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Activation of perfluoro(methyl vinyl ether) at Rh(I) complexes: metal-centered *versus* phosphine-mediated decarbonylation†

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This study investigates the reactivity of perfluoro(methyl vinyl ether) [PMVE, $\text{CF}_2=\text{CF}(\text{OCF}_3)$] towards rhodium(I) phosphine complexes. The reaction pathways are characterized by C–O and C–F bond cleavage reactions and decarbonylation steps. On using the complex $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**), unprecedented reactivity pathways were observed that are distinct from those found for previously studied fluoroolefins. Reactivity of an excess PMVE at Rh is initiated by coordination to the Rh center in **1**, followed by its insertion into the Rh–H bond and a $\beta\text{-OCF}_3$ elimination. This process ultimately results in OCF_3 ligand transformation to give *trans*- $[\text{Rh}(\text{F})(\text{CO})(\text{PEt}_3)_3]$ (**4**) and Et_3PF_2 . Reactions of stoichiometric amounts of PMVE with $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**) or an excess amount of it with $[\text{Rh}(\text{F})(\text{PEt}_3)_3]$ (**6**) led to olefin complex formation to yield *trans*- $[\text{Rh}(\text{F})(\eta^2\text{-CF}_2\text{CFH})(\text{PEt}_3)_2]$ (**7**) and *trans*- $[\text{Rh}(\text{F})(\text{CF}(\text{OCF}_3)\text{CF}_2)(\text{PEt}_3)_2]$ (**8**), respectively. In contrast, a remarkable insertion into the Rh–F bond at $[\text{Rh}(\text{F})(\text{CO})(\text{PEt}_3)_2]$ (**4**) was observed leading to the formation of *trans*- $[\text{Rh}(\text{CO})(\text{CF}(\text{OCF}_3)\text{CF}_3)(\text{PEt}_3)_2]$ (**5**). Decarbonylation of PMVE proceeds not only at Rh, but also *via* a metal-free, phosphine-mediated process. The latter is characterized by oxidative addition of PMVE at PEt_3 to form the fluorophosphoranes *E/Z*- $(\text{F}_3\text{CO})\text{CF}=\text{CF}(\text{PFEt}_3)$, which subsequently convert into Et_3PF_2 , CO and presumably tetrafluoroethene.

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Introduction

The increasing interest in hydrofluoroolefins (HFOs) stems from their significantly lower potential for ozone depletion and global warming compared to chlorofluorocarbons and hydrofluorocarbons.^{1–3} This has led to their adoption as refrigerants in automotive air conditioning systems.^{4–6} Generally, fluorinated olefins show promise as precursors for synthesizing new fluorinated building blocks.^{7–10} An interesting strategy involves the development of methods for functionalization that are mediated by main group elements or transition metals, including C–F and C–H bond activation reactions.^{11–14}

The fluoroolefin perfluoro (methyl vinyl ether) [PMVE, $\text{CF}_2=\text{CF}(\text{OCF}_3)$] can be classified as part of the PFAS family (per- and polyfluoroalkyl substances) and, therefore, understanding its reactivity will provide insights concerning its depletion.^{15–17} It is, however, valuable as a monomer for producing high-value fluorinated polymers.^{18–22} It has also been suggested as an alternative replacement for SF_6 .^{23,24} PMVE is formally an analogue of hexafluoropropene with a formal substitution of the CF_3 group in hexafluoropropene with the OCF_3 group,

which leads to a different reactivity. Note that the trifluoromethoxy group OCF_3 imparts significant biological properties to molecules, making OCF_3 compounds highly valuable targets in the pharmaceutical and agrochemical industries.^{25,26} This is primarily due to the strong electron-withdrawing effect and high lipophilicity caused by this group.^{27–32} To ensure these compounds are used safely in industrial applications, thorough research into their properties and reactivity is essential.^{17,33}

Investigations into the reactivity of PMVE towards transition metal complexes are scarce, despite extensive research on fluoroolefins bearing a CF_3 group. Noticeably, Baker *et al.* previously reported a copper catalysed hydrodefluorination of PMVE leading to the formation of difluoroethylene isomers *via* $\beta\text{-OCF}_3$ elimination.³⁴ In another recent work, they described a copper-mediated fluoroalkyl $-\text{CF}(\text{OCF}_3)(\text{CF}_2\text{H})$ transfer to organic electrophiles *via* insertion of the PMVE into Cu–H bonds of Stryker's reagent.³⁵ Note that the hydroamination of PMVE with secondary amines, as well as the addition reaction of azoles to PMVE have been reported.^{36,37}

The notable reactivity of rhodium(I) phosphine complexes $[\text{Rh}(\text{E})(\text{PEt}_3)_3]$ (E = H, F, boryl, germyl, silyl) towards fluorinated olefins, such as hexafluoropropene, has been well-documented.^{8,38,39} The identity of the anionic ligand E holds a significant importance in the activation process for several reasons, such as the formation of strong element-fluorine

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bonds like H–F, B–F, Ge–F, or Si–F bonds, as well as a kinetic control of regio- and chemoselectivities.^{8,38–43}

