Supporting Information for

Solvent- and anion-dependent rearrangement of fluorinated carbene ligands provides access to fluorinated alkenes

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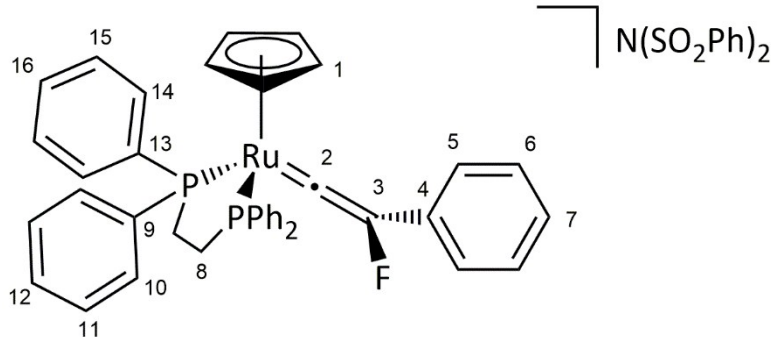
1 Experimental

All experimental procedures were performed under an atmosphere of dinitrogen using standard Schlenk Line and Glove Box techniques unless otherwise stated. Dichloromethane, pentane, hexane, tetrahydrofuran, methanol, ethanol, and diethyl ether were purified with the aid of an Innovative Technologies anhydrous solvent engineering system or distilled over sodium (under argon) before use. The d^2-dichloromethane and d^8-tetrahydrofuran used for NMR experiments were dried over CaH_2 and degassed with three freeze-pump-thaw cycles, then used in the glovebox under a nitrogen atmosphere or directly transferred to NMR tubes fitted with PTFE Young's taps under vacuum. [$RuCl_3 \cdot 3H_2O$] was purchased from Precious Metals Online.

NMR spectra were acquired on either a Jeol ECS400 (Operating frequencies; ^1H 399.78 MHz, ^{13}C 100.53 MHz, ^{19}F 376.17 MHz, ^{31}P 162 MHz), a Bruker AVANCE III 500 (Operating Frequencies; ^1H 500.23 MHz, ^{13}C 125.77 MHz, ^{19}F 470.68 MHz, ^{31}P 202.50 MHz). ^{31}P and ^{13}C spectra were recorded with proton decoupling. Assignments were completed with the aid of ^1H COSY, ^{19}F COSY, ^1H-^{13}C HSQC, ^{13}C-^{19}F HSQC, ^1H-^{13}C HMBC, and/or ^{13}C-^{19}F HMBC experiments. NMR experiments were performed in 5 mm NMR tubes fitted with PTFE J. Young's taps typically using ca. 5-20 mg of material in 0.55-0.6 mL of the appropriate solvent.

Mass spectrometry measurements were performed on a either a Bruker microTOF MS (ESI/GC-EI) or a Waters GCT Premier Acceleration TOF MS (LIFDI) instrument. Elemental analyses were performed using an Exeter Analytical Inc. CE-440 analyser, however, in most cases satisfactory values could not be obtained despite multiple attempts. This was due to the presence of either a number of different counter anions in the structure or residual solvent. Broadband UV irradiation (λ >290 nm) was carried out using a Philips HPK 125 W medium pressure mercury lamp with water filter in front of lamp output.

1.1 Synthesis of $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=C=CFPh)][N(SO_2Ph)_2]$, [1a][$N(SO_2Ph)_2$]



Prepared as described in the literature.[1]

An oven dried Schleck tube was charged with $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CCPh)]$ (100 mg, 0.15 mmol) in dichloromethane (*ca*. 3 mL); to the solution was added *N*-fluorobenzensulfonimde (47.4 mg, 0.15 mmol). After stirring the reaction for ten minutes at room temperature, a green precipitate was formed upon addition of pentane (10 mL). The solid was isolated by filtration, washed with toluene (5 mL) and pentane (2 x 5 mL), and dried *in vacuo* to yield $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CC(F)Ph)]N(SO_2Ph)$. Yield = 111 mg, 75 %.

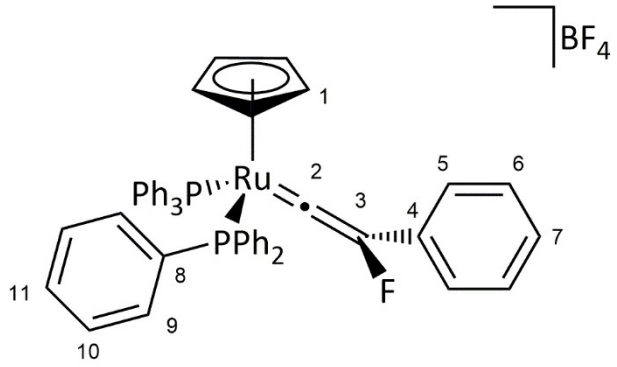
^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): 2.82 - 3.04 (m, 4H, H_8), 5.54 (s, 5H, H_1), 6.37 - 6.40 (m, 2H, H_5), 6.96 - 7.01 (m, 3H, H_{6+7}), 7.09 - 7.16 (m, 4H, Ar-H), 7.20 - 7.29 (m, 10 H, Ar-H), 7.32 - 7.40 (m, 10H, Ar-H), 7.49 - 7.50 (m, 2H, Ar-H), 7.74 - 7.75 (m, 4H, Ar-H).

^{19}F NMR (CD_2Cl_2, 376.2 MHz, 295 K): δ -209.5 (s, F_3)

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 295 K): δ 76.9 (s, PPh_2).

ESI-MS (m/z): Expected for $C_{39}H_{34}FP_2Ru$ = 685.1168; Observed: 685.1147 [M^+] (Error = 2.1 mDa).

