Oxidative addition of ether O–methyl bonds at a Pt(0) centre

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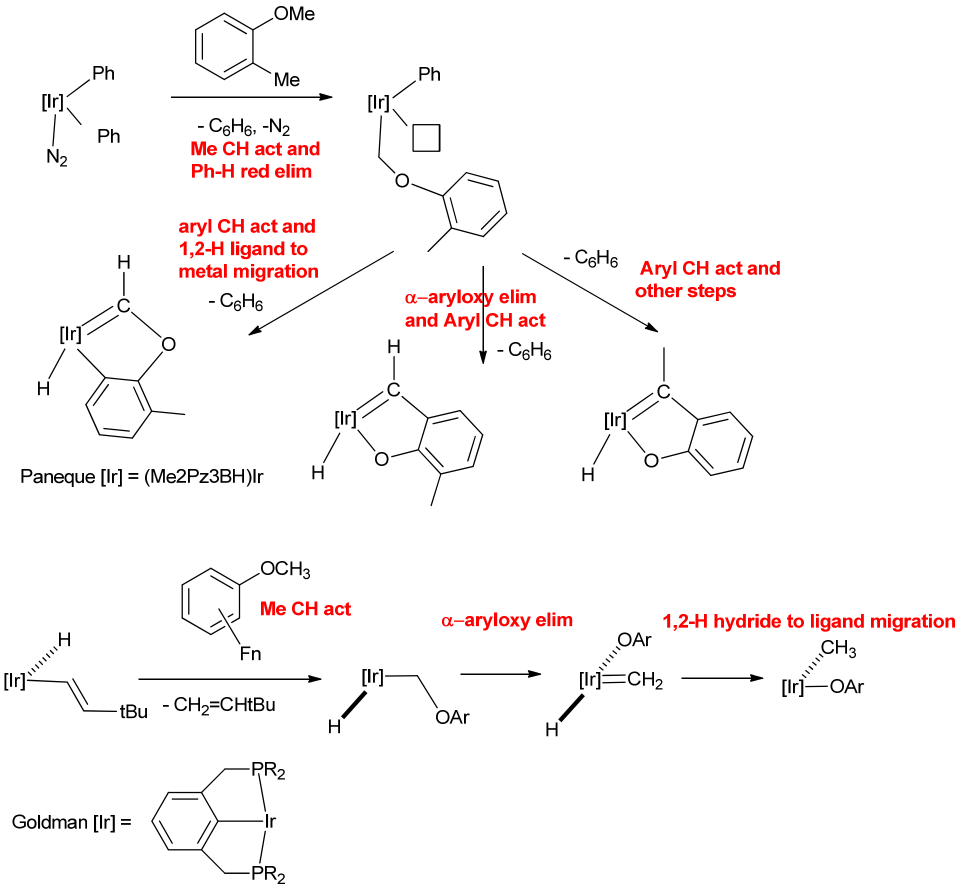
Electronic Supporting information*, revised*



Scheme S1 Paneque[1] and Goldman[2] reactions of ethers at iridium.

General Procedures.

All operations were performed under an argon atmosphere, either on a high-vacuum line (10^{-4} mbar) using modified Schlenk techniques, on standard Schlenk (10^{-2} mbar) lines or in a glovebox. Solvents for general use (hexane, benzene, toluene) were of AR grade, dried by distillation over standard reagents, or with a solvent purification system, and stored under Ar in ampoules fitted with Young's PTFE stopcocks. Deuterated solvents were dried by stirring over potassium, and were distilled under high vacuum into small ampoules with potassium mirrors.

The complex $Pt(PCyp_3)_2$ **1** was synthesized by published methods.[3] Tricyclopentylphosphine was purchased from Strem. Pentafluorophenol and pentafluoroanisole were purchased from Sigma-Aldrich. 2,3,5,6-tetrafluoro-4-methoxypyridine was synthesised according to reference 4.

The NMR spectra were recorded on Bruker AMX500 spectrometers (^{1}H 500.13, ^{31}P 202.46. ^{19}F 407.4, ^{195}Pt 107.52 MHz). The ^{1}H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15. The $^{31}P\{^{1}H\}$ NMR spectra are reported downfield of an external solution of H_3PO_4 (85%). The

^{19}F NMR spectra were referenced to external C_6F_6 at δ −162.9. The ^{195}Pt spectra were referenced relative to the absolute frequency of 86.024 MHz as *δ* 0.

EI mass spectra were measured on a Waters Micromass GCT Premier orthogonal time-of-flight instrument set to one scan per second with resolution power of 6000 fwhm. The LIFDI mass spectra were measured on a Waters Micromass GCT Premier orthogonal time-of-flight instrument set to one scan per second with resolution power of 6000 FWHM and equipped with a LIFDI probe from LINDEN GmbH. The design is very similar to that described by Gross *et al.*[5] Toluene was used for tuning the instrument. The polyethylene glycol probe was kept at ambient temperature with the emitter potential at 12 kV. Activated tungsten wire LIFDI emitters (13 μm tungsten from LINDEN) were ramped manually up to 100 mA for the emitter heating current during the experiment. m/z values are accurate to 0.01 Da.

Elemental analyses were performed by Elemental Microanalysis Ltd, Devon, UK.

Syntheses

Synthesis of 1a.

