another alternative route for the isomerization to give complexes **2** or *E*-**3** could imply a rearrangement during the nucleophilic substitution. After addition of CH_3^- to Cα, the β-carbanion formed could show a free rotation about Cα–Cβ. A Lewis-acidic cation of the type $[ZnMe]^+$ would then abstract the fluoride forming the oligomeric $[ZnFMe]_n$.

The suggested structure of complex **2** is supported by NMR spectroscopic data, in part based on the data for the ^{13}C labeled derivative [Rh(^{13}CH$_3$)(Zn^{13}CH$_3$){(*Z*)-C(^{13}CH$_3$)=CHCF$_3$}(PEt$_3$)$_2$] (**2′**) (see ESI‡). Thus, in the ^1H NMR spectrum of complex **2′** a resonance for the rhodium-bound methyl ligand is observed at −0.42 ppm as a doublet of triplets with coupling constants of 121.1 and 4.6 Hz due to the coupling to the carbon atom and the two phosphine ligands. In addition, a resonance at −0.21 ppm is assigned to the methyl group at the Zn atom. It appears as a doublet coupled with $^1J_{H-C} = 123.2$ Hz. The $^{13}C\{^1H\}$ NMR displays two resonances at −27.5 and −9.2 ppm for the rhodium- and zinc-bonded methyl moieties, respectively. The former exhibits a doublet of pseudo quartets as a result of the coupling to rhodium (9.3 Hz), the two phosphorus atoms and the carbon atom bonded to zinc with a coupling constant of 5.2 Hz. The latter signal also shows the 5.2 Hz carbon–carbon coupling together with the extra coupling to rhodium resulting in a pseudo triplet. In addition, the geometry of complex **2** was optimized by DFT calculations using toluene as a solvent (BP86/def2-SVP, see ESI‡). The complex exhibits a tetragonal pyramidal structure at rhodium in which the methylzinc group is at the apical position. The distance between the Zn nucleus and one of the fluorine atoms of the CF$_3$ moiety of 2.747 Å is shorter than the sum of van der Waals radii which might be the reason for the favored *cis* arrangement of the Zn center and the CF_3 group at the moiety containing the double bond. In fact, this product is 7.4 kJ mol^{-1} more stable than the corresponding *trans* isomer.

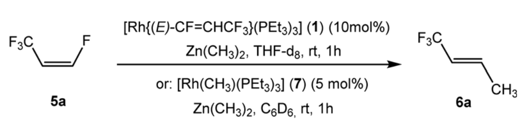
Based on the stoichiometric functionalization of the fluorinated alkenyl ligand at complex **1** to yield **6a**, a process for the catalytic methylation of fluoroolefins was developed. The reaction of *Z*-1,3,3,3-tetrafluoropropene (**5a**) with $Zn(CH_3)_2$ in THF-d_8 in the presence of 10 mol% [Rh{(*E*)-CF=CHCF$_3$}(PEt$_3$)$_3$] (**1**) as a catalyst gave full conversion of the olefin into the C–C coupling product *E*-1,1,1-trifluorobut-2-ene (**6a**) (Scheme 3, Table 1, entry 1).

Complex [Rh{(*E*)-CF=CHCF$_3$}(PEt$_3$)$_3$] (**1**) is synthesized by C–H bond activation of **5a** using [Rh(CH$_3$)(PEt$_3$)$_3$] (**7**).[33] Therefore, complex **7** was also tested as a pre-catalyst and full conversion to compound **6a** was obtained after 1 h using only 5 mol% of catalyst (Scheme 3, Table 1, entry 2). Remarkably the transformation occurs at room temperature within 1 h. Note that $Zn(CH_3)_2$ does not react with the olefin in the absence of a rhodium catalyst.

In general, there are few examples of rhodium-mediated Negishi-type cross-coupling reactions described in the literature. For these cases, C–I bond activation functionalization steps do not proceed through an outer-sphere reaction; instead they are proposed to occur *via* common oxidative addition/transmetalation cycles. Thus, Takagi *et al.* described alkyl-aryl C–C coupling reactions using [RhCl(cyclooctadiene)]$_2$ with bidentate phosphines[48] and work by Ozerov and co-workers using a PNP pincer rhodium complex as a precatalyst afforded a 7% yield in an aryl–aryl coupling.[39] It might additionally be worth noting that examples on the functionalization of fluoroaromatics by cross-coupling reactions involving C–F bond cleavage have been reported, for instance Negishi-type conversions at Ni and Pd by the research groups of Love, Ogoshi and Radius.[13,49–64]