On the other hand, examples of C(sp²)–F bond functionalization reactions by simple tertiary phosphines, without the need for activation by metals, metalloids, or a Lewis acid are still rare. Burton and colleagues demonstrated that tertiary phosphines such as PPh₃ and P^{*n*}Bu₃ could attack perfluorinated cyclic alkenes and perfluorinated linear terminal alkenes leading to the production of stable phosphonium ylides and the generation of a fluorophosphorane ^{*n*}Bu₃P(F)CF=CF(CF₃), respectively.^{44,45} Additionally, García and colleagues reported the formation of the difluorophosphorane Et₃PF₂ in the hydrodefluorination of a range of polyfluoro(hetero)aromatics, using PET₃ as the sole defluorinating agent.⁴⁶ Furthermore, the generation of fluorophosphoranes Et₃P(F)CF=C(X)CF₃ (X = H, F) or Et₃PF₂ through the reaction of various fluorinated olefins with the [Rh(E)(PET₃)₃] has been reported.^{38,41,47} Dissociation of phosphine during the C–F bond activation step at the Rh complex might be essential for these transformations.

Herein we present studies on the reactivity of PMVE towards the rhodium(I) phosphine complexes [Rh(H)(PET₃)₃] (**1**) and [Rh(F)(PET₃)₃] (**6**). PMVE serves as CO source and fluorinating agent. The observed reactivity patterns are very distinctive and involve coordination of the olefin, insertion into Rh–H and Rh–F bonds, β-OCF₃ elimination steps as well as oxidative addition at liberated PET₃.

Results and discussion

Treatment of the rhodium(I) hydrido complex [Rh(H)(PET₃)₃] (**1**) with an excess of perfluoro (methyl vinyl ether) [PMVE, CF₂=CF(OCF₃)] yielded after 30 minutes the fluoroalkyl complex *trans*-[Rh(CF₂CFH(OCF₃))(CO)(PET₃)₂] (**3**) and the Vaska type fluoroalkyl complex *trans*-[Rh(F)(CO)(PET₃)₂] (**4**) in a ratio of 1.3 : 1, as well as 1,1,2-trifluoroethylene (Scheme 1). The source of the CO ligand in **3** and **4** is the OCF₃ moiety of PMVE, and its rhodium as well as phosphine mediated-transformation is described below.

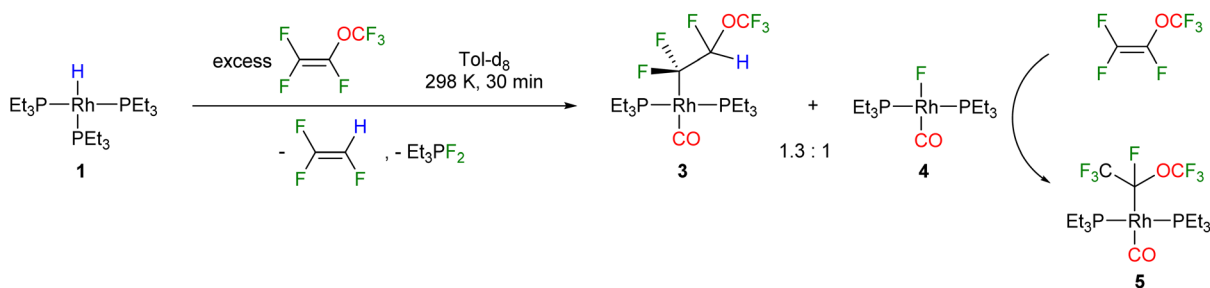
The compounds **3** and **4** were not stable at room temperature and a slow conversion into the rhodium(I) perfluoroalkyl complex *trans*-[Rh(CO)(CF(OCF₃)CF₃)(PET₃)₂] (**5**) was found (Scheme 1). The formation of complex **5** suggests an insertion of PMVE, which is present in an excess, into the rhodium–fluorine bond in complex **4**. An independent reaction of **4** with PMVE

confirmed the formation of **5** via the insertion of the olefin into the Rh–F bond. Note that examples for an insertion of fluorinated olefins into metal–fluorine bonds are rare, and have been reported previously at group 10 and 11 transition metal-complexes, but not at rhodium.^{35,48,49}

Compound **4** has been previously synthesised and fully characterised.⁵⁰ Complexes **3** and **5** were characterised by ¹H, ³¹P{¹H} and ¹⁹F NMR spectroscopy. For complex **3**, in the ³¹P{¹H} spectrum a doublet of triplets is observable due to the coupling to the rhodium centre (138.3 Hz) and the CF₂ moiety (24.4 Hz). In the ¹⁹F NMR spectrum, the resonance of the OCF₃ moiety appears at –58.4 as a broad signal, while for the CF₂ group two resonances were found with a geminal F,F coupling constant of 295 Hz, which is in accordance with the C(sp³) character of the CF₂ group.^{34,51} For the CFH group a doublet with ²J_{F,H} of 57 Hz at –134.9 ppm in ¹⁹F NMR spectrum and at 5.8 ppm in ¹H NMR spectrum are visible. The IR spectrum of **3** reveals an intense absorption band at 1945 cm^{–1}, which can be assigned to the CO stretching vibration and the data are comparable with those of known rhodium carbonyl complexes.⁵⁰ For complex **5** on the other hand, a doublet appears in ³¹P{¹H} NMR spectrum at 24.3 ppm with a P,Rh coupling constant of 120.9 Hz. In the ¹⁹F NMR spectrum, a doublet of quartets at –53.7 ppm corresponds to the CF₃ moiety, which couples to the CF group with 10 Hz and to the OCF₃ group with 1 Hz, while another doublet of quartets at –81.5 ppm with a coupling constant of 3 Hz to the CF group can be assigned to the OCF₃ moiety. Both signals correlate with the quartet of quartets at –129.5 ppm for the CF moiety. Furthermore, a CO stretching vibration band at 1938 cm^{–1} in the IR spectrum is observable for compound **5**.