1.2 Synthesis of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=CFPh)]BF_4$, [1b]$BF_4$



Prepared as described in the literature.[1]

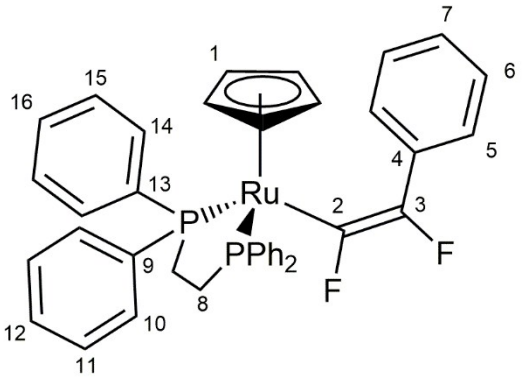
An oven dried Schlenk tube in the glovebox was charged with a solution of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(C{\equiv}CPh)]$ (145 mg, 0.18 mmol) in dichloromethane (*ca.* 5 mL) to which was added 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (37 mg, 0.16 mmol). The reaction mixture was stirred at room temperature for 20-30 min. The resultant green solution was reduced to the minimum volume and a green solid precipitated upon addition of pentane (*ca.* 10 mL). The solution was filtered and the precipitate washed with diethyl ether (3 x 5 mL). The green precipitate was isolated by filtration and dried *in vacuo* to afford a green solid. Yield = 101 mg, 64 %.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.34 (s, 5H, H_1), 7.13 (m, 35H, $H_{5\text{-}7,9\text{-}11}$).

^{19}F NMR (376 MHz, CD_2Cl_2): δ 192.8 (s).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 41.3 (s, PPh_3).

1.3 Synthesis of *E*-[Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)], [2a] from TREAT.HF



An NMR tube with a PTFE J. Young's tap was charged with [Ru(η^5-C_5H_5)(dppe)(C=C{F}Ph)][N($SO_2Ph)_2$], [**1b**][N($SO_2Ph)_2$] (15 mg, 23 μmol) and TREAT.HF (3.7 μL, 23 μmol) in CD_2Cl_2 (0.5 mL) and allowed to stand for 30 minutes, during which time a colour change was observed from green to yellow. Quantitative conversion of [**1b**][N($SO_2Ph)_2$]to [**2a**] was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

^{1}H NMR (500 MHz, d^8-THF, 295 K): δ 2.56 – 2.80 (m, 4H, H_8), 4.65 (s, 5H, H_1), 6.75 (tt, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, H_7), 6.79 – 6.84 (m, 2H, H_5), 6.90 (app. t, 2H, $^3J_{HH}$ = 7.6 Hz, H_6), 7.20 – 7.32 (m, 16H, dppe), 7.77 – 7.83 (m, 4H, dppe).

^{13}C{^{1}H} NMR (125 MHz, d^8-THF, 295 K): δ 30.1 (m, C_8), 84.1 (s, C_1), 124.0 (t, $^3J_{CF}$ = 22.6 Hz, C_5), 124.0 (s, C_7), 127.5 (d, $^4J_{CF}$ = 1.9 Hz, C_6), 128.1 (virtual t, sum of J_{CP} = 10.4 Hz, $C_{10/11/14/15}$), 128.4 (virtual t, sum of J_{CP} = 9.0 Hz, $C_{10/11/14/15}$), 129.1 (s, $C_{12/16}$), 129.7 (s, $C_{12/16}$), 131.6 (virtual t, sum of J_{CP} = 9.8 Hz, $C_{10/11/14/15}$), 133.9 (virtual t, sum of J_{CP} = 10.7 Hz, $C_{10/11/14/15}$), 134.6 (d, $^2J_{CF}$ = 30.7 Hz, C_4), 138.0 (m, $C_{9/13}$), 145.2 (m, $C_{9/13}$), 159.5 (dd, $^1J_{CF}$ = 198.1 Hz, $^2J_{CF}$ = 50.4 Hz, C_3), 187.9 (ddt, $^1J_{CF}$ = 296.6 Hz, $^2J_{CF}$ = 90.4 Hz, $^3J_{CP}$ = 18.2 Hz, C_2).

^{31}P{^{1}H} NMR (202 MHz, d^8-THF, 295 K): δ 94.3 (dd, $^3J_{PF}$ = 28.1 Hz, $^4J_{PF}$ = 2.6 Hz, dppe).

^{19}F NMR (471 MHz, d^8-THF, 295 K): δ -147.8 (d, $^3J_{FF}$ = 111.5 Hz, F_3), -82.4 (dt, $^3J_{FF}$ = 111.5 Hz, $^3J_{PF}$ = 28.1 Hz, F_2).

ESI-MS (m/z): Expected for $C_{39}H_{34}F_2P_2Ru$ = 705.1220 $[M+H]^+$; Observed: 705.1192 $[M+H]^+$ (Error = 2.8 mDa).

1.4 Synthesis of *E*-[Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)], [2a] from [NMe_4]F

An oven dried Schlenk tube was charged with [Ru(η^5-C_5H_5)(dppe)(=C=CFPh)][$N(SO_2Ph)_2$], [**1a**][$N(SO_2Ph)_2$] (100 mg, 0.10 mmol) and tetramethylammonium fluoride (37 mg, 0.40 mmol) suspended in tetrahydrofuran (15 mL). The suspension was sonicated for 20 minutes to afford a yellow solution which was evaporated to dryness *in vacuo*. The residue was extracted with dichloromethane (10 mL), filtered through a plug of alumina and the solvent removed *in vacuo*. The residue was washed with pentane (5 mL), agitated, and dried *in vacuo* to afford a yellow powder. Yield = 55 mg, 78 %.

Complex [**2a**] is formed in a 1:1 ratio of *E*- : *Z*- isomers; after standing in dichloromethane for one week the complex isomerises to the *Z*- isomer.

***E*- Isomer**

Selected ^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 2.50 (m, 2H, H_{8a}), 2.82 (m, 2H, H_{8b}), 4.19 (s, 5H, H_1).

Selected ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 295K): δ 28.8 (t, $^1J_{PC}$ = 23 Hz, C_8), 83.8 (s, C_1), 151.2 (C_3), 173.0 (C2).

^{19}F NMR (471 MHz, CD_2Cl_2, 295 K): δ -67.8 (td, $^3J_{PF}$ = 37 Hz, $^3J_{FF}$ = 10 Hz, F_2), -107.3 (d, $^3J_{FF}$ = 10 Hz, F_3).

^{31}P{^{1}H} NMR (202 MHz, CD2Cl2, 295 K): δ 90.4 (d, $^3J_{PF}$ = 37 Hz, PPh_3).

***Z*- Isomer**

Selected ^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 2.65 (m, 2H, H_{8a}), 2.75 (m, 2H, H_{8b}), 4.73 (s, 5H, H_1), 6.83 (d, $^3J_{HH}$ = 8 Hz, 2H, H_5), 6.90 (t, $^3J_{HH}$ = 7Hz, 1H, H_7), 7.05 (app. t, $^3J_{HH}$ = 8 Hz, 2H, H_6).

