Supporting Information

Stepwise Addition of Difluorocarbene to a Transition Metal Complex

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1. General Information

Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glove box. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, diethyl ether (DEE) and tetrahydrofuran (THF) were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour®) solvent purification system. Benzene-d_6 (C_6D_6) was dried by stirring over activated alumina (*ca.* 10 wt. %) overnight, followed by filtration. All solvents were stored over activated (heated at *ca.* 250°C for >10 h under vacuum) 4 Å molecular sieves. Glassware was oven-dried at 150°C for >2 h. The following chemicals were obtained commercially, as indicated: [$CpCo(CO)_2$] (Cp = cyclopentadienyl) (Strem, 95%), sodium (Alfa Aesar, 99%), mercury (Strem, 99.998%), Me_3SiCF_3 (Synquest, 98%). Compounds **2b** and **4** were prepared as previously reported.[2] Compounds **1b** and **1c** were prepared according to slightly modified literature procedures.[3] Tetrafluoroethylene (TFE) was made by pyrolysis of polytetrafluoroethylene (Scientific Polymer Products, powdered) under vacuum, using a slightly modified literature procedure (10-20 mTorr, 650°C, 30 g scale, product stabilized with R(+)-limonene (Aldrich, 97%), giving TFE of *ca.* 97% purity).[1] ^{1}H, ^{19}F and ^{31}P{^{1}H}NMR spectra were recorded on either a 300 MHz Bruker Avance or 300 MHz Bruker Avance II instrument at room-temperature (21-23°C). ^{1}H NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (C_6D_6: 7.16 ppm). ^{19}F NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)benzene (BTB) (Aldrich, 99%, deoxygenated by purging with nitrogen, stored over activated 4 Å molecular sieves), set to –63.5 ppm. Note: for NMR solutions containing both BTB and hexafluorobenzene (C_6F_6) (Aldrich, 99%), the chemical shift of C_6F_6 appears at –163.6 in C_6D_6 (with BTB at –63.5 ppm). ^{1}H NMR data for BTB: (300 MHz, C_6D_6) δ 6.60 (m, 1H, Ar-5-H), 7.12 (m, 2H, Ar-4,6-H), 7.76 (m, 1H, Ar-2-H); (300 MHz, CD_3CN) δ 7.76-7.84 (m, 1H, Ar–H), 7.95-8.04 (m, 3H, Ar–H). ^{31}P{^{1}H}NMR data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. IR data were collected on a Varian 640 FT-IR spectrometer. Elemental analyses were performed by the Elemental Analysis Service, Université de Montréal (Montréal, Québec).

[1] Hunadi, R. J.; Baum, K. *Synthesis* **1982**, *39*, 454.

[2] D. J. Harrison, S. I. Gorelsky, G. M. Lee, I. Korobkov and R. T. Baker, *Organometallics*, **2012**, *32*, 12-15.

[3] *Inorganic Synthesis, vol. 26,* H. D. Kaesz, ed., John Wiley & Sons, Inc., **1989**, p.191.

2. Experimental Section

General procedure for reactions of 1 with Me_3SiCF3

Complex **1** (0.1 mmol), NaI (0.02 mmol) and THF (3 mL) were charged into a 50 mL ampoule. Me_3SiCF_3 (0.2 mmol) was added, and the ampoule was sealed and stirred at 65 ^oC in an oil bath. After 2.5 hours, the ampoule was allowed to cool to room temperature. Internal standard (BTB, 15 mol%) was added and the mixture was analyzed using ^{19}F NMR.

CpCo(=CF_2)(P(O^iPr)$_3$) (2c) A solution of CpCoI(CO)CF_3 (500 mg, 1.44 mmol in toluene (5 mL) was stirred in a schlenk tube, and a solution of P(O^iPr)$_3$ (330 mg, 1.58 mmol) in toluene (5 mL) was then added via cannula transfer over 5 minutes. The resulting solution was stirred under dynamic N_2 (to accommodate the release of CO) for 3 hours. The solution was then degassed using 3 freeze-pump-thaw cycles. The dark brown solution was transferred to a 100 mL round bottom flask containing an amalgam of Na (69 mg, 3 mmol) and Hg (0.064 mL) (0.8 wt% Na/Hg) in toluene (10 mL), which had been stirred vigorously for 10 minutes. This solution was stirred for 20 hours, and the color changed from dark brown to dark red/orange. The volatiles were removed under vacuum, and the resulting red/orange residue was extracted with hexanes/DEE (1:1) (20 mL) and filtered through a plug of celite. The solvent was removed from the filtrate under vacuum, giving 422 mg of **2c** as red/orange oil (76% yield). ^1H NMR (300 MHz, C_6D_6) δ 1.16 (d, 18H, Me, ^{i}Pr), 4.72 (m, 3H, ^{i}Pr), 4.82 (s, 5H, Cp). ^{19}F NMR (282 MHz, C_6D_6) δ 63.95 (dd, 1F, $^2J_{FF}$ = 101 Hz, $^3J_{FP}$ = 45 Hz), 94.97 (dd, 1F, $^3J_{FP}$ = 18 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ 164.7.