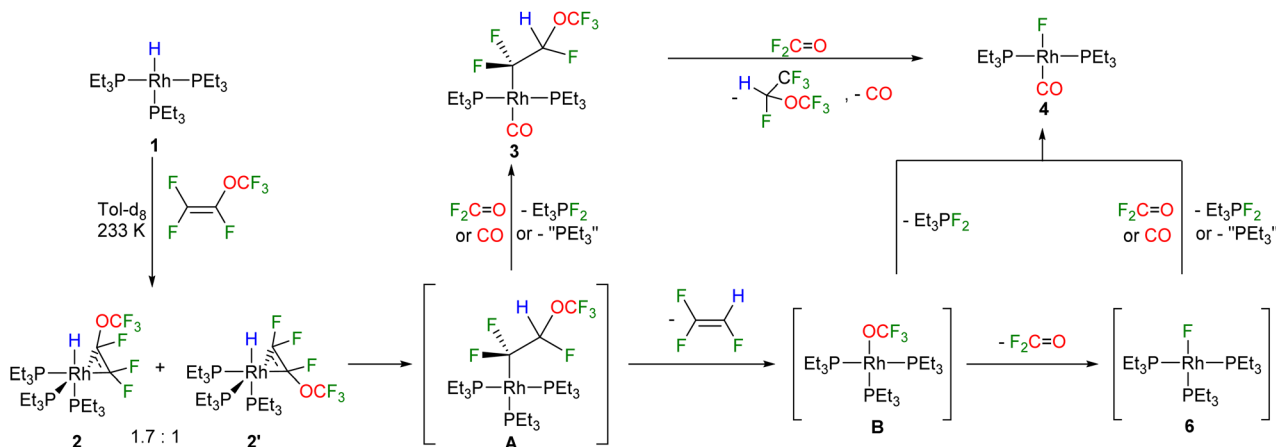
Moreover, the formation of the fluorophosphorane Et₃PF₂ and 1,2,2,2-tetrafluoroethyl trifluoromethyl ether, CHF(OCF₃)(CF₃) was observed (see also below, Scheme 2).⁴⁷ The presence of CHF(OCF₃)(CF₃) was revealed by the ¹⁹F and ¹H NMR spectra data, which were in accordance with the literature.⁵²

The reaction of **1** with PMVE was then monitored by NMR spectroscopy at 233 K and the isomeric rotational intermediates *fac*-[Rh(H)(η²-CF₂=C(OCF₃)F)(PET₃)₃] (**2/2'**) in a ratio of 1.7 : 1 were identified (Scheme 2). These olefin complexes were only stable below 273 K, therefore, identification was possible by ¹H, ³¹P{¹H} and ¹⁹F NMR spectroscopy. Another identified intermediate at this temperature was a fluorophosphorane, Z-(F₃CO)CF=CF(PFET₃), which indicates the reaction of PMVE



Scheme 1 Reactivity of complex **1** towards PMVE.





Scheme 2 Mechanistic proposal for the reactivity of complex 1 towards PMVE.

with PEt_3 (for further explanation see below). Above 273 K the transformation of this compound together with **2** and **2'** into **3**, **4**, trifluoroethylene, $\text{CHF}(\text{OCF}_3)(\text{CF}_3)$, and Et_3PF_2 was observed. Previously, coordination of fluorinated olefins to $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**) at low temperatures has been described.^{38,43,53} Characteristic features in the ^1H NMR spectrum are the signals for the hydrido ligands at -12.1 ppm with a large $\text{H,P}_{\text{trans}}$ coupling constant of 152.3 Hz for **2** and at -11.9 ppm for **2'** with 152.8 Hz. Additionally, in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, a doublet of doublets appears for **2** due to the coupling to Rh and the one fluorine atom in *syn* position, while for **2'** a doublet of triplets due to the coupling to Rh and two fluorine atoms in *syn* position is visible. Due to the high structural similarities of the two isomers, the three sets of signals for the inequivalent phosphine ligands at 14.0–12.8 ppm, 11.2–9.4 ppm and 4.8–2.6 ppm, which integrate in a 1:1:1 ratio, overlap in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (242 MHz) at 273 K. However, the Rh,P coupling constants are in accordance with the oxidation state +III at rhodium and a metallacyclopropane structure.^{38,43} In order to further support the metallacyclopropyl configuration of the complexes **2** and **2'**, the structures of the corresponding PMe_3 derivatives **2*** and **2'*** were optimized by DFT calculations and a C–C bond distance of 1.472 Å for **2*** and **2'*** was obtained (Fig. 1).^{54–56} Calculations on the PEt_3 complexes **2** and **2'** were not conclusive as the energy

differences of the converged structures were highly dependent on slight structural differences in the PEt_3 ligand sphere, thus making it hard to identify the global minima. However, based on the DFT calculations on the simplified PMe_3 derivatives, complex **2*** is more stable than complex **2'*** by 10.7 kJ mol^{-1} .^{54–56}