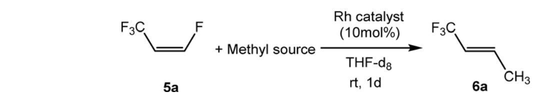
Other rhodium complexes as catalysts for the derivatization of **5a** were then studied using $Zn(CH_3)_2$ as a nucleophile. Accordingly, $Zn(CH_3)_2$ methylates the Rh–F bond of [Rh(F)(PEt$_3$)$_3$] and in the presence of *Z*-1,3,3,3-tetrafluoropropene (**5a**), the generation of *E*-1,1,1-trifluorobut-2-ene (**6a**) with 70% conversion was achieved (Table 1, entry 3). A comparable outcome was obtained when [Rh(H)(PEt$_3$)$_3$] was tested as a catalyst (Table 1, entry 4). Note that the rhodium hydrido complex is known to activate preferentially vinylic C–F bonds followed by C–H bond activation of another equivalent of olefin.[65–68]

As an alternative to $Zn(CH_3)_2$, $BrMgCH_3$ and $LiCH_3$ were applied for the catalytic methylation of **5a**, but the formation of the methylated derivative was not observed within one day (Table 1, entries 5 and 6). Note that an oligomerization of the



Scheme 3 Catalytic Negishi cross-coupling reaction of **5a**.

Table 1 Catalyst and methyl source screening to obtain **6a**



Entry	Catalyst	Methyl source	Conversion[a] (%)
1	Complex **1**	$Zn(CH_3)_2$	99
2[b]	Complex **7**	$Zn(CH_3)_2$	99
3	[Rh(F)(PEt$_3$)$_3$]	$Zn(CH_3)_2$	70
4	[Rh(H)(PEt$_3$)$_3$]	$Zn(CH_3)_2$	70
5	Complex **7**	$MgBrCH_3$	—
6	Complex **7**	$LiCH_3$	—
7	Complex **7**	$Zn(CH_3)Cl$	15

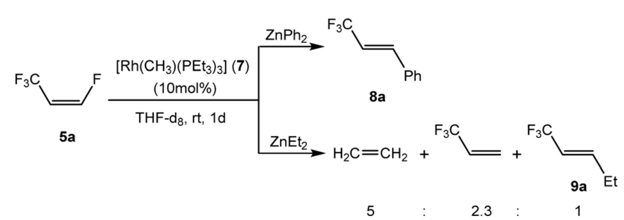
[a] Conversion based on the consumption of $Zn(CH_3)_2$ and determined by ^{1}H NMR spectroscopy. [b] 1 h reaction time, 5 mol% of complex **7**.

nucleophilic reagents in solution can attenuate the nucleophilicity of their methyl anion. On the other hand, mono organylzinc chloride derivatives can also be used for cross-coupling reactions. Indeed, chloromethylzinc could be employed to yield **6a**, but only with 15% conversion (Table 1, entry 7).

Further functionalization of *Z*-1,3,3,3-tetrafluoropropene (**5a**) was attempted using $ZnEt_2$ and $ZnPh_2$ as nucleophile sources. Indeed, reaction of **5a** with $ZnPh_2$ in the presence of complex **7** as a catalyst gave, within 1 d, *E*-3-phenyl-1,1,1-trifluoropropene (**8a**) with 90% conversion (Scheme 4), but after one week at room temperature, full conversion was achieved. Interestingly, $ZnEt_2$ provided a different outcome. The reaction of **5a** with $ZnEt_2$ using complex **7** as a catalyst gave, after 1 day a mixture of ethylene, *E*-1,1,1-trifluoropent-2-ene (**9a**) and 3,3,3-trifluoropropene in a 5 : 1 : 2.3 ratio with 60% conversion (Scheme 4).