Selected ^{13}C{^{1}H} NMR (126 MHz, CD2Cl2, 295K): δ 29.4 (t, $^1J_{PC}$ = 22 Hz, C_8), 83.6 (s, C_1), 123.6 (t, $^4J_{CF}$ = 8Hz, C_5), 124.0 (s, C_7), 127.3 (s, C_6), 158.8 (dd, $^1J_{CF}$ = 198 Hz, $^2J_{CF}$ = 51 Hz, C_3), 188.2 (ddt, $^1J_{CF}$ = 294 Hz, $^2J_{CF}$ = 89 Hz, $^2J_{PC}$ = 19 Hz, C_2).

^{19}F NMR (471 MHz, CD_2Cl_2, 295 K): δ -83.0 (dt, $^3J_{FF}$ = 113 Hz, $^3J_{PF}$ = 28 Hz, F_2), -107.3 (d, $^3J_{FF}$ = 113 Hz, F_3).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 295 K): δ 92.8 (dd, $^3J_{PF}$ = 28 Hz, $^4J_{PF}$ = 3 Hz, PPh_3).

ESI-MS (m/z): Expected for $C_{39}H_{35}F_2P_2Ru$ = 705.1231 m/z; Observed: 705.1235 m/z [$M.^+$] (Error = -0.4 mDa).

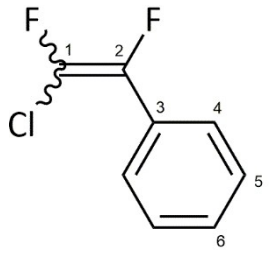
1.5 Broadband UV Irradiation of [Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)] [2a] in DCM

An NMR tube charged with [Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)] (5 mg, 7.1 µmol) in CD_2Cl_2 was irradiated with broadband UV light (125 W) for 1 and 2 hours. The sample was analysed without purification.

Irradiation resulted in the formation of numerous phosphorus- and fluorine-containing species, of which trifluorostyrene and 1-chloro-1,2-difluorostyrene were identified in the ^{19}F NMR spectrum.

Due to the complexity of the ^{1}H NMR spectrum it was not possible to distinguish between the overlapping aromatic resonances.

1-chloro-1,2-difluorostyrene[2]



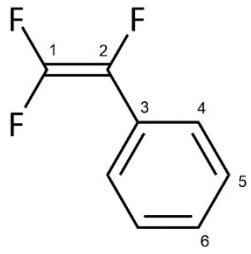
Z -Isomer

^{19}F NMR (CD_2Cl_2, 376.2 MHz, 295 K): δ -118.3 (d, $^3J_{FF}$ = 127 Hz), -148.1 (d, $^3J_{FF}$ = 127 Hz).

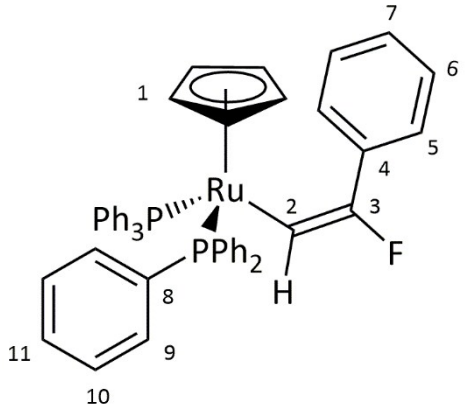
E-Isomer

^{19}F NMR (CD_2Cl_2, 376.2 MHz, 295 K): δ -102.1 (d, $^3J_{FF}$ = 11 Hz), -132.0 (d, $^3J_{FF}$ = 11 Hz).

Trifluorostyrene[3]



^{19}F NMR (CD_2Cl_2, 376.2 MHz, 295 K): δ -100.0 (dd, *J* = 32, 72 Hz), -114.8 (dd, *J* = 72, 110 Hz), and -177.1 (dd, *J* = 32, 110 Hz).



1.6 Synthesis of *E*-[Ru(η^5-C_5H_5)(PPh_3)$_2$(-CF=CFPh)], [2b]

To an oven-dried ampoule was added [Ru(η^5-C_5H_5)(PPh_3)$_2$(C=C{F}Ph)]BF_4, [**1b**]BF4 (50 mg, 0.56 µmol) and tetramethylammonium fluoride (5.2 mg, 0.56 µmol, 1 equivalent) in dichloromethane (10 mL) which was left to stir for 3 days.

Alternative Procedure: An NMR tube with a PTFE J. Young's tap was charged with [Ru(η^5-C_5H_5)(PPh_3)$_2$(C=C{F}Ph)]BF_4, [**1b**]BF4 (20 mg, 0.02 mmol) and TREAT.HF (triethylamine trihydrofluoride, 3.6 µL, 0.02 mmol) in deuterated tetrahydrofuran (0.5 mL), and the reaction turned from green to yellow. The NMR spectra reported were recorded 5 days after addition. Samples of [**2b**] synthesised via this route tended to be cleaner and reduce the formation of [**3b**]BF4.

^{1}H NMR (C_4D_8O, 500 MHz, 298 K): δ 4.39 (s, 5H, H1), 6.81 – 7.82 (m, 50H, ar)

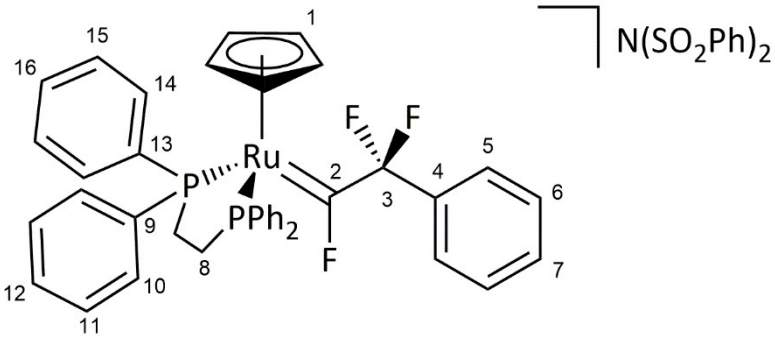
^{13}C{^{1}H} NMR (C_4D_8O, 126 MHz, 298 K): δ 85.8 (d, $^3J_{CF}$ = 1.8 Hz, C1), 124.3 (dd, $^3J_{CF}$ = 10.2 Hz, $^4J_{CF}$ = 8.2 Hz, C5), 127.9 (virtual t, sum of J_{CP} = 9.2 Hz, C9/10), 129.0 (s, C6/7), 129.2 (s, C11), 134.6 (virtual t, sum of J_{CP} = 10.4 Hz, C9/10), 139.8 (m, C8), 140.4 (dd, J_{CF} = 20.8 Hz, J_{CF} = 19.3 Hz, C4), 145.7 (dd, $^1J_{CF}$ = 186.7 Hz, $^2J_{CF}$ = 21.3 Hz, C3), 160.8 (dd, $^1J_{CF}$ = 197.3 Hz, $^2J_{CF}$ = 51.7 Hz, C2)