Mechanistically, the transformation of intermediates **2** and **2'** into complexes **3** and **4** requires an insertion of the olefin into the Rh–H bond to yield the intermediate **A** (Scheme 2). **A** then undergoes a $\beta\text{-OCF}_3$ elimination accompanied by the release of the trifluoroethylene. It is likely that the complex $[\text{Rh}(\text{OCF}_3)(\text{PEt}_3)_3]$ (**B**) is then formed as an unstable intermediate, which converts into **4** and F_2PEt_3 . Alternatively, the fluorido complex $[\text{Rh}(\text{F})(\text{PEt}_3)_3]$ (**6**) and fluorophosgene $\text{O}=\text{CF}_2$ are generated. The rapid decomposition of a trifluoromethoxide anion OCF_3^- into fluorophosgene $\text{O}=\text{CF}_2$ and fluoride has been reported in literature.³¹ Fluorophosgene can react with **A** or **6** to yield Et_3PF_2 as well as the carbonyl complexes **3** and **4**, respectively. In addition, it is also feasible that complex **3** reacts with fluorophosgene to convert into **4** upon the release of the observed $\text{CHF}(\text{OCF}_3)(\text{CF}_3)$ and CO (Scheme 2). Note that olefin insertion into the metal–hydrogen bond and $\beta\text{-OCF}_3$ elimination steps have been proposed for a copper complex that mediates the catalytic hydrodefluorination of PMVE to yield a mixture of *cis*- and *trans*-1,2-difluoroethylene in a 4:1 ratio.³⁴

Furthermore, it is important to consider that for the conversion of **A** into **3** and for the formation of the fluorido complex **4** from $[\text{Rh}(\text{F})(\text{PEt}_3)_3]$ (**6**) at least two equivalents of PMVE as an excess source of CO are required. Hence, initially the role of olefin was investigated further by the reaction of $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**) with stoichiometric amounts of PMVE at room temperature, which led to the formation of *trans*- $[\text{Rh}(\text{F})(\eta^2\text{-CF}_2\text{CFH})(\text{PEt}_3)_2]$ (**7**) as well as the fluorophosphorane Et_3PF_2 (Scheme 3). Formation of **7** implies the generation of the reaction products as described above, whereas subsequently a phosphine ligand is substituted by trifluoroethylene at $[\text{Rh}(\text{F})(\text{PEt}_3)_3]$ (**6**) (Scheme 2). The latter step was confirmed independently by treatment of the rhodium fluorido complex $[\text{Rh}(\text{F})(\text{PEt}_3)_3]$ (**6**) with trifluoroethylene to yield

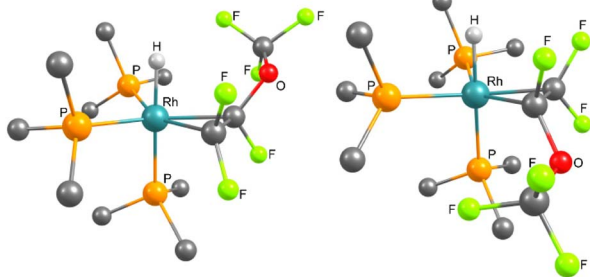
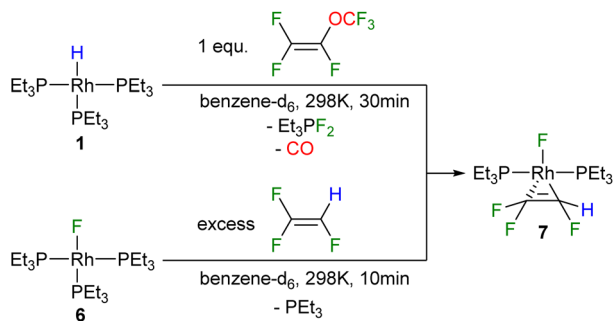


Fig. 1 DFT optimised structures ((B3LYP/cc-pvtz and cc-pvdz, see ESI†) of left: *fac*- $[\text{Rh}(\text{H})(\eta^2\text{-CF}_2\text{=CF}(\text{OCF}_3))(\text{PMe}_3)_3]$ (**2***), and right: (**2'***). Hydrogen atoms of the phosphine ligands are omitted for clarity.



