

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

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

Maria Talavera, *^{ab} Soodeh Mollasalehi ^b and Thomas Braun *^b

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.

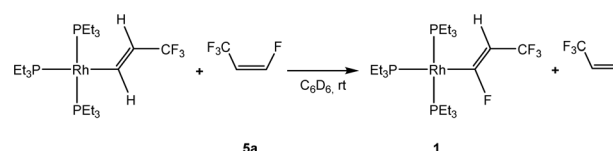
Introduction

Fluorinated compounds are of eminent importance as they are used in a broad range of fields such as pharmaceuticals, agrochemicals and materials science.^{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 $\text{C}(\text{sp}^2)\text{-F}$ 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 difluoro-vinyl 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 $\text{C}(\text{sp}^2)\text{-F}$ 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.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 $\text{C}(\text{sp}^2)\text{-F}$ 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 $[\text{Rh}\{\text{(E)-CH=CHCF}_3\}(\text{PEt}_3)_3]$ 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.³³



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

^aFacultad de Química, Universidade de Vigo, Campus Universitario, 36310 Vigo, Spain. E-mail: matalaveran@uvigo.gal

^bDepartment of Chemistry, Humboldt Universität zu Berlin, Brook-Taylor Straße 2, 12489 Berlin, Germany. E-mail: thomas.braun@cms.hu-berlin.de

† 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

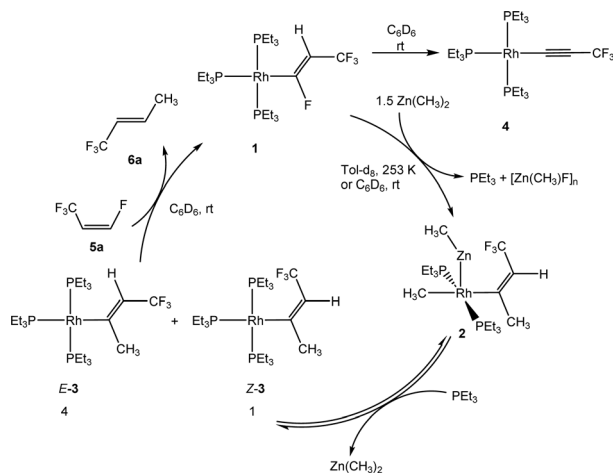
Treatment of complex $[\text{Rh}\{\text{(E)-CF}=\text{CHCF}_3\}(\text{PET}_3)_3]$ (**1**) with one equivalent of $\text{Zn}(\text{CH}_3)_2$ in C_6D_6 yielded after 20 min at room temperature a mixture of complexes, which included a heterobimetallic compound, for which the structure $[\text{Rh}(\text{CH}_3)(\text{ZnCH}_3)\{\text{(Z)-C}(\text{CH}_3)=\text{CHCF}_3\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

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 heterobimetallic 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 $\text{C}=\text{C}$ 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 $[\text{Rh}(\text{¹³CH}_3)(\text{Zn¹³CH}_3)\{\text{(Z)-C}(\text{¹³CH}_3)=\text{CHCF}_3\}(\text{PET}_3)_2]$ (**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 phosphorus 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 ¹³C{¹H} 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 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.

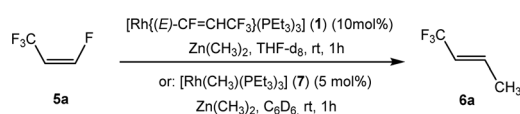
Based on the stoichiometric functionalization of the fluorinated alkenyl ligand at complex **1** to yield **6a**, a process for the catalytic methylation of fluoroolefins was developed. The reaction of *Z*-1,3,3,3-tetrafluoropropene (**5a**) with Zn(CH₃)₂ in THF-d₈ in the presence of 10 mol% [Rh{(E)-CF=CHCF₃}(PET₃)₃] (**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

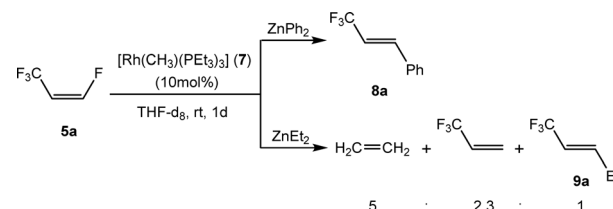
^a Conversion based on the consumption of Zn(CH₃)₂ and determined by ¹H NMR spectroscopy. ^b 1 h reaction time, 5 mol% of complex **7**.