^{19}F NMR (C_4D_8O, 471 MHz, 298 K): δ -146.8 (d, $^3J_{FF}$ = 113.7 Hz, F3), -72.6 (dt, $^3J_{FF}$ = 113.7 Hz, $^3J_{PF}$ = 32.3 Hz, F2)

^{31}P{^{1}H} NMR (C_4D_8O, 162 MHz, 298 K): δ 52.5 (dd, $^3J_{PF}$ = 32.3 Hz, $^4J_{PF}$ = 2.4 Hz, PPh_3)

All attempts to obtain elemental analysis for [**2b**] were unsuccessful due to the presence of low concentration impurities which could not be removed by washing with pentane or diethyl ether. Attempts to crystallise [**2b**] were also unsuccessful.

1.7 Synthesis of [Ru(η^5-C_5H_5)(dppe)(=CFCF$_2$Ph)]NSI, [4a][N(SO$_2$Ph)$_2$]



An oven dried Schlenk tube was charged with [Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)] (55 mg, 78 µmol) and NFSI (28 mg, 78 µmol) in dichloromethane (5 mL). After the reaction was stirred for 10 minutes at room temperature, the solvent was removed *in vacuo*. The residue was washed with toluene (2 x 5 mL) and diethyl ether (2 x 5 mL), and the resultant green powder was dried *in vacuo*. Yield = 61 mg, 77 %.

^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 3.05- 3.19 (m, 2H, H_8), 3.23- 3.36 (m, 2H, H_8), 5.46 (s, 5H H_1), 7.12-7.18 (m, 6H, H_5 + $H_{10/11/14/15}$), 7.20-7.38 (m, 6H, H_6 + $H_{10/11/14/15}$), 7.39-7.44 (m, 4H, $H_{10/11/14/15}$), 7.48-7.56 (m, 9H, H_7 + $H_{10/11/14/15}$ + H_{12} + H_{16}).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 295 K): δ 28.6 (C_8), 94.1 (s, C_1), 119.2 (C_3), 125.8 (t, J_{CF}= 6 Hz, C_5), 128.9-129.0 ($C_{10/11/14/15}$ + C_6), 129.4 (t, $^nJ_{CP}$ + $^{n+2}J_{CP}$= 5 Hz, $C_{10/11/14/15}$), 130.3 (t, $^nJ_{CP}$ + $^{n+2}J_{CP}$= 5 Hz, $C_{10/11/14/15}$), 130.5 (t, $^2J_{CF}$= 28 Hz, C_4), 131.1 (s, C_7), 131.4 (s, $C_{12/16}$), 131.8 (s, $C_{12/16}$), 131.8 ($C_{9/13}$), 132.4 (t, $^nJ_{CP}$+ $^{n+2}J_{CP}$= 5 Hz, $C_{10/11/14/15}$), 136.7 ($C_{9/13}$), 284.5 (d, $^2J_{CF}$ = 398.8 Hz).

^{19}F NMR (471 MHz, CD_2Cl_2, 295 K): δ 113.6 (tt, $^3J_{FP}$ = 33 Hz, $^3J_{FF}$ = 12 Hz, 1F, F_2), -90.3 (d, $^3J_{FF}$= 11 Hz, 2F, F_3).

^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2, 295 K): δ 85.5 (d, $^3J_{FP}$ = 33 Hz, PPh_2).

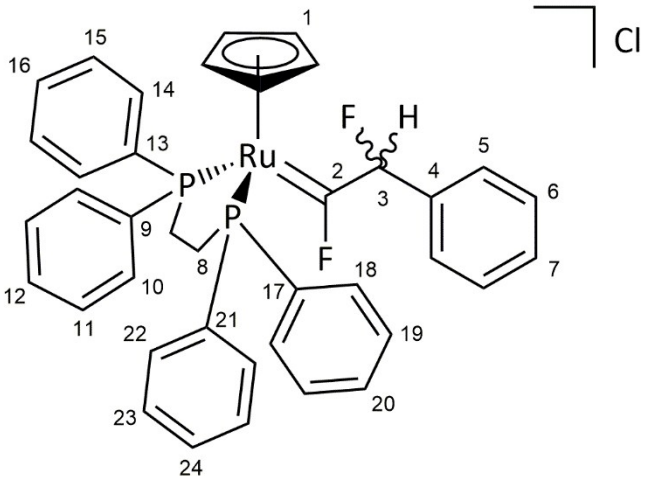
ESI-MS (m/z): Expected for $C_{48}H_{46}FP_2Ru$ = 805.2096 [M$^+$]; Observed = 805.2092 [M$^+$] (Error = 0.4 mDa).

UV-Vis: λ_{max} = 395 nm, ε = 4214 mol^{-1} dm^2 at a concentration of approximately 1 mmol dm^{-3} and a path length of 1 cm.

To obtain crystallographic data the dibenzenesulfonimide anion was exchanged for the hexafluorophosphate anion through ion metathesis. This was achieved by dissolving the dibenzenesulfonimide salt in dichloromethane with 20 equivalents of sodium hexafluorophosphate

and stirred for 1 hour. Crystals of the hexafluorophosphate salt were grown from a dichloromethane: pentane solvent system via slow diffusion.

1.9 Synthesis of [Ru(η^5-C_5H_5)(dppe)(=CFCFHPh)]Cl, [5a]Cl



An NMR tube charged with [Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)] (5 mg, 7.1 µmol) in CD_2Cl_2 was treated with anhydrous 2M HCl in diethyl ether (259 µg, 3.5 µL, 7.1 µmol). The sample was used without further purification. The sample was found to contain the desired complex as the major product (88 % conversion), as well as [Ru(η^5-C_5H_5)(dppe)(=CCFPh)]Cl, **[5a]**Cl, and an additional unknown species (6% each).

