

Cite this: *Chem. Sci.*, 2024, **15**, 8472

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 8th February 2024
Accepted 28th April 2024

DOI: 10.1039/d4sc00951g
rsc.li/chemical-science

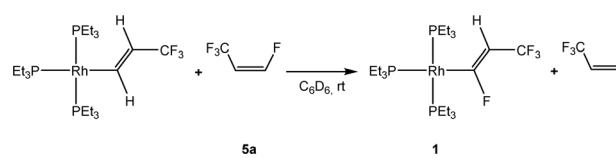
Introduction

Fluorinated compounds are of eminent importance as they are used in a broad range of fields such as pharmaceuticals, 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 $CF_2=CH(1\text{-naphthyl})$ with arylzinc derivative MeC_6H_4ZnCl 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 $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ can activate higher fluorinated olefins (Scheme 1). For the latter, in a C-H activation step $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**1**) and 3,3,3-trifluoropropene were produced.³³



Scheme 1 Reaction of $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ 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(sp²)–F and C(sp²)–H bond activation and, remarkably, involving a C–C coupling step in the outer coordination sphere.

Results and discussion

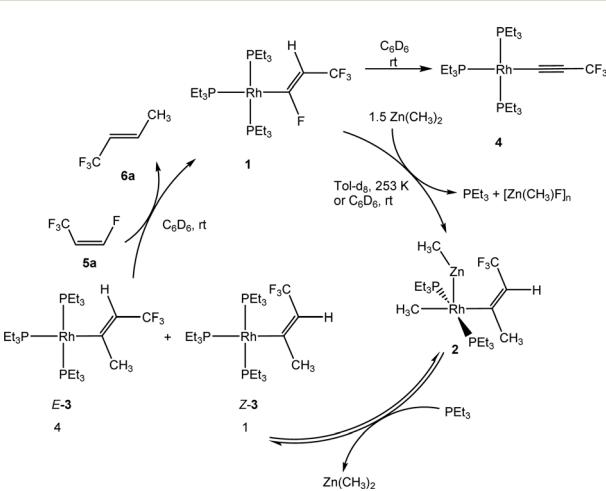
Treatment of complex $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**1**) with one equivalent of $\text{Zn}(\text{CH}_3)_2$ in C_6D_6 yielded after 20 min at room temperature a mixture of complexes, which included a heterobimetallic compound, for which the structure $[\text{Rh}(\text{CH}_3)(\text{ZnCH}_3)\{(Z)\text{-C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) is suggested, as well as the isomers $[\text{Rh}\{(E)\text{-C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PEt}_3)_3]$ (**E-3**), $[\text{Rh}\{(Z)\text{-C}(\text{CH}_3)=\text{CHCF}_3\}(\text{PEt}_3)_3]$ (**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 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 $\text{Z}-1,3,3,3\text{-tetrafluoropropene}$ (**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

In an alternative approach in which complex **1** was treated with 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 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 metallacyclopene-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 $\text{C}=\text{C}$ 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 $\text{C}\alpha$, the β -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 ¹³C labeled derivative $[\text{Rh}^{(13)\text{CH}_3}](\text{Zn}^{13}\text{CH}_3)\{(Z)\text{-C}^{(13)\text{CH}_3}=\text{CHCF}_3\}(\text{PEt}_3)_3$ (**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 $^1J_{\text{H-C}} = 123.2$ Hz. The ¹³C{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



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 CF₃ 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.

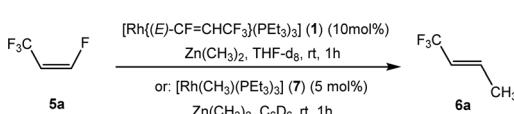
Based on the stoichiometric functionalization of the fluorinated alkenyl ligand at complex **1** to yield **6a**, a process for the catalytic methylation of fluoroolefins was developed. The reaction of *Z*-1,3,3,3-tetrafluoropropene (**5a**) with Zn(CH₃)₂ in THF-d₈ in the presence of 10 mol% [Rh{(E)-CF=CHCF₃}(PEt₃)₃] (**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=CHCF₃}(PEt₃)₃] (**1**) is synthesized by C–H bond activation of **5a** using [Rh(CH₃)(PEt₃)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(CH₃)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 phosphines⁴⁸ 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(CH₃)₂ as a nucleophile. Accordingly, Zn(CH₃)₂ methylates the Rh–F bond of [Rh(F)(PEt₃)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)(PEt₃)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(CH₃)₂, BrMgCH₃ and LiCH₃ 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

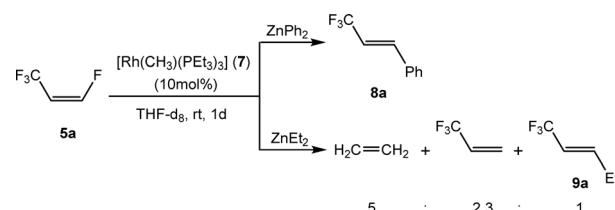
^a Conversion based on the consumption of Zn(CH₃)₂ and determined by ¹H NMR spectroscopy. ^b 1 h reaction time, 5 mol% of complex **7**.

nucleophilic reagents in solution can attenuate the nucleophilicity of their methyl anion. On the other hand, mono 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 ZnEt₂ and ZnPh₂ as nucleophile sources. Indeed, reaction of **5a** with ZnPh₂ 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, ZnEt₂ provided a different outcome. The reaction of **5a** with ZnEt₂ 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)(PEt₃)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=CHCF₃}(PEt₃)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(CH₃)(PEt₃)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 ZnPh₂ and ZnEt₂.



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

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

^a Determined by 1H 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.

Acknowledgements

We acknowledge the DFG (Deutsche Forschungsgemeinschaft) for financial support (BR 2065/13-1). M. T. thanks the Spanish Government and NextGenerationEU/PRTR funds for a María Zambrano contract. We thank Dr N. Otero for fruitful discussions.

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