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).

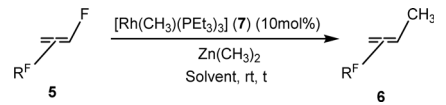
The formation of **9a** should take place through a comparable mechanism as for the generation of **6a**, leading to a Rh–Zn bimetallic intermediate which would bear an ethyl group at the olefin and an ethyl ligand bound to rhodium. This intermediate can produce ethene together with [Rh(H)(PET₃)₃] by 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








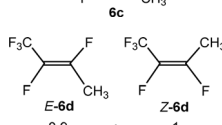






The scope of the rhodium defluorinative methylation was then investigated using other olefinic substrates and complex [Rh(CH₃)(PET₃)₃] (**7**) as a catalyst (Table 2, see also the ESI† for further optimizations). Thus, *E*-1,3,3,3-tetrafluoropropene (**5b**) was converted into compound **6a** with 95% 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 ($R^F = F$ 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 Maria Zambrano contract. We thank Dr N. Otero for fruitful discussions.

Notes and references

- 1 T. Hiyama, *Organofluorine Compounds: Chemistry and Applications*, Springer, Berlin, 2000.
- 2 Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J. L. Aceña, V. A. Soloshonok, K. Izawa and H. Liu, *Chem. Rev.*, 2016, **116**, 422–518.
- 3 S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320–330.
- 4 P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis, Reactivity and Applications*, Wiley-VCH, Weinheim, 2nd edn, 2013.
- 5 P. Javidmand and K. A. Hoffmann, *Int. J. Refrig.*, 2016, **69**, 114–135.
- 6 V. F. Cardoso, D. M. Correia, C. Ribeiro, M. M. Fernandes and S. Lanceros-Méndez, *Polymers*, 2018, **10**, 161–187.
- 7 R. Dams and K. Hintzer, in *Fluorinated Polymers: Volume 2: Applications*, ed. B. Ameduri and H. Sawada, RSC, 2017, vol. 24, pp. 1–31.