^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 3.07- 3.41 (m, 4H, H_8), 4.61 (dd, $^2J_{HF}$= 46 Hz, $^3J_{HF}$= 8 Hz, H_3), 5.43 (s, 5H H_1), 7.04 (td, J_{HH}= 3, 8 Hz, 2H, Ar-H), 7.13 (d, J_{HH}= 8 Hz, 2H, H_5), 7.16-7.24 (m, 6H, Ar-H), 7.36 (d, J_{HH}= 8 Hz, 2H, H_6), 7.44-7.63 (m, 11H, Ar-H), 7.67 (d, J_{HH}= 8 Hz, 1H, Ar-H), 7.69 (d, J_{HH}= 8 Hz, 1H, Ar-H).

Selected ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 295 K): δ 29.1 (C_8), 93.3 (s, C_1), 103.4 (dd, $^3J_{CF}$= 45 Hz, $^2J_{CF}$= 185 Hz, C_3), 299.0 ($^1J_{CF}$ = 388 Hz, C_2).

Assignment of the aromatic carbon environments was challenged by the broken symmetry of the complex and presence of [Ru(η^5-C_5H_5)(dppe)(=CCFPh)]Cl, **[1a]**Cl, and an additional unknown species (6% each).

^{19}F NMR (471 MHz, CD_2Cl_2, 295 K): δ 115.8 (app. tdm, $^3J_{FF}$ + $^3J_{PF}$ = 43 Hz, $^3J_{PF}$ = 26 Hz, 1F, F_2), -90.3 (app. t, $^3J_{FF}$ + $^2J_{HF}$ = 44 Hz, 1F, F_3).

^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2, 295 K): δ 83.9 (dd, $^3J_{PP}$ = 19 Hz, $^4J_{FP}$ = 26 Hz), 88.8 (dd, $^3J_{PP}$ = 19 Hz, $^3J_{FP}$ = 42 Hz).

ESI-MS (m/z): Expected for $C_{39}H_{35}F_2P_2Ru$ = 705.1231 [M $^+$]; Observed= 705.1226 [M$^+$] (Error = -0.5 mDa).

To obtain crystallographic data the chloride anion was exchanged for the hexafluorophosphate anion through ion metathesis. This was achieved by dissolving the chloride salt in dichloromethane with 20 equivalents of sodium hexafluorophosphate and stirred for 1 hour. Crystals of the hexafluorophosphate salt were grown from a dichloromethane: pentane solvent system via slow diffusion. The crystal structure obtained consisted of a mixture of the desired carbene and the HF elimination product, $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=C=CFPh)]PF_6$.

1.10 Formation of $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=CFCFHPh)]BF_4$ [5a]BF_4 with tetrafluoroboric acid and liberation of *E*-1,2-difluorostyrene.

Formation of $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=CFCFHPh)]BF_4$ with tetrafluoroboric acid

In the glovebox, $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CFCFPh)]$ (5 mg, 7.1 µmol) in THF (0.6 mL) was transferred into a in a Youngs tap NMR tube. Under a flow of nitrogen outside the box, tetrafluoroboric acid (1.0 µL, 1.2 mg, 7.1 µmol) and the sample submitted for NMR spectroscopic analysis. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra revealed the formation of $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CFCFHPh)]BF_4$, but there was no evidence for the formation of 1,2-fluorostyrene.

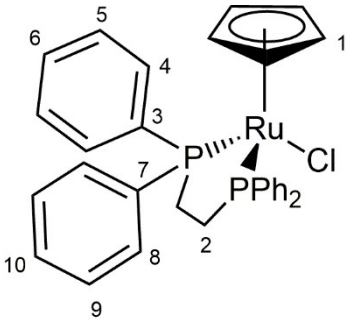
Similarly, $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CFCFPh)]$ (5 mg, 7.1 µmol) in dichloromethane (0.6 mL) was transferred into a in a Youngs tap NMR tube. Under a flow of nitrogen outside the box, tetrafluoroboric acid (1.0 µL, 1.2 mg, 7.1 µmol) was added and the sample submitted for NMR spectroscopic analysis. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra revealed the formation of $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CFCFHPh)]BF_4$, but there was no evidence for the formation of 1,2-fluorostyrene.

Liberation of E-1,2-difluorostyrene from $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=CFCFHPh)]BF_4$

In the glovebox, $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CFCFPh)]$ (5 mg) in THF (0.6 mL) was transferred into a in a Young's tap NMR tube. Under a flow of nitrogen outside the box, tetrafluoroboric acid (1.0 µL, 1.2 mg, 7.1 µmol) was added to form $[Ru(\eta^5\text{-}C_5H_5)(dppe)(CFCFHPh)]BF_4$. The NMR spectra were recorded prior to addition of Bu_4NCl; the $^{31}P\{^1H\}$ NMR spectrum contained a minor species, but the majority of the sample was the desired carbene complex.

In the glovebox, Bu_4NCl (3.9 mg, 14.2 µmol) was added to the reaction mixture and the solution turned a dark orange. The phosphorus NMR spectrum revealed the carbene complex was converted to $[Ru(\eta^5C_5H_5)(dppe)Cl]$ at 81.1ppm. The fluorine signals for the carbene are replaced by the fluorine signals for *E*-1,2-difluorostyrene at -167.7 (dd, J = 5, 125 Hz) and -174.8 (dd, J = 75, 125 Hz).

1.11 Synthesis of [Ru(η^5-C_5H_5)(dppe)Cl], [6a]



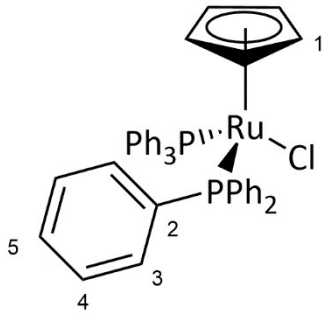
Prepared as described in the literature.[4]

An oven dried Schlenk was charged with [Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (2.00 g, 2.75 mmol) and 1,2-bis(triphenylphosphino)ethane (dppe, 1.15 g , 2.89 mmol) in toluene (40 mL). The reaction mixture was heated under reflux for 16 hours or until the phosphorus NMR spectrum indicated the reaction had reached completion. The solvent was removed *in vacuo* and the orange oil purified by alumina column chromatography. Dichloromethane was first used to elute free triphenylphosphine and acetone used to elute the orange band of the product. Removal of the solvent *in vacuo* afforded an orange oil; the unreacted dppe was removed by washing the oil with diethyl ether (2 x 5 mL) to afford [Ru(η^5-C_5H_5)(dppe)Cl] as an orange powder (yield: 974 mg, 59 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): δ 2.37 - 2.49 (m, 2H, $H_{2a/b}$), 2.60 - 2.74 (m, 2H, $H_{2a/b}$), 4.57 (s, 5H, H_1), 7.14 - 7.20 (m, 4H, Ar-H), 7.28 - 7.36 (m, 6H, Ar-H), 7.42 - 7.46 (m, 6H, Ar-H), 7.88 - 7.92 (m, 4H, Ar-H)

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 295 K): δ 81.8 (s, PPh_3).