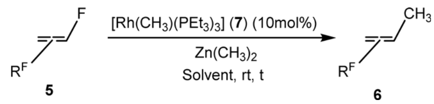
The formation of **9a** should take place through a comparable mechanism as for the generation of **6a**, leading to a Rh–Zn bimetallic intermediate which would bear an ethyl group at the olefin and an ethyl ligand bound to rhodium. This intermediate can produce ethene together with [Rh(H)(PEt$_3$)$_3$] by β-H elimination. The rhodium hydrido complex would then react with **5a** to give 3,3,3-trifluoropropene and complex [Rh{(*E*)-CF=CHCF$_3$}(PEt$_3$)$_3$] (**1**) as described before in the literature.[33]

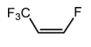
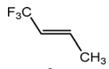
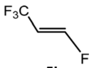
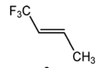
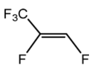
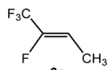
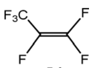
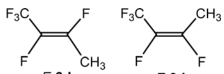
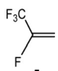
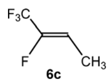
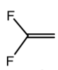
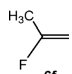
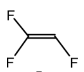
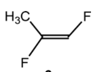
The scope of the rhodium defluorinative methylation was then investigated using other olefinic substrates and complex [Rh(CH$_3$)(PEt$_3$)$_3$] (**7**) as a catalyst (Table 2, see also the ESI‡ for further optimizations). Thus, *E*-1,3,3,3-tetrafluoropropene (**5b**) was converted into compound **6a** with 95% conversion. Higher fluorinated derivatives were also attempted and both *Z*-



Scheme 4 Activation of compound **5a** with $ZnPh_2$ and $ZnEt_2$.

Table 2 Negishi cross-coupling methylation of fluorinated olefins (R^F = F and/or CF_3)



Olefin	Solvent	Time	Conv.[a] (%)	Products
 5a	C_6D_6	1 h	99	 6a
 5b	C_6D_6	6 d	95	 6a
 5c	THF-d_8	1 d	25[c]	 6c
 5d	THF-d_8	1 d	10	 E-6d : Z-6d 0.9 : 1
 5e	THF-d_8	6 d	11	 6c
 5f	C_6D_6	4 d[b]	Traces	 6f
 5g	THF-d_8	1 d	17	 6g

[a] Determined by ^{1}H and ^{19}F NMR. [b] At 60 °C. [c] Main product.

1,2,3,3,3-pentafluoropropene (**5c**) and perfluoropropene (**5d**) were used. In the first case *Z*-1,1,1,2-tetrafluorobut-2-ene (**6c**) was identified in 25% conversion as the main product, while in the second case a mixture of *Z*/*E*-1,2,3,3,3-pentafluorobut-2-ene isomers (**6d**) in a 1 : 0.9 ratio was formed (10% conversion). The latter stoichiometric conversion and decrease in reactivity for the perfluorinated substrate could be due to the preference of complex 7 for the activation of C–H over C–F bonds.[67] Then, 2,3,3,3-tetrafluoropropene (HFO-1234yf, **5e**) was used as a substrate, but only 11% conversion was achieved to form **6c** and unidentified compounds. Finally, to investigate the influence of a CF_3 group on the catalytic methylation of fluoroolefins, 1,1-difluoroethane (**5f**) and trifluoroethane (**5g**) were employed as reagents. While **5f** yielded only traces of the methylated product 2-fluoropropene (**6f**) even at 60 °C, compound **5g** provided a mixture of *E*-1,2-difluoropropene (**6g**) and an unknown compound in a 5 : 1 ratio with 17% conversion. These results also suggest a preference of the rhodium system for olefins with a geminal CHF group facilitating the initial C–H bond activation.

Conclusions

In conclusion, Negishi-type cross-coupling reactions of fluorinated alkenes were developed. The conversions follow an unprecedented reaction pathway: (I) the C–F bond activation and C–C coupling steps occur by an outer-sphere nucleophilic attack at the fluorinated alkenyl ligand. (II) Another crucial step comprises C–H bond activation to convert the olefinic substrate into a Rh derivative, whereas at the same time the lower-fluorinated olefinic product is released. Stoichiometric model reactions give insight into key-steps of a putative catalytic cycle. A heterobinuclear Rh/Zn complex might play a certain role for the C–C coupling step. Note that in the past Rh-catalyzed hydrodefluorination, germylation, silylation and borylation reactions of fluorinated olefins were studied, but cross coupling reactions were elusive.[65–71]

Data availability

Details of experimental procedures, characterization of the complexes can be found in the ESI.‡

Author contributions

Conceptualization, M. T. and T. B.; investigation, M. T., S. M.; writing—original draft preparation, M. T.; writing—review and editing, M. T., S. M. and T. B.; funding acquisition, T. B.

Conflicts of interest

There are no conflicts to declare.

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