- 8 R. Britton, V. Gouverneur, J.-H. Lin, M. Meanwell, C. Ni, G. Pupo, J.-C. Xiao and J. Hu, *Nat. Rev. Methods Primers*, 2021, **1**, 47.
- 9 S.-J. Lou, D.-Q. Xu and Z.-Y. Xu, *Angew. Chem., Int. Ed.*, 2014, **53**, 10330–10335.
- 10 H. Amii and K. Uneyama, *Chem. Rev.*, 2009, **109**, 2119–2183.
- 11 R. D. Chambers and J. F. S. Vaughan, in *Organofluorine Chemistry. Fluorinated Alkenes and Reactive Intermediates*, ed. R. D. Chambers, Springer-Verlag, Germany, 1997, vol. 192.
- 12 M. Ohashi and S. Ogoshi, *Top. Organomet. Chem.*, 2015, **52**, 197–216.
- 13 T. Ahrens, J. Kohlmann, M. Ahrens and T. Braun, *Chem. Rev.*, 2015, **115**, 931–972.
- 14 *Metal-Catalyzed Cross-Coupling Reactions*, ed. F. Diederich and P. J. Stang, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2nd edn, 2008.
- 15 *Metal-Catalyzed Cross-Coupling Reactions and More*, ed. A. d. Meijere, S. Bräse and M. Oestreich, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2013.
- 16 Y. Wang, X. Qi, Q. Ma, P. Liu and G. C. Tsui, *ACS Catal.*, 2021, **11**, 4799–4809.
- 17 W. Dai, X. Zhang, J. Zhang, Y. Lin and S. Cao, *Adv. Synth. Catal.*, 2016, **358**, 183–187.
- 18 R. T. Thornbury and F. D. Toste, *Angew. Chem., Int. Ed.*, 2016, **55**, 11629–11632.
- 19 L. Xu, Q. Zhang, Q. Xie, B. Huang, J.-J. Dai, J. Xu and H.-J. Xu, *Chem. Commun.*, 2018, **54**, 4406–4409.
- 20 W. Heitz and A. Knebelkamp, *Makromol. Chem., Rapid Commun.*, 1991, **12**, 69–75.
- 21 Y. Xiong, T. Huang, X. Ji, J. Wu and S. Cao, *Org. Biomol. Chem.*, 2015, **13**, 7389–7392.
- 22 X. Tong, S.-S. Luo, H. Shen, S. Zhang, T. Cao, Y.-P. Luo, L.-L. Huang, X.-T. Ma and X.-W. Liu, *Org. Chem. Front.*, 2021, **8**, 4533–4542.
- 23 H. Shi, W. Dai, B. Wang and S. Cao, *Organometallics*, 2018, **37**, 459–463.
- 24 T. Fujita, T. Fukuda, N. Suzuki and J. Ichikawa, *Eur. J. Org. Chem.*, 2022, **2022**, e202200600.
- 25 Y. Ishibashi, T. Fujita and J. Ichikawa, *Org. Lett.*, 2022, **24**, 9306–9310.
- 26 Q. Ma, Y. Wang and G. C. Tsui, *Angew. Chem., Int. Ed.*, 2020, **59**, 11293–11297.
- 27 W. Dai, J. Xiao, G. Jin, J. Wu and S. Cao, *J. Org. Chem.*, 2014, **79**, 10537–10546.
- 28 K. T. Keasler, M. E. Zick, E. E. Stacy, J. Kim, J.-H. Lee, L. Aeindartehran, T. Runčevski and P. J. Milner, *Science*, 2023, **381**, 1455–1461.
- 29 Y. Zeng, H. Yang, J. Du, Q. Huang, G. Huang and Y. Xia, *Chem. Sci.*, 2022, **13**, 12419–12425.
- 30 T. Saeki, Y. Takashima and K. Tamao, *Synlett*, 2005, **2005**, 1771–1774.
- 31 Y.-C. Luo, M.-K. Wang, L.-C. Yu and X. Zhang, *Angew. Chem., Int. Ed.*, 2023, **62**, e202308690.
- 32 M. Ohashi, T. Kambara, T. Hatanaka, H. Saijo, R. Doi and S. Ogoshi, *J. Am. Chem. Soc.*, 2011, **133**, 3256–3259.
- 33 M. Talavera and T. Braun, *Chem. Sci.*, 2022, **13**, 1130–1135.
- 34 O. Eisenstein, J. Milani and R. N. Perutz, *Chem. Rev.*, 2017, **117**, 8710–8753.
- 35 M. Molon, T. Cadenbach, T. Bollermann, C. Gemel and R. A. Fischer, *Chem. Commun.*, 2010, **46**, 5677–5679.
- 36 O. Ekkert, A. J. P. White, H. Toms and M. R. Crimmin, *Chem. Sci.*, 2015, **6**, 5617–5622.
- 37 M. D. Fryzuk, D. H. McConville and S. J. Rettig, *Organometallics*, 1993, **12**, 2152–2161.
- 38 J. J. Gair, Y. Qiu, R. L. Khade, N. H. Chan, A. S. Filatov, Y. Zhang and J. C. Lewis, *Organometallics*, 2019, **38**, 1407–1412.
- 39 C. J. Pell, W.-C. Shih, S. Gatard and O. V. Ozerov, *Chem. Commun.*, 2017, **53**, 6456–6459.
- 40 A. L. Raza and T. Braun, *Chem. Sci.*, 2015, **6**, 4255–4260.
- 41 T. Braun, B. Blöcker, V. Schorlemer, B. Neumann, A. Stammler and H.-G. Stammler, *J. Chem. Soc., Dalton Trans.*, 2002, 2213–2218.
- 42 L. M. Milner, N. E. Pridmore, A. C. Whitwood, J. M. Lynam and J. M. Slattery, *J. Am. Chem. Soc.*, 2015, **137**, 10753–10759.
- 43 L. M. Milner, L. M. Hall, N. E. Pridmore, M. K. Skeats, A. C. Whitwood, J. M. Lynam and J. M. Slattery, *Dalton Trans.*, 2016, **45**, 1717–1726.
- 44 J. Cid, J. J. Carbó and E. Fernández, *Chem.–Eur. J.*, 2012, **18**, 1512–1521.
- 45 R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.*, 1990, **112**, 7984–7989.
- 46 R. J. Pawley, M. A. Huertos, G. C. Lloyd-Jones, A. S. Weller and M. C. Willis, *Organometallics*, 2012, **31**, 5650–5659.
- 47 I. Ojima, N. Clos, R. J. Donovan and P. Ingallina, *Organometallics*, 1990, **9**, 3127–3133.
- 48 S. Ejiri, S. Odo, H. Takahashi, Y. Nishimura, K. Gotoh, Y. Nishihara and K. Takagi, *Org. Lett.*, 2010, **12**, 1692–1695.
- 49 Y. P. Budiman, S. A. Westcott, U. Radius and T. B. Marder, *Adv. Synth. Catal.*, 2021, **363**, 2224–2255.
- 50 L. Fu, Q. Chen and Y. Nishihara, *Chem. Rec.*, 2021, **21**, 3394–3410.
- 51 S. Iqbal, M. Sharif and P. Langer, *Synlett*, 2021, **32**, 1784–1795.
- 52 Z. Zhu, L. Lin, J. Xiao and Z. Shi, *Angew. Chem., Int. Ed.*, 2022, **61**, e202113209.
- 53 Y. Li and J. Zhu, *J. Org. Chem.*, 2022, **87**, 8902–8909.
- 54 B. C. Figula, D. L. Kane, K. Balaraman and C. Wolf, *Org. Lett.*, 2022, **24**, 8719–8723.
- 55 R. Doi, Y. Zhou and S. Ogoshi, *Synthesis*, 2023, **55**, 857–867.
- 56 X. Lu, Y. Wang, B. Zhang, J.-J. Pi, X.-X. Wang, T.-J. Gong, B. Xiao and Y. Fu, *J. Am. Chem. Soc.*, 2017, **139**, 12632–12637.
- 57 T. W. Butcher, J. L. Yang, W. M. Amberg, N. B. Watkins, N. D. Wilkinson and J. F. Hartwig, *Nature*, 2020, **583**, 548–553.
- 58 X. Li, Y. Li, Z. Wang, W. Shan, R. Liu, C. Shi, H. Qin, L. Yuan, X. Li and D. Shi, *ACS Catal.*, 2023, **13**, 2135–2141.
- 59 T. Schaub, M. Backes and U. Radius, *J. Am. Chem. Soc.*, 2006, **128**, 15964–15965.
- 60 O. He, B. Cula and T. Braun, *Helv. Chim. Acta*, 2023, **106**, e202200156.
- 61 D. Breyer, T. Braun and P. Kläring, *Organometallics*, 2012, **31**, 1417–1424.