1.12 Synthesis of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$, [6b]



Prepared as described in the literature.[5]

Dicyclopentadiene (50 mL) was freshly cracked to afford cyclopentadiene using distillation apparatus, with the temperature at the top of the Vigreux column being maintained at 35 °C in order to prevent transfer of the dimer.

Ethanol (1 L) was degassed with nitrogen in a 2 litre, 3-necked round bottom flask for approximately 60 minutes. Anti-bumping granules and triphenylphosphine (21 g, 0.08 mol) were added and the mixture was heated to reflux.

$RuCl_3.3H_2O$ (4.98 g, 0.02 mol) was dissolved in deoxygenated ethanol (*ca.* 80 mL). Separately, freshly-distilled cyclopentadiene (10 mL) was added to degassed ethanol (approximately 10 mL).

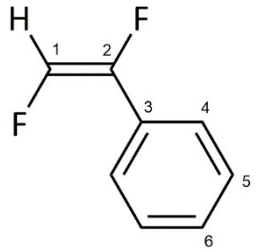
The solution of $RuCl_3.3H_2O$ was added to the refluxing triphenylphosphine via syringe, followed by the cyclopentadiene solution. The reaction mixture was heated at reflux for 1 hour. The solution was allowed to cool to room temperature and stored at -20 °C overnight to produce bright red crystals. The air-stable crystals were collected by vacuum filtration in air and washed with ethanol (4 x 25 mL) and diethyl ether (4 x 25 mL). Further batches of crystals could be obtained by reduction of the solvent volume and storing the subsequent solutions in the freezer at -20 °C overnight. Yield = 11.2 g, 77 %.

^{1}H NMR (CD_2Cl_2, 400 MHz, 295 K): δ 4.10 (s, 5H, H_1), 7.15 (app.t, 12H, $^3J_{HH}$ = 7.2 Hz, H_3), 7.26 (t, 6H, $^3J_{HH}$ = 7.4 Hz, H_5), 7.33 – 7.37 (m, 12H, H_4).

^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz, 295 K): δ 39.5 (s, PPh_3).

1.13 Liberation of *E*-1,2-difluorostyrene, *E*-7 from [Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)]

In the glovebox, a Young's tap NMR tube was charged with a THF-d^8 solution of [Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)] (5 mg, 7.1 µmol). Anhydrous 2M hydrochloric acid in diethyl ether (772 µg, 11 µL, 21.3 µmol) was added and the sample analysed by ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy and GC-EI-mass spectrometry. Protonation affords quantitative conversion to *E*-1,2-difluorostyrene and [Ru(η^5-C_5H_5)(dppe)Cl] according to NMR spectroscopy.[6]



^{1}H NMR (THF-d^8, 500 MHz, 298 K): δ 7.61 (dd, $^2J_{HF}$ = 75 Hz, $^3J_{HF}$ = 6 Hz, H_1).

Aromatic resonances hidden under overlapping signals.

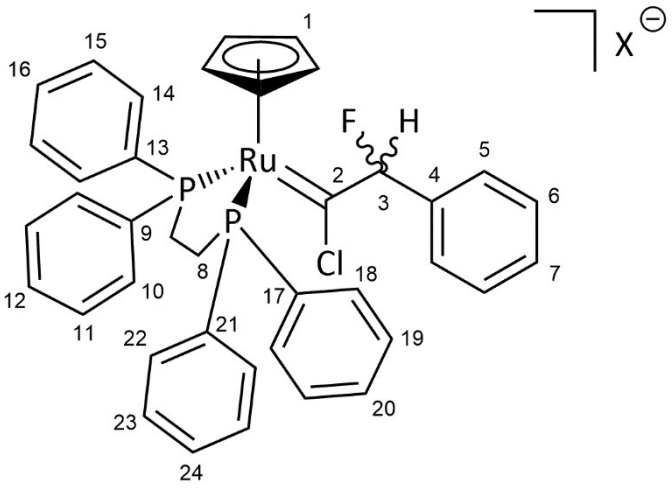
^{19}F NMR (THF-d^8, 471MHz, 295 K): δ -170.5 (dd, $^3J_{FF}$ = 125 Hz, $^3J_{HF}$ = 6 Hz, F_2), -177.6 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 75 Hz, F_1).

GC-EI-MS (m/z): Expected for $C_8H_6F_2$ = 140.0438 m/z [$M^{+\cdot}$]; Observed: 140.0441 m/z [M^+] (Error = 0.3mDa).

1.14 Liberation of *E*-1,2-difluorostyrene *E*-7 from [Ru(η^5-C_5H_5)(dppe)(=CFCFHPh)]Cl

In the glovebox, a Young's tap NMR tube was charged [Ru(η^5-C_5H_5)(dppe)(-CF=CFPh)] (5 mg, 7.1 µmol) in dichloromethane was treated with anhydrous 2M HCl in diethyl ether (259 µg, 3.5 µL, 7.1 µmol). The solvent and hydrogen chloride were removed *in vacuo*. The residue of [Ru(η^5-C_5H_5)(dppe)(=CFCHFPh)] was dissolved in THF and submitted for ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy. Dissolution in THF results in quantitative conversion to *E*-1,2-difluorostyrene and [Ru(η^5-C_5H_5)(dppe)Cl].

1.15 Synthesis of [Ru(η^5-C_5H_5)(dppe)(=CClCFHPh)]Cl, [11a]Cl



X = Cl or BF_4

An NMR tube charged with [Ru(η^5-C_5H_5)(dppe)(=C=CFPh)]BF_4 (5 mg, 6.5 µmol) in CD_2Cl_2 was treated with anhydrous 2M HCl in diethyl ether (709 µg, 9.5 µL, 19.5 µmol). The sample was left to react over three hours and used without further purification. The compound could not be isolated due to loss of hydrogen chloride in the solid state. Attempts to obtain an ESI-mass spectrum of the complex were unsuccessful, numerous products were observed including [Ru(η^5-C_5H_5)(dppe)(=C=CFPh)]$^+$ (by loss of HCl).