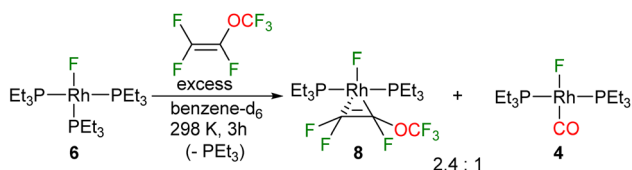


Scheme 3 Reactivity of complex 1 towards one equivalent of PMVE (top), and reactivity of complex 6 towards trifluoroethylene (bottom).

complex 7 (Scheme 3). Thus, the result demonstrates that a replacement of the phosphine ligand in $[\text{Rh}(\text{F})(\text{PEt}_3)_3]$ (6) by an olefin can compete with the substitution of the phosphine by CO, when less amounts of PMVE as a CO source are provided. Note that the dissociation of a phosphine ligand upon the coordination of a fluoroolefin to the fluoro complex 6 has been previously reported for 1,1,3,3,3-pentafluoropropene in a similar manner.³⁸

The resonances of the two inequivalent phosphine ligands of complex 7 appear at 32.3 and 25.9 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and are coupled to each other by $^{trans}J_{\text{P,P}} = 368.2$ Hz. The phosphorus–rhodium coupling constants of 138.9 Hz and 133.3 Hz, respectively, demonstrate the presence of a Rh(I) complex. The signal at 25.9 ppm represents a doublet of doublet of doublets due to its coupling to phosphorus, rhodium, one fluorine atom of the CF_2 moiety and the fluoro ligand, while the second signal displays a doublet of doublet of triplets due to couplings to phosphorus and rhodium, as well as coupling to one fluorine atom of the CF_2 moiety and the fluorine atom of the CFH group. In the ^{19}F NMR spectrum, a geminally coupled pair is observed at -89.4 and -90.8 ppm ($^2J_{\text{F,F}} = 109$ Hz) associated with the CF_2 fluorine resonances along with an upfield CFH peak at -194.9 ppm and the signal of the fluoro ligand at -218.3 ppm. A distinctive doublet of doublet of doublets appears at 5.5 ppm in the ^1H NMR spectrum, corresponding to the CFH hydrogen atom ($^2J_{\text{FH}} = 73.3$ Hz).

The reactivity described above of the fluoro complex $[\text{Rh}(\text{F})(\text{CO})(\text{PEt}_3)_2]$ (4) towards PMVE (Scheme 1) prompted us to also study the behaviour of the fluoro compound $[\text{Rh}(\text{F})(\text{PEt}_3)_3]$ (6) towards PMVE, in order to assess a possible coordination *versus* insertion in a Rh–F bond, as the latter step was found for $[\text{Rh}(\text{F})(\text{CO})(\text{PEt}_3)_2]$ (4). However, treatment of 6 with PMVE gave after 3 hours a mixture of complexes $[\text{Rh}(\text{F})(\eta^2\text{-CF}(\text{OCF}_3)\text{CF}_2)(\text{PEt}_3)_2]$ (8) and 4 in a 2.4 : 1 ratio, and the



Scheme 4 Reactivity of complex 6 towards PMVE.

Et_3PF_2 (Scheme 4). At the beginning of this reaction the phosphorane $\text{Z}(\text{F}_3\text{CO})\text{CF}=\text{CF}(\text{PFEt}_3)$ was present, but there was no indication for the formation of complex 4. The latter was formed upon depletion of the phosphonium salt indicating a crucial role of $\text{Z}(\text{F}_3\text{CO})\text{CF}=\text{CF}(\text{PFEt}_3)$ as an alternative CO source (see below). It can be presumed that initially $\text{Z}(\text{F}_3\text{CO})\text{CF}=\text{CF}(\text{PFEt}_3)$ was generated by reaction of liberated PEt_3 with PMVE, which indicates that a dissociation of phosphine takes place and that any rebinding process is slower than the reactivity of the free phosphine towards the excess of olefin. Note that when 6 was treated with PMVE in the presence of oxygen only $^{trans}\text{-}[\text{Rh}(\text{F})(\eta^2\text{-CF}(\text{OCF}_3)\text{CF}_2)(\text{PEt}_3)_2]$ (8) was generated as the liberated phosphine can be trapped as $\text{Et}_3\text{P}=\text{O}$.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz) of complex 8 displayed two resonances for inequivalent phosphorus atoms at 34.1 and 30.5 ppm. Both signals show a *trans* P–P coupling of 366.7 Hz and P–Rh coupling constants typical of Rh(I) complexes (133.4 and 134.1 Hz). The signal at 30.5 ppm appears as a doublet of doublet of doublet of doublets due to the couplings to phosphorus and rhodium as well as coupling to one of the fluorine atoms at the CF_2 moiety and the fluoro ligand. In contrast, the second resonance shows a doublet of doublet of triplet of doublets due to the additional coupling to the CF moiety. In the ^{19}F NMR spectrum, five inequivalent resonances for the OCF_3 moiety at -57.1 ppm, the two fluorine atoms of the CF_2 group at -96.8 and -98.2 ppm, the CF group at -116.1 ppm and the rhodium bound fluoro ligand at -206.3 ppm are displayed. A correlation between the olefinic fluorine signals and fluoro ligand was confirmed by ^{19}F , ^{19}F -COSY NMR spectroscopy. The C–C bond distance of the olefin obtained by DFT calculations (1.44 Å) suggests a metal-lacyclopropane configuration (Fig. 2).^{54–56} Note that the NMR as well as the DFT calculation results are in agreement with those that have been previously reported for 1,1,3,3,3-pentafluoropropene.³⁸