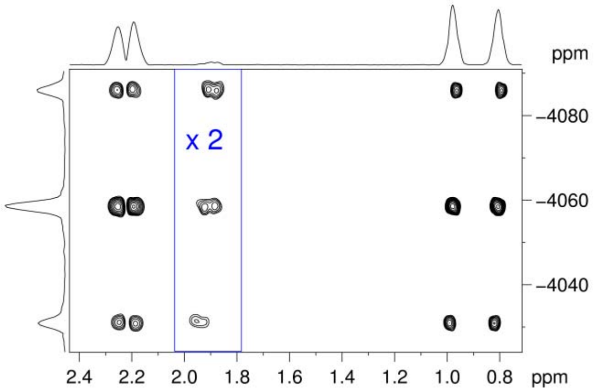
2,3,5,6-tetrafluoro-4-methoxypyridine (3 mg, 0.0181 mmol) was added into a J Young's NMR tube containing a pale yellow hexane solution of **1** (10 mg, 0.0194 mmol). The contents of the tube were heated 60° C for two days. The product was recrystallized from benzene/hexane to give colourless crystals of complex **1a**.

Mass spec: LIFDI, *m/z+,* 852.3 (9%, M^+), 837.3 (70%, $M^+ - CH_3$), 686.4 (10%, $M^+ - C_5NF_4O$)

Calculated isotope pattern for molecular ion of $C_{36}H_{57}F_4NOP_2Pt$ 851.3 (70%), 852.4 (100%), 853.4 (88%) 854.4 (28%), 855.4 (20%), 856.4 (8%)

Experimental isotope pattern: 851.3 (78%), 852.3 (100%), 853.3 (88%), 854.3 (30%), 855.3(20%), 856.3 (9%)

Anal. calcd for $C_{36}H_{57}F_4NOP_2Pt$ C, 50.70; H, 6.74; N, 1.64. Found: C, 50.72; H, 6.75; N, 1.65.



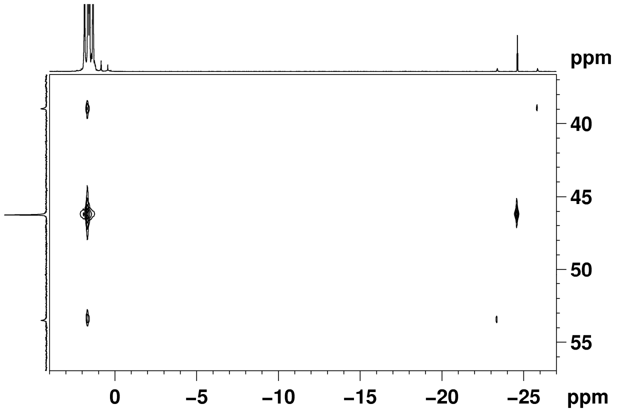


Figure S1. Above: 500 MHz ^{195}Pt{^{1}H}-^{1}H HSQC in C_6D_6 for **1a** with internal projections. Below: 500 MHz ^{31}P-^{1}H HSQC in C_6D_6 for **1c**.

Synthesis of 1b.

The reaction was conducted in a similar manner to that described for complex **1a.** Pentafluoroanisole (4 mg, 0.02 mmol) was added into a J Young's NMR tube containing a pale yellow hexane solution of **1** (10 mg, 0.0194 mmol) to form **1b**. It was heated at 60° C for 2 days and crystals form after cooling to room temperature. It was recrystallised from benzene/hexane.

Mass spectrum (LIFDI, *m/*z, +) 686.3 (100%, $M^+ - OC_6F_5$)

Calculated isotope pattern for $C_{31}H_{57}P_2Pt$: 685.4 (72%), 686.6 (100%), 687.4 (86%), 688.4 (25%), 689.4 (19%), 690.4 (6%)

Experimental isotope pattern: 685.3 (6%), 686.3 (100%), 687.3 (83%), 688.3 (23%), 690.3 (6%)

Anal. calcd for $C_{31}H_{57}P_2Pt$ C, 51.09; H, 6.60. Found C, 51.54; H, 6.56.

Synthesis of 1c.

2,3,5,6-tetrafluoro-4-ethoxypyridine (5 mg, 0.022 mmol) was added into a J Young's NMR tube containing a pale yellow hexane solution of Pt(PCyp$_3$)$_2$ (10 mg, 0.0194 mmol). The reaction was conducted in a similar manner to that described for complex **1a** and formed the hydride complex **1c.** The sample was at 60^o C for 2 days. Crystals form on cooling. It was recrystallized from hexane. The ^{31}P-^{1}H HSQC spectrum is shown in Figure S1.

Anal. calcd for $C_{35}H_{55}F_4NOP_2Pt$ C, 50.11; H, 6.61; N, 1.67. Found C, 50.5; H, 6.72; N, 1.64.

Calculated isotope pattern for $C_{35}H_{55}F_4NOP_2Pt$: 837.3 (70%), 838.3 (100%), 839.3 (90%), 840.3 (29%), 841.3 (20%), 842.3 (8%).

Experimental isotope pattern: 837.4 (52%), 838.3 (100%), 839.3 (75%), 840.3 (23%), 841.1 (5%)

Synthesis of 1d

Pentafluorophenol (4 mg, 0.0217 mmol) was added into a J Young's NMR tube containing a pale yellow hexane solution of Pt(Cyp$_3$)$_2$ (10 mg, 0.0194 mmol). The solution color changed immediately to colorless at room temperature. Colorless crystals were formed by slow evaporation.