^{1}H NMR (500 MHz, CD_2Cl_2, 295 K): δ 3.26- 3.41 (m, 2H, H_8), 3.54-3.69 (m, 2H, H_8), 5.10 (d, $^2J_{HF}$= 48 Hz, H_3), 5.30 (s, 5H H_1), 7.10 (td, J_{HH}= 8, 3 Hz, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 7.23 (m, 2H, Ar-H), 7.30 (dd, J_{HH}= 12, 8 Hz, 2H, Ar-H), 7.42-7.56 (m, 14H, Ar-H), 7.60-7.64 (m, 3H, Ar-H).

Selected ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 295 K): δ 28.9 (t, $^1J_{CP}$ + $^3J_{CP}$ = 11 Hz, C_8), 29.2 (t, $^1J_{CP}$ + $^3J_{CP}$ = 11 Hz, C_8), 94.5 (s, C_1), 109.5 (d, $^1J_{CF}$ = 191 Hz, C_3), 128.6 (s, C_{Ar}), 128.7 (s, C_{Ar}), 128.8 (s, C_{Ar}), 128.9 (s, C_{Ar}), 129.0 (s, C_{Ar}), 129.3 (s, C_{Ar}), 129.4 (s, C_{Ar}), 129.5 (s, C_{Ar}), 129.6 (s, C_{Ar}), 129.8 (d, $^nJ_{CP}$ = 10 Hz, C_{Ar}), 130.1 (d, $^nJ_{CP}$ = 10 Hz, C_{Ar}), 130.9 (d, $^nJ_{CP}$ = 2 Hz, C_{Ar}), 131.1 (d, $^nJ_{CP}$ = 3 Hz, C_{Ar}), 131.4 (d, $^nJ_{CP}$ = 3 Hz, C_{Ar}), 131.7 (s, C_{Ar}), 131.9 (d, $^nJ_{CP}$ = 3 Hz, C_{Ar}), 133.0 (d, $^nJ_{CP}$ = 10 Hz, C_{Ar}), 133.2 (d, $^nJ_{CP}$ = 11 Hz, C_{Ar}), 138.5 (d, $^nJ_{CP}$ = 20 Hz, C_{Ar}), 138.9 (d, $^nJ_{CP}$ = 20 Hz, C_{Ar}), 292.2 (dt, $^2J_{CF}$ = 48 Hz, $^2J_{PF}$ = 10 Hz, C_2).

Assignment of the aromatic carbon environments was challenged by the broken symmetry of the complex.

^{19}F NMR (471 MHz, CD_2Cl_2, 295 K): δ -130.2 (d, $^2J_{HF}$ = 48 Hz, F_3).

^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2, 295 K): δ 89.6 (d, $^3J_{PP}$ = 16 Hz), 93.8 (d, $^3J_{PP}$ = 16 Hz).

1.16 Liberation of *E*-1-Chloro-2-fluorostyrene from $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=C=CFPh)]BF_4$ or $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=CFPh)]BF_4$

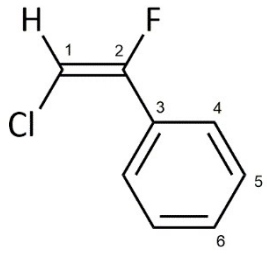
From $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=C=CFPh)]BF_4$

In the glovebox, a Youngs tap NMR tube was charged with a THF solution of $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=C=CFPh)]BF_4$ (5 mg, 6.5 µmol). The solution was treated with anhydrous 2M HCl in diethyl ether (709 µg, 9.8 µL, 19.5 µmol) and the reaction monitored by ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy and MS. Protonation affords *E*-1-chloro-2-fluorostyrene and $[Ru(\eta^5\text{-}C_5H_5)(dppe)Cl]$.

Alternatively, the reaction can be carried out in CD_2Cl_2 with the addition of 100 µL of THF.

From $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=CFPh)]BF_4$

In the glovebox, a Youngs tap NMR tube was charged with a THF solution of $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=C=CFPh)]BF_4$ (5 mg, 5.1 µmol). The solution was treated with anhydrous 2M HCl in diethyl ether (554 µg, 7.65 µL, 15.3 µmol) and the reaction monitored by ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy and MS. Protonation affords *E*-1-chloro-2-fluorostyrene and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$.



Selected ^{1}H NMR (THF-d^8, 400 MHz, 295 K): δ 6.45 (d, $^3J_{HF}$ = 14 Hz, H_1).[7]

Aromatic resonances hidden under overlapping signals.

^{19}F NMR (THF-d^8, 376 MHz, 295 K): δ -111.2 (d, $^3J_{HF}$ = 14 Hz, F_2)

GC-EI-MS (m/z): Expected for C_8H_6FCl = 156.0142 m/z [$M^{+\cdot}$]; Observed: 156.0410 m/z [M^+] (Error = -0.4 mDa).

2 Crystallographic Data

Diffraction data were collected using a dual source Oxford Diffraction SuperNova diffractometer using either Mo-Kα radiation (0.71073 Å), or Cu-Kα radiation (1.54184 Å), and an EOS CCD camera. The crystals were cooled with an Oxford Instruments CryoJet to 110 K. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with "CrysalisPro".[8] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm and analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark and Reid,[9] implemented within "CrysalisPro".[8] Olex2[10] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Using Olex2, the structure was solved using the ShelXT "dual space" algorithm (ref SHELXT – Integrated space-group and crystal-structure determination,).[11] Refinement was carried out with the ShelXL refinement package using Least Squares minimisation.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions

2.1 $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=CFCF_2Ph)]PF_6$, $[4a]PF_6$

CCDC	1952189
Empirical formula	$C_{39}H_{34}F_9P_3Ru$
Formula weight	867.64
Temperature/K	110.00(10)
Crystal system	monoclinic
Space group	Cc
a/Å	20.7451(2)
b/Å	9.98170(10)
c/Å	17.2999(2)
α/°	90
β/°	97.2290(10)
γ/°	90
Volume/Å^3	3553.84(6)
Z	4
ρ_{calc}g/cm^3	1.622
μ/mm^{-1}	0.653
F(000)	1752.0
Crystal size/mm^3	0.255 × 0.163 × 0.115
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.744 to 60.062
Index ranges	-28 ≤ h ≤ 29, -14 ≤ k ≤ 14, -23 ≤ l ≤ 24
Reflections collected	20324
Independent reflections	9932 [R_{int} = 0.0191, R_{sigma} = 0.0269]
Data/restraints/parameters	9932/2/469
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0191, wR_2 = 0.0451
Final R indexes [all data]	R_1 = 0.0198, wR_2 = 0.0455
Largest diff. peak/hole / e Å^{-3}	0.25/-0.26
Flack parameter	-0.028(8)