Independent reactivity studies on the reactivity of PEt_3 towards PMVE demonstrated that *Z/E*- $\text{Z}(\text{F}_3\text{CO})\text{CF}=\text{CF}(\text{PFEt}_3)$ in a 10 : 1 ratio can be formed by an oxidative addition at the

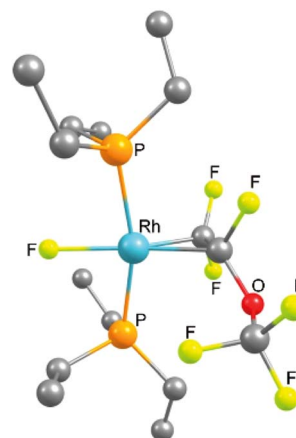
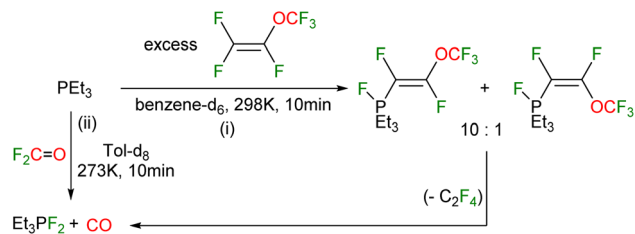
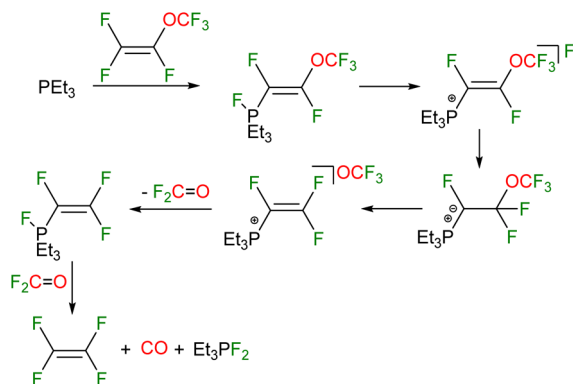


Fig. 2 DFT optimised structure (B3LYP/cc-pvdz) of complex 8. Hydrogen atoms of the phosphine ligands are omitted for clarity.





Scheme 5 Reactivity of triethylphosphine towards: (i) perfluoro (methyl vinyl ether), and (ii) fluorophosgene.



Scheme 6 Mechanistic proposal for the decomposition of the fluorophosphorane $Z-(F_3CO)CF=CF(PFet_3)$.

phosphorus center (Scheme 5). A similar reactivity pattern of phosphines with other fluoroolefins, for instance by Burton and Röscenthaler, or fluoroaromatics was previously reported.^{38,41,45,47,57,58} Monitoring the reaction solution after the generation of $Z/E-(F_3CO)CF=CF(PFet_3)$ at room temperature revealed a conversion into F_2PET_3 , CO, and presumably C_2F_4 along with other decomposition products. The latter could not be identified, possibly because of oligomerization. The formation of the CO gas was confirmed by $^{13}C\{^1H\}$ NMR spectroscopy as well as gas chromatography. In the $^{31}P\{^1H\}$ NMR spectrum of $Z/E-(F_3CO)CF=CF(PFet_3)$ two signals at -63.8 ppm with a $^1J_{P,F}$ coupling constant of 598.8 Hz and 592.2 Hz are visible. The corresponding signals in the ^{19}F NMR appeared at -19.6 and -22.3 ppm for the *Z* and *E* isomers, respectively. Additionally, resonances for the OCF_3 moiety and the two CF groups with a $^3J_{F,F}^{trans}$ of 116 Hz (for the *Z* isomer) and a $^3J_{F,F}^{cis}$ of 25 Hz (for the *E* isomer) are displayed.

Mechanistically it can be assumed that $(F_3CO)CF=CF(PFet_3)$ converts initially into the phosphonium salt $(F_3CO)CF=CF(PEt_3)^+F^-$ (Scheme 6). A nucleophilic attack of the fluoride at the vinyl carbon yields the ylide $CF_2(OCF_3)CF(PEt_3)$. Then $CF_2=CF(PFet_3)$ and $O=CF_2$ might be generated *via* $CF_2=CF(PEt_3)^+OCF_3^-$. The former $CF_2=CF(PFet_3)$ might convert into F_2PET_3 , CO, and C_2F_4 . Note that an independent reaction shows that F_2PET_3 and CO can also be obtained by the reaction of the phosphine with fluorophosgene (Scheme 5).⁵⁹