Mass spec LIFDI m/z + 855.3 (98%, M$^+$), 672.3 (100%, M$^+$ – OC_6F_5)

Calculated isotope pattern for $C_{36}H_{55}F_5OP_2Pt$ 854.3 (70%), 855.3 (100%), 856.3 (88%), 857.3 (30%) 858.3 (20%), 859.3 (6%)

Experimental isotope pattern: 854.3 (60%), 855.3 (100%), 856.3 (80%), 857.3 (30%) 858.3 (20%), 859.3 (5%)

Anal. calcd for $C_{36}H_{55}F_5OP_2Pt$ C, 50.52; H, 6.48;. Found: C, 50.45; H, 6.39; N, <0.05.

Synthesis of 1e.

2,3,5,6-tetrafluoro-4-methoxybenzene (3 mg, 0.0167 mmol) was added into a J Young's NMR tube containing a pale yellow hexane solution of **1** (10 mg, 0.0194 mmol). The contents of the tube were heated 60° C for 5 days. The product was recrystallized from hexane to give colourless crystals of **1e**.

Mass spec LIFDI m/z + 851.4 (30%, M$^+$), 686.4 (100%, M-OC_6F_4H)

Calculated isotope pattern for $C_{37}H_{58}F_4OP_2Pt$, 850.35 (71%), 851.36 (100%), 852.36 (90%), 853.36 (33%), 854.36 (22%)

Experimental isotope pattern, 850.24(70%), 851.35 (100%), 852.37 (84%), 8553.36 (30%), 854.47 (25%)

Anal. calcd for $C_{37}H_{58}F_4OP_2Pt$ C, 52.17; H, 6.86; Found: C, 52.45; H, 6.84

Synthesis of 1f

2,3,6-trifluoro-4-methoxybenzene (10 mg, 0.055 mmol) was added into a J Young's NMR tube containing a pale yellow hexane solution of **1** (10 mg, 0.0194 mmol) and the solution was heated for 30 h at 60° C. A white precipitate was formed on cooling which was pumped to dryness.

Mass spec LIFDI m/z+ 833.4 (7%, M^+), 686.4 (60%, M^+-$OC_6F_3H_2$)

Calculated isotope pattern for $C_{37}H_{59}F_3OP_2Pt$, 832.36 (70%), 833.36 (100%), 834.37 (90%), 835.37 (32%), 836.37 (19%)

Experimental isotope pattern, 832.4 (64%), 833.4 (100%), 834.4, (95%), 835.2 (10%)

Anal. calcd for $C_{37}H_{59}F_3OP_2Pt$ C, 53.29, H 7.13; Found C, 53.06, H 7.02

Synthesis of 2,3,5,6-tetrafluoro-4-ethoxypyridine

A mixture of pentafluoropyridine (3 g, 17.7 mmol) and NaOEt (1.203 g, 17.7 mmol) was dissolved in ethanol (35 mL) and refluxed for 3 h. The product was treated with water (50 mL) and extracted with ether (4 × 30 mL). The ethereal phase was dried ($MgSO_4$) and distilled at 81° C to yield 2,3,5,6-tetrafluoro-4-ethoxypyridine. Bp 81° C.

^{1}H NMR (300 MHz, C_6D_6) δ 1.08 (t, 3H, J_{HH} 6.8 Hz), 3.51 (q, 2H J_{HH} 6.8, 13.9 Hz).

^{19}F NMR (300 MHz, C_6D_6) δ –91.8(m,2F), –159.7 (m,2F).

EI mass spec: m/z 195.0297 (calculated 195.0307, difference 1 mDa)

Synthesis of d_3-2,3,5,6-tetrafluoro-4-methoxypyridine

Small scale: Small pieces of sodium (68 mg, 2.96 mmol) were added slowly to deuterated methanol (5 mL). Upon complete reaction, pentafluoropyridine (500 mg, 2.96 mmol) was added dropwise and the solution was stirred and heated at 60° C for 15 min. The product was treated with water (15 mL) and extracted with ether (3 × 10 mL). The organic extract was dried over $MgSO_4$ and the solvent removed by rotary evaporator giving a colourless oil which needed no further purification.

Larger scale: Small pieces of sodium (140 mg, 6.1 mmol) were added slowly to deuterated methanol (5 mL). Upon complete reaction, pentafluoropyridine (1g, 5.9 mmol) was added dropwise to the sodium methoxide solution cooled in ice. The solution was stirred and heated at 60° C for 10 min. The product was treated with water (30 mL) and extracted with ether (3 × 15 mL). The organic extract was dried over $MgSO_4$ and the solvent removed by rotary evaporator giving a colourless oil. The product was purified by fractional distillation under vacuum but still contained 8% *d_3*-3,5,6-trifluoro-2,4,-dimethoxypyridine.

Mono-substituted:

^{2}D NMR (C_6H_6, 300 K): δ 3.28 (CD_3).

^{19}F NMR: δ – 91.9 (2 F, m) δ – 160.9 (2 F, m).

Mass-spec EI, *m/z* 184.0336 (M^+, 100%), (calcd for $C_6D_3F_4NO$ 184.0339, difference 0.3 mDa).

IR (liquid film/cm^{-1}**)** 2082 (s, ν(CD)), 1648 (s, ν(CN)), 1480 (s, ν(ring vibration)) 900-1000 (s, ν(CF)).

