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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  $[\text{Rh}\{\text{(E)-CF=CHCF}_3\}(\text{PEt}_3)_3]$  with  $\text{Zn}(\text{CH}_3)_2$  results in the methylation of the alkenyl ligand to give  $[\text{Rh}\{\text{(E/Z)-C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PEt}_3)_3]$ . Variable temperature NMR studies allowed the identification of a heterobinuclear rhodium–zinc complex as an intermediate, for which the structure  $[\text{Rh}(\text{CH}_3)(\text{ZnCH}_3)\{\text{(Z)-C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PEt}_3)_2]$  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.

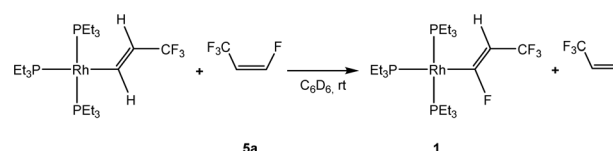
## Introduction

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

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.<sup>14,15</sup> For fluoroalkenes, C–C couplings have been less studied and examples include group 10 catalysts and the use of *gem*-difluoroalkenes.<sup>16–28</sup> 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  $\beta$ -fluorine elimination. Cao and Wu developed a Suzuki–Miyaura cross coupling arylation of *gem*-difluoroalkenes using a nickel

catalyst,<sup>21</sup> whereas Tsui and Liu applied a palladium catalyst.<sup>16</sup> Xu *et al.* published the arylation of an *in situ* formed difluoro-vinyl ketone in the presence of a palladium catalyst and aryl boronic acids.<sup>19</sup> 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.<sup>29</sup> Negishi-type cross-coupling reactions based on vinyl  $\text{C}(\text{sp}^2)\text{-F}$  bond oxidative addition steps are rare. Saeki *et al.* functionalized the olefin  $\text{CF}_2=\text{CH}(1\text{-naphthyl})$  with arylzinc derivative  $\text{MeC}_6\text{H}_4\text{ZnCl}$  in the presence of a palladium catalyst.<sup>30</sup> 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  $\text{C}(\text{sp}^2)\text{-F}$  bond alkylations of 2,3,3,3-tetrafluoropropene or tetrafluoroethylene, respectively.<sup>31,32</sup>

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  $[\text{Rh}\{\text{(E)-CH=CHCF}_3\}(\text{PEt}_3)_3]$  can activate higher fluorinated olefins (Scheme 1). For the latter, in a C–H activation step  $[\text{Rh}\{\text{(E)-CF=CHCF}_3\}(\text{PEt}_3)_3]$  (**1**) and 3,3,3-trifluoropropene were produced.<sup>33</sup>



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

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

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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<sup>2</sup>)–F and C(sp<sup>2</sup>)–H bond activation and, remarkably, involving a C–C coupling step in the outer coordination sphere.

## Results and discussion

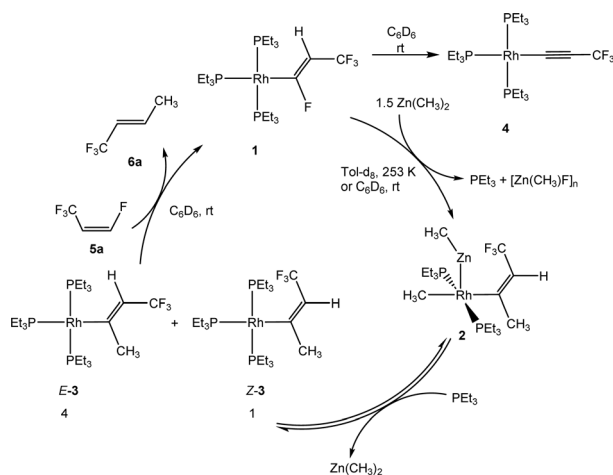
Treatment of complex  $[\text{Rh}\{\text{E}-\text{CF}=\text{CHCF}_3\}(\text{PET}_3)_3]$  (**1**) with one equivalent of  $\text{Zn}(\text{CH}_3)_2$  in  $\text{C}_6\text{D}_6$  yielded after 20 min at room temperature a mixture of complexes, which included a heterobimetallic compound, for which the structure  $[\text{Rh}(\text{CH}_3)(\text{ZnCH}_3)\{\text{Z}-\text{C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PET}_3)_2]$  (**2**) is suggested, as well as the isomers  $[\text{Rh}\{\text{E}-\text{C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PET}_3)_3]$  (*E*-**3**),  $[\text{Rh}\{\text{Z}-\text{C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PET}_3)_3]$  (*Z*-**3**), the alkynyl complex  $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PET}_3)_3]$  (**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  $\text{PET}_3$ , 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  $\text{Zn}(\text{CH}_3)_2$  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.<sup>34</sup> As previously reported, complex **1** is not stable and after a dehydrofluorination step complex **4** is obtained.<sup>33</sup>