Conclusions

The paper demonstrates that the rhodium(I) hydrido complex $[Rh(H)(PEt_3)_3]$ (**1**) exhibits distinct reactivity pathways towards PMVE when compared to the reactivity of other fluorinated olefins. These pathways lead to metal- and phosphine-mediated decarbonylation reactions. Both processes involve the generation of a OCF_3^- moiety that can convert into CO, fluoride and fluorophosgene. While at Rh trifluoroethylene is generated, the phosphine-mediated process presumably leads to the formation of tetrafluoroethene. The studies provide valuable insights into the reactivity of PMVE which is considered a PFAS.¹⁵ Decarbonylation processes allow for its decomposition and open up new avenues for transforming fluorinated fragments. Remarkably, It is shown that the formation of the rhodium carbonyl fluorido complex **4** allows the insertion of PMVE into the Rh-F bond forming the $-CF(OCF_3)(CF_3)$ ligand. Additionally, this paper highlights that phosphines might be suitable tools for a transformation of fluorinated compounds.¹⁴

Data availability

Details of the experimental procedures, characterization of the complexes and DFT calculations can be found in the ESI.†

Author contributions

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

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 E. A. Heath, *Int. Leg. Mater.*, 2017, **56**, 193–205.
- 2 T. J. Wallington, M. P. Sulbaek Andersen and O. J. Nielsen, *Chemosphere*, 2015, **129**, 135–141.
- 3 A. J. Sicard and R. T. Baker, *Chem. Rev.*, 2020, **120**, 9164–9303.
- 4 S. E. Manahan, *Fundamentals of environmental and toxicological chemistry: sustainable science*, CRC press, 2013.
- 5 P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis, Reactivity and Applications*, Wiley-VCH, Weinheim, 2nd edn, 2013.
- 6 P. Javidmand and K. A. Hoffmann, *Int. J. Refrig.*, 2016, **69**, 114–135.