Di-substituted:

^{2}D NMR (C_6H_6, 300 K): δ 4.1(s) (*p*-CD_3), 3.8(s) (*o*-CD_3).

^{19}F NMR: δ – 95.2 (*t,* J_{FF} 24 Hz, 1 F) δ –162.6 (d, J_{FF} 25 Hz, 1 F) δ –167.0 (d, J_{FF} 22Hz, 1 F)

Mass-spec EI, *m/z* 199.0711 (M^+, 100%), (calcd for $C_7D_6FNO_2$ 199.0727, difference 0.16 mDa).

Kinetic isotope effect; reaction of Pt(PCyp$_3$)$_2$ with mixture of *d*$_3$-2,3,5,6-tetrafluoro-4-methoxypyridine and *h*$_3$-2,3,5,6-tetrafluoro-4-methoxypyridine

A solution was made up containing a mixture of *d*$_3$-2,3,5,6-tetrafluoro-4-methoxypyridine (41.1 mg, 0.223 mmol) and *h*$_3$-2,3,5,6-tetrafluoro-4-methoxypyridine (40.0 mg, 0.221 mmol) in hexane (0.5 mL). Additionally, the deuterated sample contained 3.9 mg (0.019 mmol, 8%) of *d*$_3$-3,5,6-trifluoro-2,4-dimethoxypyridine. This impurity is unreactive towards **1**. Complex **1** (15 mg, 0.022 mmol) was added and allowed to react at room temperature (with 20 times excess substrate, heating is not required). The product was isolated and investigated by ^{31}P{^{1}H} NMR spectra with inverse gated decoupling (quantitative phosphorus) and with ^{195}Pt{^{1}H} NMR spectra. Figure S2 compares the spectra obtained with *h*$_3$-2,3,5,6-tetrafluoro-4-methoxypyridine to those obtained with the isotopic mixture.

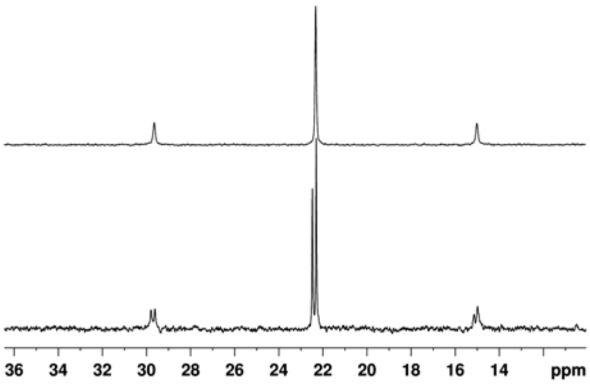
The isotopic shifts on deuteration are as follows:

^{31}P δ 22.28 shifted to 22.45: difference 0.17 ppm = 35.32 Hz

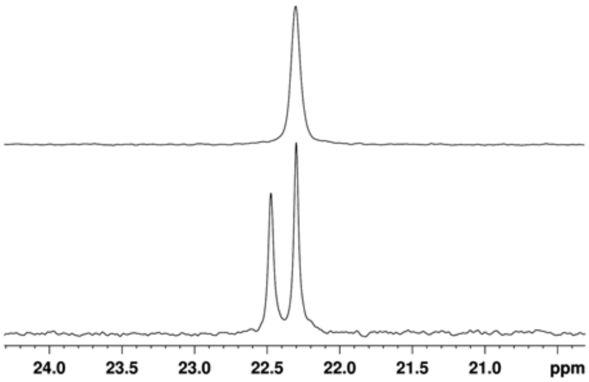
Integration ratio is [Pt(CH_3)]/[Pt(CD_3)] = 1.097

^{195}Pt δ –4060.0 shifted to –4045.8: difference is 14.2 ppm = 1527 Hz

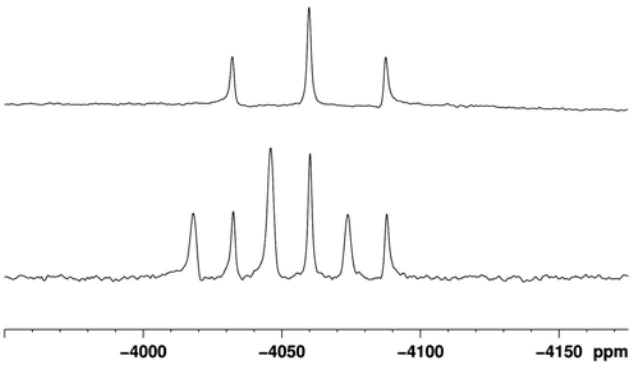
Kinetic isotope effect (k_H/k_D) = 1.097 x 0.223/0.221 = 1.11



(a) $^{31}P\{^1H\}$ NMR spectra: above **1a**, below **1a** + **1a**-*d*3



(b) $^{31}P\{^1H\}$ NMR spectra expansion: above **1a**, below **1a** + **1a**-*d*3



(c) $^{195}Pt\{^1H\}$ NMR spectra: above **1a**, below **1a** + **1a**-*d*3

Figure S2. $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of **1a** and of mixture of **1a** and **1a-d$_3$** obtained by reaction of **1** with 10-fold excess of each of **a** and **a-d$_3$.**