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

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.<sup>40</sup> The attack of  $\text{PET}_3$  at the  $\beta$ -carbon atom of a perfluorovinyl ligand at nickel was also described.<sup>41</sup> In addition, outer-sphere electrophilic fluorination was reported by Lynam, Slattery and co-workers.<sup>42,43</sup> 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.<sup>44–46</sup> In addition, a negative hyperconjugation of the  $\pi$ -electron density into antibonding orbitals at the  $\text{CF}_3$  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.<sup>47</sup> 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  $\text{CH}_3^-$  to  $\text{C}\alpha$ , the  $\beta$ -carbanion formed could show a free rotation about  $\text{C}\alpha$ – $\text{C}\beta$ . A Lewis-acidic cation of the type  $[\text{ZnMe}]^+$  would then abstract the fluoride forming the oligomeric  $[\text{ZnFMe}]_n$ .

The suggested structure of complex **2** is supported by NMR spectroscopic data, in part based on the data for the <sup>13</sup>C labeled derivative  $[\text{Rh}(\text{C}^{13}\text{CH}_3)(\text{Zn}^{13}\text{CH}_3)\{\text{Z}-\text{C}(\text{C}^{13}\text{CH}_3)=\text{CHCF}_3\}(\text{PET}_3)_2]$  (**2'**) (see ESI†). Thus, in the <sup>1</sup>H 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 <sup>1</sup>J<sub>H–C</sub> = 123.2 Hz. The <sup>13</sup>C{<sup>1</sup>H} NMR displays two resonances at –27.5 and –9.2 ppm for the rhodium- and zinc-bound 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  $\text{CF}_3$  moiety of 2.747 Å is shorter



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



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<sub>3</sub> group at the moiety containing the double bond. In fact, this product is 7.4 kJ mol<sup>-1</sup> more stable than the corresponding *trans* isomer.

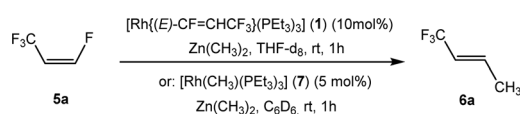
Based on the stoichiometric functionalization of the fluorinated alkenyl ligand at complex **1** to yield **6a**, a process for the catalytic methylation of fluoroolefins was developed. The reaction of *Z*-1,3,3,3-tetrafluoropropene (**5a**) with Zn(CH<sub>3</sub>)<sub>2</sub> in THF-d<sub>8</sub> in the presence of 10 mol% [Rh{(E)-CF=CHCF<sub>3</sub>}(PET<sub>3</sub>)<sub>3</sub>] (**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<sub>3</sub>}(PET<sub>3</sub>)<sub>3</sub>] (**1**) is synthesized by C–H bond activation of **5a** using [Rh(CH<sub>3</sub>)(PET<sub>3</sub>)<sub>3</sub>] (**7**).<sup>33</sup> 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<sub>3</sub>)<sub>2</sub> 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)]<sub>2</sub> with bidentate phosphines<sup>48</sup> 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.<sup>39</sup> 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.<sup>13,49–64</sup>