2.2 $[Ru(\eta^5\text{-}C_5H_5)(dppe)(=CFCFHPh)]PF_6/SiF_5$, $[5a]PF_6/SiF_5$

CCDC	1952190
Empirical formula	$C_{39}H_{34.25}F_{6.53}P_{2.27}RuSi_{0.72}$
Formula weight	818.78
Temperature/K	110.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.4924(2)
b/Å	15.7881(2)
c/Å	17.8372(3)
α/°	90
β/°	97.0299(14)
γ/°	90
Volume/Å^3	3491.59(9)
Z	4
ρ_{calc}g/cm^3	1.558
μ/mm^{-1}	5.414
F(000)	1661.0
Crystal size/mm^3	0.157 × 0.082 × 0.072
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.13 to 134.154
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -20 ≤ l ≤ 21
Reflections collected	24639
Independent reflections	6231 [R_{int} = 0.0299, R_{sigma} = 0.0250]
Data/restraints/parameters	6231/5/515
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0932
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0982
Largest diff. peak/hole / e Å^{-3}	1.21/-0.93

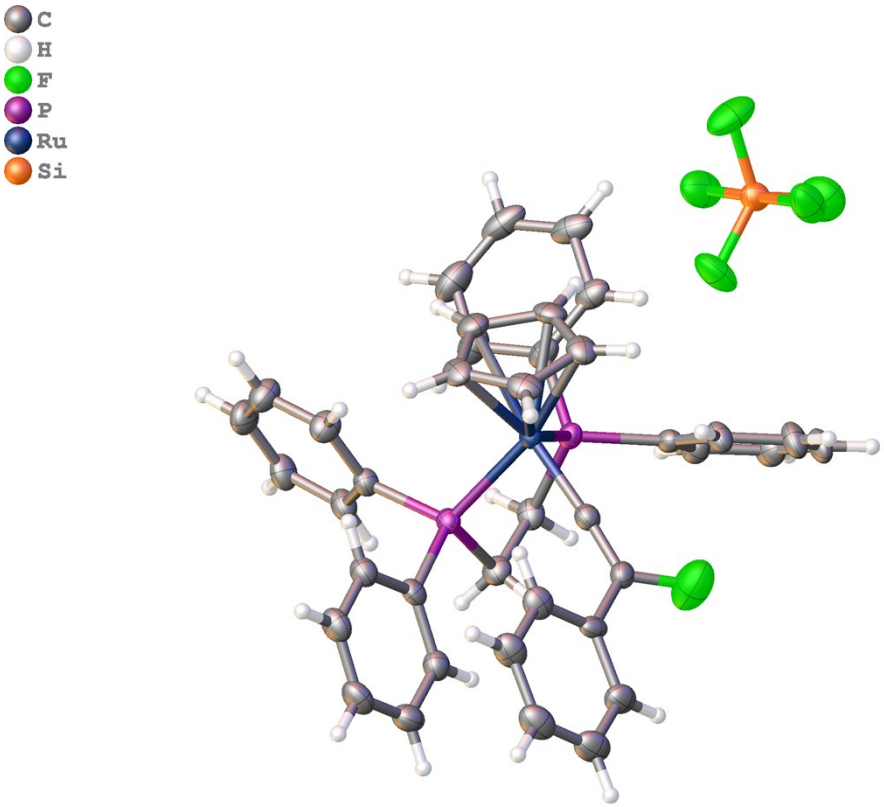
Refinement Special Details

The crystal contained a mixture of two cationic complexes and two anions (Figure S1).

The cations were a mixture of the fluorocarbene and fluorovinylidene complexes in a refined ratio of 0.749:0.251(4). The latter complex was present as two diasteroisomers with refined occupancies of 0.173:0.077(6). For the vinylidene complex, the phenyl ring was constrained to be a regular hexagon with the monofluoromethylene group and phenyl restrained to be planar. The ADP of pairs of the

phenyl carbons were constrained to be equal (ie. C9 & C9A, C10 & C10a etc) as were the ADP of F7 & F7a.

The anion was a mixture of pentafluorosilicate and hexafluorophosphate in a refined ratio of 0.730:0.270(8). The ADP of the silicon and phosphorus were constrained to be equal.



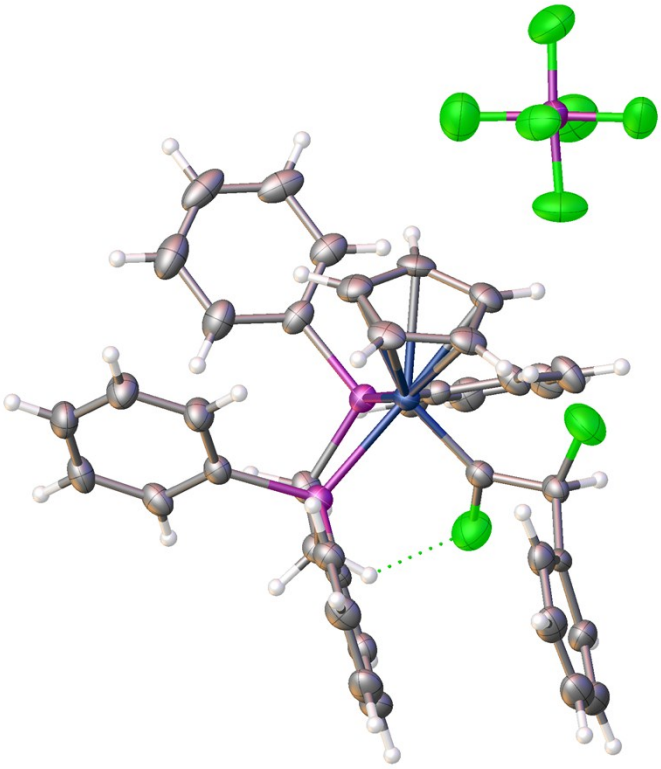


Figure S1 Structure of the different cations and anions in the structure.

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