In-situ monitoring of reaction of formation of 1b

The reaction of **1** with pentafluoroanisole (2 eqv) was monitored at 50° C in situ by ^{31}P NMR spectroscopy (unlocked, protiosolvents) in hexane and in THF (Figure S3, S4). Measurements were made every 68 min in THF up to 680 min and every 30 min in hexane up to 1050 min. The half-lives were 200 min (THF) and 620 min (hexane). An intermediate was observed at δ 26.9 (s, J_{PtP} 3956 Hz) in THF and δ 27.4 (J_{PtP} 3962 Hz) in hexane. Its intensity was at a maximum in the first spectra after mixing. The reaction was also followed by ^{19}F NMR in THF revealing the following resonances of the intermediate:

δ –185.0 (broad), –175.6 (t, J = 21 Hz), –173.6 (t, J = 21 Hz), –170.0 (broad), –164.0 (broad)

The intermediate is assigned as Pt(PCyp$_3$)$_2$(η^2-C=C-C$_6$F$_5$OMe). The site of coordination on the aromatic ring cannot be identified unambiguously.

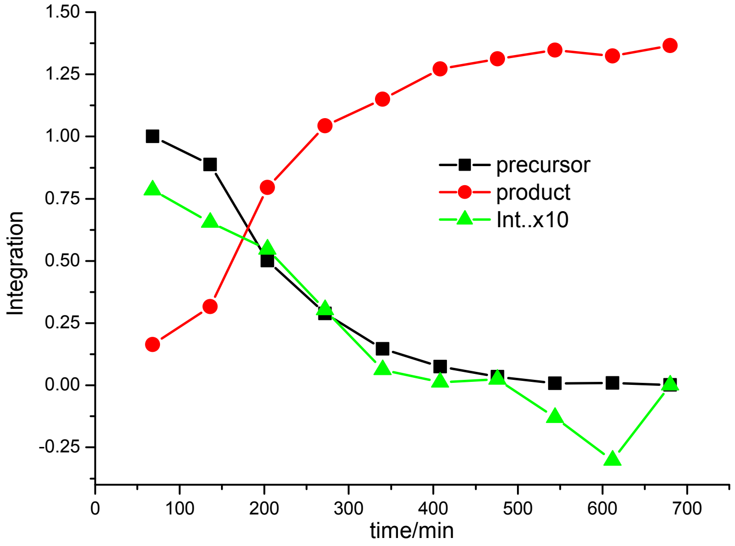


Figure S3. Kinetic plot of reaction of **1** with pentafluoroanisole followed by ^{31}P{^{1}H} NMR at 50 °C in THF showing decay of **1** (black), growth of product (red) and evolution of intermediate (green, integration expanded ten times)

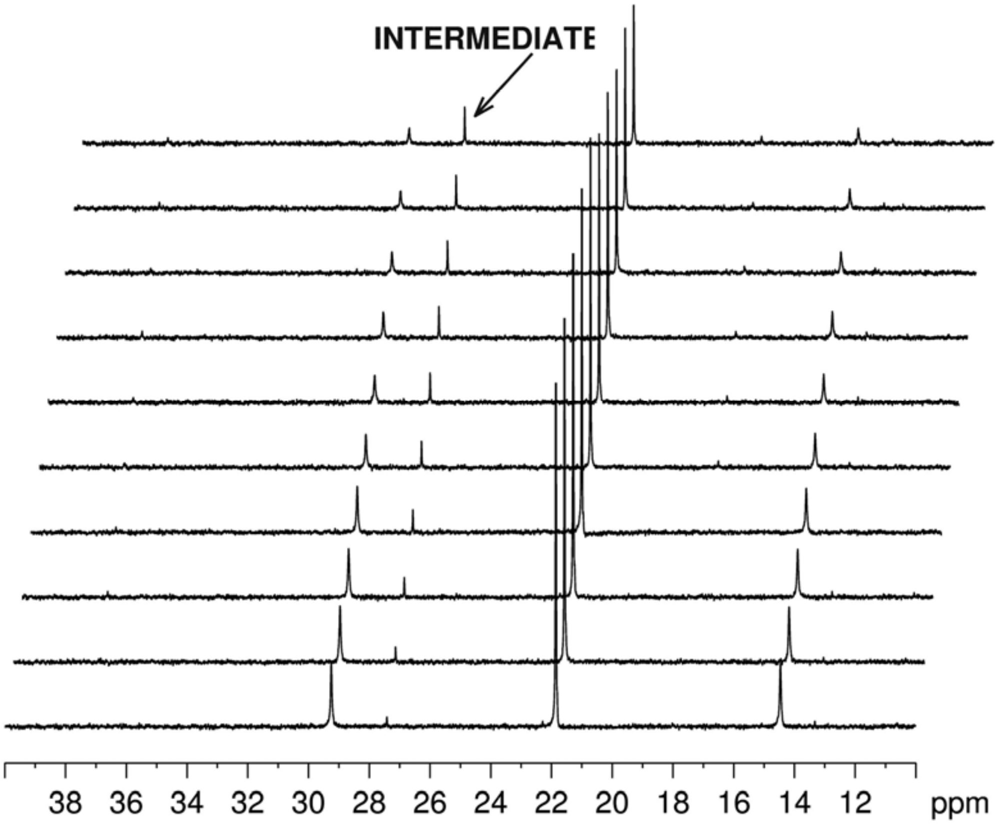


Figure S4. $^{31}P\{^1H\}$ NMR spectra following time course of reaction of **1** with pentafluoroanisole at 50 °C in hexane. Spectra are recorded at the following times starting from the top: 90, 150, 180, 240, 270, 360, 570, 630, 780 and 1020 min.