- 7 G. Coates, H. Y. Tan, C. Kalff, A. J. P. White and M. R. Crimmin, *Angew Chem. Int. Ed. Engl.*, 2019, **58**, 12514–12518.
- 8 M. Talavera and T. Braun, *Synlett*, 2020, **31**, 1760–1774.
- 9 B. J. Murray, L. T. Boulton and G. Sandford, *J. Fluorine Chem.*, 2021, **245**, 109774.
- 10 B. Ameduri and H. Sawada, *Fluorinated polymers: volume 1: synthesis, properties, Processing and Simulation*, Royal Society of Chemistry, 2016.
- 11 M. Ohashi and S. Ogoshi, *Top. Organomet. Chem.*, 2015, **52**, 197–215.
- 12 M. Talavera, S. Mollasalehi and T. Braun, *Chem. Sci.*, 2024, **15**, 8472–8477.
- 13 H. Amii and K. Uneyama, *Chem. Rev.*, 2009, **109**, 2119–2183.
- 14 J. M. Bayne and D. W. Stephan, *Chem.–Eur. J.*, 2019, **25**, 9350–9357.
- 15 K. M. Wollin, M. Batke, G. Damm, A. Freyberger, U. Gundert-Remy, A. Mangerich, J. G. Hengstler, F. Partosch, T. Schupp, A. Sonnenburg and H. Foth, *Arch. Toxicol.*, 2023, **97**, 3305–3312.
- 16 M. A. Adi and M. Altarawneh, *Atmos. Environ.*, 2023, **307**, 119843.
- 17 L. Vereecken, J. N. Crowley and D. Amedro, *Phys. Chem. Chem. Phys.*, 2015, **17**, 28697–28704.
- 18 F. Reis da Cunha, I. Davidovich, Y. Talmon and B. Ameduri, *Polym. Chem.*, 2020, **11**, 2430–2440.
- 19 Q. Quan, Y. Zhao, K. Chen, H. Zhou, C. Zhou and M. Chen, *ACS Catal.*, 2022, **12**, 7269–7277.
- 20 A. Zharov and O. Nikolaeva, *Russ. J. Phys. Chem. B*, 2010, **4**, 839–845.
- 21 R. E. Banks, B. E. Smart and J. Tatlow, *Organofluorine chemistry: principles and commercial applications*, 1994.
- 22 M. A. Sidebottom, C. P. Junk, H. L. S. Salerno, H. E. Burch, G. S. Blackman and B. A. Krick, *Macromolecules*, 2018, **51**, 9700–9709.
- 23 N. Sinha, H. Choi, M.-Y. Song, H.-J. Jang, Y.-H. Oh and K.-D. Song, *J. Comput. Theor. Chem.*, 2023, **1225**, 114159.
- 24 S. Xiao, Y. Chen, M. Tang, S. Tian, H. Xia, Y. Wang, J. Tang, Y. Li and X. Zhang, *High Volt.*, 2024, **9**, 509–517.
- 25 O. Marrec, T. Billard, J.-P. Vors, S. Pazenok and B. R. Langlois, *J. Fluorine Chem.*, 2010, **131**, 200–207.
- 26 C. Bonnefoy, E. Chefdeville, A. Panosian, G. Hanquet, F. R. Leroux, F. Toulgoat and T. Billard, *Chem.–Eur. J.*, 2021, **27**, 15986–15991.
- 27 A. Tlili, F. Toulgoat and T. Billard, *Angew Chem. Int. Ed. Engl.*, 2016, **55**, 11726–11735.
- 28 E. Castagnetti and M. Schlosser, *Chem.–Eur. J.*, 2002, **8**, 799–804.
- 29 Q. W. Zhang and J. F. Hartwig, *Chem. Commun.*, 2018, **54**, 10124–10127.
- 30 P. Golz, K. Shakeri, L. Maas, M. Balizs, A. Perez-Bitrian, H. D. Kemmler, M. Kleoff, P. Vossnacker, M. Christmann and S. Riedel, *Chem.–Eur. J.*, 2024, **30**, e202400861.
- 31 C.-P. Zhang and D. A. Vasic, *Organometallics*, 2012, **31**, 7812–7815.
- 32 A. Turksoy, T. Scattolin, S. Bouayad-Gervais and F. Schoenebeck, *Chem.–Eur. J.*, 2020, **26**, 2183–2186.
- 33 C. M. Tovar, M. B. Blanco, I. Barnes, P. Wiesen and M. A. Teruel, *Atmos. Environ.*, 2014, **88**, 107–114.
- 34 N. O. Andrella, N. Xu, B. M. Gabidullin, C. Ehm and R. T. Baker, *J. Am. Chem. Soc.*, 2019, **141**, 11506–11521.
- 35 B. Ghaffari, L. L. T. N. Porto, N. Johnson, J. S. Ovens, C. Ehm and R. T. Baker, *ACS Org. Inorg. Au.*, 2024, **4**, 628–639.
- 36 K. I. Petko and A. A. Filatov, *Chem. Heterocycl. Compd.*, 2021, **57**, 666–671.
- 37 E. Schmitt, S. Bouvet, B. Pégot, A. Panossian, J.-P. Vors, S. Pazenok, E. Magnier and F. R. Leroux, *Org. Lett.*, 2017, **19**, 4960–4963.
- 38 M. Talavera and T. Braun, *Chem.–Eur. J.*, 2021, **27**, 11926–11934.
- 39 M. Talavera and T. Braun, *Chem. Sci.*, 2022, **13**, 1130–1135.
- 40 A. L. Raza and T. Braun, *Chem. Sci.*, 2015, **6**, 4255–4260.
- 41 A. L. Raza, M. F. Kuehnel, M. Talavera, M. Teltewskoi, M. Ahrens, P. Kläring, T. Braun and D. Lentz, *J. Fluorine Chem.*, 2018, **214**, 80–85.
- 42 M. Teltewskoi, J. A. Panetier, S. A. Macgregor and T. Braun, *Angew Chem. Int. Ed. Engl.*, 2010, **49**, 3947–3951.
- 43 M. Talavera, C. N. von Hahmann, R. Muller, M. Ahrens, M. Kaupp and T. Braun, *Angew Chem. Int. Ed. Engl.*, 2019, **58**, 10688–10692.
- 44 M. A. Howells, R. D. Howells, N. C. Baenziger and D. J. Burton, *J. Am. Chem. Soc.*, 1973, **95**, 5366–5370.
- 45 D. J. Burton, S. Shin-ya and R. D. Howells, *J. Fluorine Chem.*, 1980, **15**, 543–546.
- 46 A. A. Facundo, A. Arévalo, G. Fundora-Galano, M. Flores-Álamo, E. Orgaz and J. J. García, *New J. Chem.*, 2019, **43**, 6897–6908.
- 47 D. Noveski, T. Braun, M. Schulte, B. Neumann and H.-G. Stammer, *Dalton Trans.*, 2003, 4075–4083.
- 48 S. Wada and R. F. Jordan, *Angew Chem. Int. Ed. Engl.*, 2017, **56**, 1820–1824.
- 49 N. O. Andrella, K. Liu, B. Gabidullin, M. Vasiliu, D. A. Dixon and R. T. Baker, *Organometallics*, 2018, **37**, 422–432.
- 50 N. Pfister, T. Braun, P. Wittwer and M. Ahrens, *Z. Anorg. Allg. Chem.*, 2018, **644**, 1064–1070.
- 51 Y. Zong and G. C. Tsui, *Org. Lett.*, 2024, **26**, 1261–1264.
- 52 A. Foris, *Magn. Reson. Chem.*, 2004, **42**, 534–555.
- 53 T. Ahrens, M. Teltewskoi, M. Ahrens, T. Braun and R. Laubenstein, *Dalton Trans.*, 2016, **45**, 17495–17507.
- 54 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar,



- J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, 2016.
- 55 K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2007, **126**, 124101.
- 56 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
- 57 U. Allwörden and G. V. Rösenthaller, *Chem. Ztg.*, 1988, **112**, 69–76.
- 58 S. Bonfante, C. Lorber, J. M. Lynam, A. Simonneau and J. M. Slattery, *J. Am. Chem. Soc.*, 2024, **146**, 11578.
- 59 M. H. Holthausen, M. Mehta and D. W. Stephan, *Angew Chem. Int. Ed. Engl.*, 2014, **53**, 6538–6541.