- 62 M. Ohashi, R. Doi and S. Ogoshi, *Chem.–Eur. J.*, 2014, **20**, 2040–2048.
- 63 A. D. Sun, K. Leung, A. D. Restivo, N. A. LaBerge, H. Takasaki and J. A. Love, *Chem.–Eur. J.*, 2014, **20**, 3162–3168.
- 64 M. W. Kuntze-Fechner, C. Kerpen, D. Schmidt, M. Häring and U. Radius, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1767–1775.
- 65 T. Ahrens, M. Teltewskoi, M. Ahrens, T. Braun and R. Laubenstein, *Dalton Trans.*, 2016, **45**, 17495–17507.
- 66 M. Talavera, R. Müller, T. Ahrens, C. N. von Hahmann, B. Braun-Cula, M. Kaupp and T. Braun, *Faraday Discuss.*, 2019, **220**, 328–349.
- 67 M. Talavera, C. N. von Hahmann, R. Müller, M. Ahrens, M. Kaupp and T. Braun, *Angew. Chem., Int. Ed.*, 2019, **58**, 10688–10692.
- 68 M. Talavera and T. Braun, *Chem.–Eur. J.*, 2021, **27**, 11926–11934.
- 69 M. Talavera and T. Braun, *Synlett*, 2020, **31**, 1760–1774.
- 70 T. Braun, F. Wehmeier and K. Altenhöner, *Angew. Chem., Int. Ed.*, 2007, **46**, 5321–5324.
- 71 T. Braun, M. Ahijado Salomon, K. Altenhöner, M. Teltewskoi and S. Hinze, *Angew. Chem., Int. Ed.*, 2009, **48**, 1818–1822.