Table S1. NMR Data measured in C_6D_6 at 298 K 1H at 500 MHz

Complex	^{1}**H** δ, **(*J*/Hz)**	^{31}**P{**^{1}**H}** δ, **(*J*/Hz)**	^{19}**F** δ, **(*J*/Hz)**	^{195}**Pt** δ, **(*J*/Hz)**	^{13}**C{**^{1}**H}** δ, **(*J*/Hz)**
1a	0.89 (t, J_{PH} 6.3, J_{PtH} 83.8, 3H) 1.50 (m, 12H, Cyp) 1.71 (m, 12 H, Cyp) 1.89 (m, 24H, Cyp) 2.22 (quintet of triplets with satellites, J_{HH} 9.3, 1.8, 6H, J_{PtH} 128 Hz, Cyp),	22.3 (J_{PtP} 2962)	–168.3 (m, 2F, F meta to N) –99.0 (m, 2F, F ortho to N)	–4060 (t, J_{PtP} 2995)	–34.3 (t, J_{CP} 7.0, J_{CPt} 695, Me) 26.3 (s, Cyp) 29.9 (s, Cyp) 34.9 (vt, J_{CP} 13.7, Cyp) 137 (dm, J_{CF} 247, CF) 146 (dm, J_{CF} 230, CF) 158 (s, CO)
1b	0.77 (t, J_{PH} 6.1, J_{PtH} 82.6, 3H Hz, Me) 1.40 (m, 12H, Cyp) 1.62 (m, 12H, Cyp) 1.81 (b, 24H, Cyp) 2.15 (quin with satellites, J_{HH} 9.4, J_{PtH} 127, 6H, Cyp)	22.0 (s, J_{PtP} 2990)	–166.2 (m, 2F, F^2 & F^4) –169.0 (t, J 23.1, 2F, F^3 & F^5) –183.8 (tt, J 23.1, 11.6, 1F, F^4)	–4040 (t, J_{PtP} 2997)	–34.7 (t, J_{CP} 6.9, Me) 26.4 (vt, J_{CP} 4.4, Cyp) 29.8 (s, Cyp) 34.9 (vt, J_{CP} 14.3, Cyp) 139.7 (dm, J_{CF} 242, CF) 141 (m, CO) 143.9 (dm, J_{CF} 256, CF)
1c	–24.62 (t, J_{PH} 13.1, J_{PtH} 1234, 1H, PtH) 1.34 (m, 12H, Cyp) 1.55 (m, 12H, Cyp) 1.65 (m, 24H, Cyp) 1.86 (quin, J_{HH} 9.5, Cyp)	46.2 (s, J_{PtP} 2940)	–99.3 (m, 2F) –169.8 (m, 2F)	–4704 (t, J_{PtP} 2938)	26.0 (t, J_{CP} 4.4, Cyp) 30.0 (s, J_{CPt} 21.3, Cyp) 36.0 (t, J_{CP} 15.7, Cyp) 136.7 (dm, J_{CF} 244, CF) 146.0 (dm, J_{CF}, 235, CF) 158.9 (m, CO)
1d	–24.27 (t, J_{PH} 13.4, J_{PtH} 1178, 1H, PtH) 1.38 (m, 12 H, Cyp) 1.59 (m, 12H, Cyp) 1.70 (b, 24H. Cyp) 1.92 (quin with satellites, J_{HH} 9.4, J_{PtH} 59 Hz, 6H, Cyp)	45.5 (s, J_{PtP} 2974)	–168.56 (m, 2F) –170.76 (m, 2F) –185.5 (tt, J 23.3, 12.1, 1F)	–4696 (td J_{PtP} 2964, J_{PtH} 1176)	26.5 (t, J_{CP} 4.5, Cyp) 30.4 (s with Pt satellites, J_{CPt} 21.2, Cyp) 36.5 (t with Pt satellites, J_{CP} 15.4, J_{CPt} 62.9, Cyp) 139.7 (dm, J_{CF} 243.5, CF) 142.0 (dm, J_{CF} 234.0, CF) 146.3 (t, J_{CF} 12.8, CF)
1e	0.79 (t, J_{PH} 6.0, J_{PtH} 82.5, 3H, PtMe) 1.41 (m, 12H, Cyp)	21.6 (s, J_{PtP} 2986)	–166.0 (dm, J_{FH} 10.4, 2F, F^3 & F^5) –146.2 (dm, J_{FH} 6.4, 2F, F^2 &	–4040 (t, J_{PtP} 2988)	–34.9 (t, J_{CP} 6.9, J_{CPt} 680 Me) 26.5 (t, J_{CP} 3.8, Cyp) 29.8 (s, Cyp)