Other rhodium complexes as catalysts for the derivatization of **5a** were then studied using Zn(CH<sub>3</sub>)<sub>2</sub> as a nucleophile. Accordingly, Zn(CH<sub>3</sub>)<sub>2</sub> methylates the Rh–F bond of [Rh(F)(PET<sub>3</sub>)<sub>3</sub>] 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<sub>3</sub>)<sub>3</sub>] 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.<sup>65–68</sup>

As an alternative to Zn(CH<sub>3</sub>)<sub>2</sub>, BrMgCH<sub>3</sub> and LiCH<sub>3</sub> 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 <sup>a</sup> (%)
1	Complex <b>1</b>	Zn(CH <sub>3</sub> ) <sub>2</sub>	99
2 <sup>b</sup>	Complex <b>7</b>	Zn(CH <sub>3</sub> ) <sub>2</sub>	99
3	[Rh(F)(PET <sub>3</sub> ) <sub>3</sub> ]	Zn(CH <sub>3</sub> ) <sub>2</sub>	70
4	[Rh(H)(PET <sub>3</sub> ) <sub>3</sub> ]	Zn(CH <sub>3</sub> ) <sub>2</sub>	70
5	Complex <b>7</b>	MgBrCH <sub>3</sub>	—
6	Complex <b>7</b>	LiCH <sub>3</sub>	—
7	Complex <b>7</b>	Zn(CH <sub>3</sub> )Cl	15

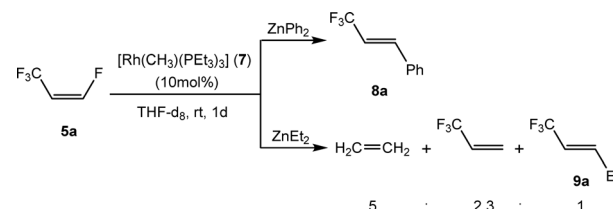
<sup>a</sup> Conversion based on the consumption of Zn(CH<sub>3</sub>)<sub>2</sub> and determined by <sup>1</sup>H NMR spectroscopy. <sup>b</sup> 1 h reaction time, 5 mol% of complex **7**.

nucleophilic reagents in solution can attenuate the nucleophilicity of their methyl anion. On the other hand, mono organozinc 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<sub>2</sub> and ZnPh<sub>2</sub> as nucleophile sources. Indeed, reaction of **5a** with ZnPh<sub>2</sub> 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<sub>2</sub> provided a different outcome. The reaction of **5a** with ZnEt<sub>2</sub> 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<sub>3</sub>)<sub>3</sub>] 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<sub>3</sub>}(PET<sub>3</sub>)<sub>3</sub>] (**1**) as described before in the literature.<sup>33</sup>

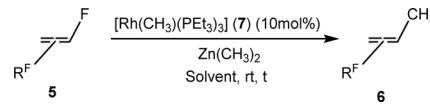
The scope of the rhodium defluorinative methylation was then investigated using other olefinic substrates and complex [Rh(CH<sub>3</sub>)(PET<sub>3</sub>)<sub>3</sub>] (**7**) as a catalyst (Table 2, see also the ESI† for further optimizations). Thus, *E*-1,3,3,3-tetrafluoropropene (**5b**) was converted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








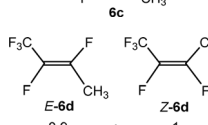








Scheme 4 Activation of compound **5a** with ZnPh<sub>2</sub> and ZnEt<sub>2</sub>.



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



Olefin	Solvent	Time	Conv. <sup>a</sup> (%)	Products
	$C_6D_6$	1 h	99	
	$C_6D_6$	6 d	95	
	THF- $d_8$	1 d	25 <sup>c</sup>	
	THF- $d_8$	1 d	10	
	THF- $d_8$	6 d	11	
	$C_6D_6$	4 d <sup>b</sup>	Traces	
	THF- $d_8$	1 d	17	

<sup>a</sup> Determined by  $^1H$  and  $^{19}F$  NMR. <sup>b</sup> At 60 °C. <sup>c</sup> 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.<sup>67</sup> 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.<sup>65–71</sup>

## 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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