	1.64 (m, 12H, Cyp) 1.84 (m, 24H, Cyp) 2.17 (quin of t, J_{HH} 9.2, J_{PH} 2.0, 6H, Cyp) 6.03 (tt, J_{HF} 10.5, 6.5, 1H, aromatic)		F^4)		34.9 (t, J_{CP} 14.4, Cyp) 86.5 (t, J_{CF} 24.1 CH) 142.0 (d, J_{CF} 231, CF) 148.5 (dm, J_{CF} 238, CF) 149.6 (m, CO)
1f	0.79 (t, J_{HP} 6.0, J_{HPt} 82, 3H, Me) 1.43 (m, 12H, Cyp) 1.65 (m, 12H, Cyp) 1.87 (m, 24H, Cyp) 2.22 (quin of t, J_{HH} 9.3, J_{HP} 1.7 6H, Cyp) 6.04 (m, 1H, CH) 6.60 (m,1H, CH)	21.2 (s, J_{PtP} 2997)	–159.7 (m, 1F) –145.3 (m, 1F) –139.7 (m, 1F)	–4034 (J_{PtP} 3013)	–35.1 (t, J_{CP} 6.9, J_{CPt} 686, Me) 26.5 (t, J_{CP} 4.3, Cyp) 29.9 (s, Cyp) 34.9 (t, J_{CP} 14.4, Cyp) 96.0 (dd, J_{CF}, 19.9, 8.6, CH) 109.9 (ddd, J_{CF} 22.1, 10.1, 2.8) 145.2 (dm, J_{CF} 236.0, CF) 148.6 (m, CO) 150.3 (dd, J_{CF} 239.5, 12.1, CF) 153.5 (dd, J_{CF} 233.6, 6.2)

Crystallographic methods.

Diffraction data for **1a** were collected at 110 K on a Bruker Smart Apex diffractometer with Mo-Kα radiation (λ = 0.71073 Å) using a SMART CCD camera. The crystal was cooled with an Oxford Crysostream. Diffractometer control, data collection and initial unit cell determination was performed using "SMART".[6] Frame integration and unit-cell refinement was carried out with "SAINT+".[7] Absorption corrections were applied by SADABS.[8] Diffraction data for **1b** were collected at 110 K on an Agilent SuperNova diffractometer with MoKα radiation (λ = 0.71073 Å). Data collection, unit cell determination and frame integration were carried out with "CrysalisPro". Absorption corrections were applied using crystal face-indexing and the ABSPACK absorption correction software within CrysalisPro.

For **1a**, **1b**, **1e and 1f** structures were solved and refined using Olex2[9] implementing SHELX algorithms. Structures were solved by either Patterson or direct methods using SHELXS-97 and refined by full-matrix least squares using SHELXL-97.[10] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed at calculated positions and refined using a "riding model" except for the Pt-methyl hydrogens which were located by difference map after all other atoms had been located. The largest peak in the difference map of **1a**, Q1, corresponds to the Pt in a minor non-merohedral twin, Q14 and Q19 correspond to twin sites of P1 and P2, respectively. The minor twin component is estimated to be ~2.5% of the major component. The relationship between the coordinates of the major and minor components is –x, y+0.21, –z, ie a 2-fold rotation about the b-axis with a translation of 0.21 along the same axis. For **1b** two of the cyclopentyl ligands exhibited disorder. For the cyclopentyl C28–C32, C31 was modelled in two positions with occupancies of 0.611:0.389(7); similarly for cyclopentyl C33–C37, C36 was modelled in two positions with occupancies of 0.924:0.076(7). For **1e**, one of the cyclopentyl groups was disordered and modelled with a carbon (C20) in two positions with refined occupancies of 0.838:0.162(9). For **1f**, the trifluorophenoxy moiety was disordered and modelled in two positions which differed by a 180° rotation about the C-O bond coupled with a slight difference in the Pt-O-C angle. The occupancy of each form refined to 0.678:0.322(3). The ADPs of carbons of the trifluorophenoxy group which were spatially close were constrained to be equal, for example, C3 and C7a. One of the cyclopentyl groups was disordered and modelled in two positions. When refined independently, the occupancies of the two forms were very close to those of the phenoxy group and were therefore made to be the same as the phenoxy group, *i.e*. 0.678:0.322(3). Crystallographic parameters are listed in Table S2. Structures of **1e** and **1f** are shown in Figure S4.

Table S2. Crystallographic data for **1a**, **1b, 1e** and **1f**

Identification code	rnp1020m **1a**	rnp1103 **1b**	rnp1341 **1e**	rnp1344 **1f**
Empirical formula	$C_{36}H_{57}F_4NOP_2Pt$	$C_{37}H_{57}F_5OP_2Pt$	$C_{37}H_{58}F_4OP_2Pt$	$C_{37}H_{59}F_3OP_2Pt$
Formula weight	852.86	869.86	851.86	833.87
Temperature / K	110(2)	110(2)	110(2)	110.05(10)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å, b / Å, c / Å	9.6998(8), 26.160(2), 13.9557(12)	9.8789(6), 26.7643(10), 13.7600(5)	10.28091(16), 24.3536(4), 14.17425(19)	9.72738(15) 26.6352(4) 13.74424(18)
β/°	100.507(2)	103.677(5)	101.1202(14)	102.3566(14)
Volume / Å^3	3481.8(5)	3535.0(3)	3482.28(9)	3478.51(9)
Z	4	4	4	4
ρ_{calc} / mg mm^{-3}	1.627	1.634	1.625	1.592
μ / mm^{-1}	4.173	4.116	4.172	4.171
F(000)	1728	1760	1728	1696.0
Crystal size / mm^3	0.45 × 0.12 × 0.10	0.41 × 0.231 × 0.18	0.20 × 0.096 × 0.066	0.36 × 0.17 × 0.17
2Θ range for data collection	3.12 to 60.00°	5.78 to 58.24°	5.6 to 60.1°	5.6 to 60.1°
Index ranges	–13<=h<=13, –36<=k<=36, –19<=l<=19	–13 ≤ h ≤ 13, –35 ≤ k ≤ 31, –17 ≤ l ≤ 18	–14 ≤ h ≤ 14, –30 ≤ k ≤ 34, –19 ≤ l ≤ 19	-13 ≤ h ≤ 13, -37 ≤ k ≤ 37, -19 ≤ l ≤ 19
Reflections collected	52381	27536	30583	41481
Independent reflections	10111 [R(int) = 0.0367]	8391[R(int) = 0.0294]	10221[R(int) = 0.0260]	10210 [R_{int} = 0.0335]

Data/restraints/parameters	10111 / 0 / 415	8391/4/424	10221/0/417	10210/12/450
Goodness-of-fit on F^2	1.055	1.052	1.064	1.069
Final R indexes [I>2σ(I)]	R_1 = 0.0235, wR_2 = 0.0511	R_1 = 0.0224, wR_2 = 0.0455	R_1 = 0.0221, wR_2 = 0.0418	R_1 = 0.0217, wR_2 = 0.0441
Final R indexes [all data]	R_1 = 0.0295, wR_2 = 0.0533	R_1 = 0.0261, wR_2 = 0.0469	R_1 = 0.0271, wR_2 = 0.0432	R_1 = 0.0257, wR_2 = 0.0457
Largest diff. peak/hole / e $Å^{-3}$	2.088 and –0.467	0.603/–0.747	0.70/-0.67	0.87/-0.91
CCDC reference number	CCDC966767	CCDC966768	CCDC 983216	CCDC 983215

Table S3. Selected bond lengths (Å) and angles (º) of **1a**, **1b, 1e** and **1f**.

	1a	**1b**	**1e**	**1f**
O(1)–Pt(1)	2.1586(15)	2.1306(15)	2.1419(14)	2.1325(13)
C(1)–Pt(1)	2.044(2)	2.047(2)	2.0520(19)	2.0546(19)
P(1)–Pt(1)	2.3322(6)	2.3021(6)	2.3166(5)	2.3023(5)
P(2)–Pt(1)	2.3072(6)	2.3200(6)	2.3059(5)	2.3222(5)
Pt···F(6)/F(7)	3.110(2)	3.117(2)	2.972(1)	3.046(9)/3.196(20) occupancy 0.678:0.322(3)
C(1)–Pt(1)–O(1)	176.46(9)	179.56(9)	176.37(7)	179.14(8)
P(1)–Pt(1)–P(2)	171.397(19)	176.43(2)	164.957(18)	175.207(18)
O(1)–Pt(1)–P(1)	92.03(4)	90.86(5)	91.53(4)	90.95(4)
O(1) –Pt(1)–P(2)	89.08(4)	90.81(5)	89.42(4)	90.60(4)
C(1)–Pt(1)–P(1)	89.44(7)	89.26(7)	89.35(6)	89.32(6)
C(1)–Pt(1)–P(2)	89.95(7)	89.05(7)	90.65(6)	89.19(6)
C(2)–O(1)–Pt(1)	130.10(15)	126.78(14)	126.90(13)	123.3(3)
C(3)–C(2)–O(1)–Pt	21.2(3)	27.3(3)	-1.00(14)	23.8(6)

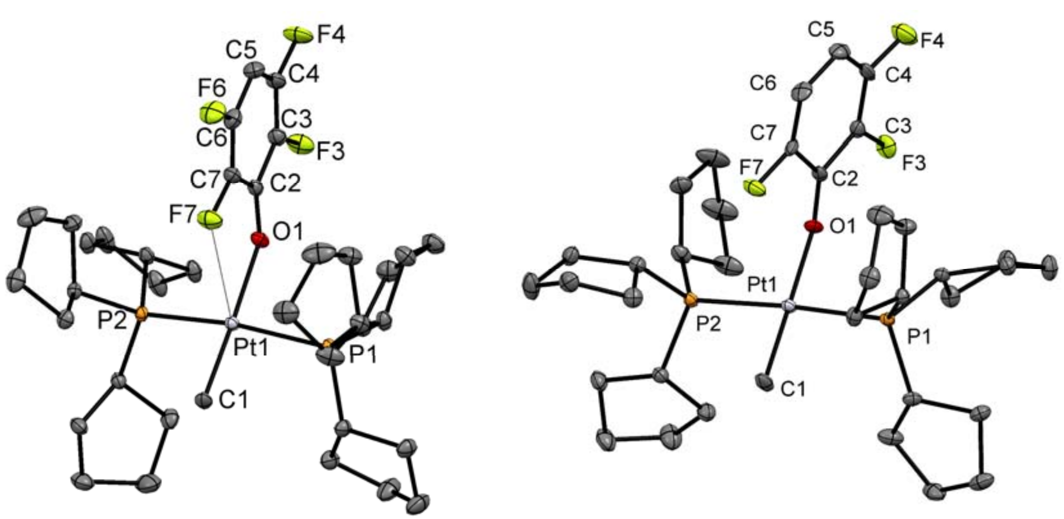


Figure S5. Molecular structure of **1e** (left) and **1f** (right). Hydrogen atoms omitted, anisotropic displacement parameters shown at the 50% level. The minor disordered components are not shown.

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