CpCo(η^2-C_2F_4)(CO) (3a) $CpCo(CO)_2$ (200 mg, 1.11 mmol), NaI (33 mg, 0.22 mmol), and THF (10 mL) were charged into a 100 mL ampoule, resulting in a dark red solution. Me_3SiCF_3 (400 mg, 2.81 mmol) was added, and the ampoule was sealed and stirred at 65 ^oC in an oil bath. After approximately 30 minutes, the red solution turned yellow in color, and the solution was heated for an additional 1.5 hours. The volatiles were removed under vacuum, leaving a brown oily residue. The residue was extracted with hexane (8 mL) and filtered through a plug of celite. The hexane solution was dried under vacuum, giving 193 mg of **3a** as golden-brown oil (69% yield). IR (cm^{-1}) : 2050 (s br, ν_{CO}). ^1H NMR (300 MHz, C_6D_6) δ 4.39 (s, 5H, Cp). ^{19}F NMR (282 MHz, C_6D_6) δ –113.2 (m, 2F, CF_2=CF_2), -107.1 (m, 2F, CF_2=CF_2). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 88.86 (s, Cp), 121.8 (m, CF_2=CF_2), 199.04 (br s, CO). Anal. Calc. for $C_8H_5F_4Co_1O_1$: C, 38.12, H, 2.00. Found: C, 38.25, H, 2.08.

CpCo(η^2-C_2F_4)(PPh_3) (3b) Complex **2b** (200mg, 0.458 mmol), NaI (13 mg, 0.086 mmol), and THF (10 mL) were charged into a 100 mL ampoule. To the red solution, Me_3SiCF_3 (163 mg, 1.15 mmol) was added, and the ampoule

was sealed and stirred at 65 °C in an oil bath. After 2.5 hours, volatiles were removed under vacuum, leaving a brown oily residue. The residue was extracted with toluene (6 mL), and filtered through a plug of celite. Volatiles were again removed under vacuum, and the residue was recrystallized from a concentrated solution in toluene/hexanes at -35 °C, giving **3b** as brown/orange crystalline solid (150 mg, 67% yield). Crystals of **3b** suitable for X-ray analysis were grown from concentrated toluene/hexanes at -35 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 4.53 (s, 5H, Cp), 6.97 (ov m, 9H), 7.63 (m, 6H). ^{19}F NMR (282 MHz, C_6D_6) δ –114.1 (m, 2F, CF_2=CF_2), -110.2 (m, 2F, CF_2=CF_2). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ 58.1. Anal. Calc. for $C_{25}H_{20}F_4Co_1P_1$: C, 61.74, H, 4.15. Found: C, 64.28, H, 4.58.

CpCo(η^2-C_2F_4)(P(O^{i}Pr)$_3$) (3c) $CpCo(P(O^iPr)_3)_2$ (150 mg, 0.28 mmol), NaI (9 mg, 0.06 mmol), and THF (6 ml) were charged into a 100 mL ampoule. Me_3SiCF_3 (118 mg, 0.83 mmol) was added, and the ampoule was sealed and stirred at 65 °C in an oil bath. After 2.5 hours, the volatiles were removed under vacuum, leaving an orange residue. The residue was extracted with hexane (6 mL) and filtered through celite. The filtrate was concentrated to ca. 1 mL and cooled to -35 °C. A yellow solid precipitated from the solution, and was collected and washed with cold hexanes. The solid was died under vacuum, giving **3c** as yellow crystals (75 mg, 62 % yield). ^{1}H NMR (300 MHz, C_6D_6) δ 1.08 (d, 18H, Me, ^{i}Pr), 4.55 (m, 3H, ^{i}Pr), 4.79 (s, 5H, Cp). ^{19}F NMR (282 MHz, C_6D_6) δ –115.7 (m, 2F, CF_2=CF_2), -111.2 (m, 2F, CF_2=CF_2). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ 151.6. Anal. Calc. for $C_{16}H_{26}F_4Co_1P_1O_3$: C, 44.46, H, 6.06. Found: C, 44.49, H, 6.06.

CpCo(η^2-$CF_2CF(CF_3)$)(PPh_3) (5) Complex **4** (200 mg, 0.413 mmol), NaI (13 mg, 0.086 mmol), and THF (10 mL) were charge into a 100 mL ampoule. To the blue solution, Me_3SiCF_3 (146 mg, 1.028 mmol) was added, and the ampoule was sealed and stirred at 65 °C in an oil bath. After 2.5 hours, volatiles were removed under vacuum, leaving a yellow/brown residue. The residue was extracted with toluene and hexanes (4 mL: 4 mL), and filtered through a plug of celite. Volatiles were again removed under vacuum, and the residue was recrystallized from a concentrated solution of toluene/hexanes at -35 °C, giving **5** as orange crystals (120 mg, 54% yield). Crystals of **5** suitable for x-ray analysis were grown from concentrated toluene/hexanes at -35 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 4.49 (s, 5H, Cp), 6.98 (ov m, 9H), 7.64 (m, 6H). ^{19}F NMR (282 MHz, C_6D_6) δ –195.4 (m, 1F), -96.3 (dtm, 1F, $^2J_{FF(gem)}$ = 125 Hz), -94.6 (ddm, 1F, $^2J_{FF(gem)}$ = 125 Hz), -66.2 (t, 3F, CF_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ 52.3. Anal. Calc. for $C_{26}H_{20}F_6Co_1P_1$: C, 58.23, H, 3.76. Found: C, 58.23, H, 3.83.

3. Spectroscopic Data

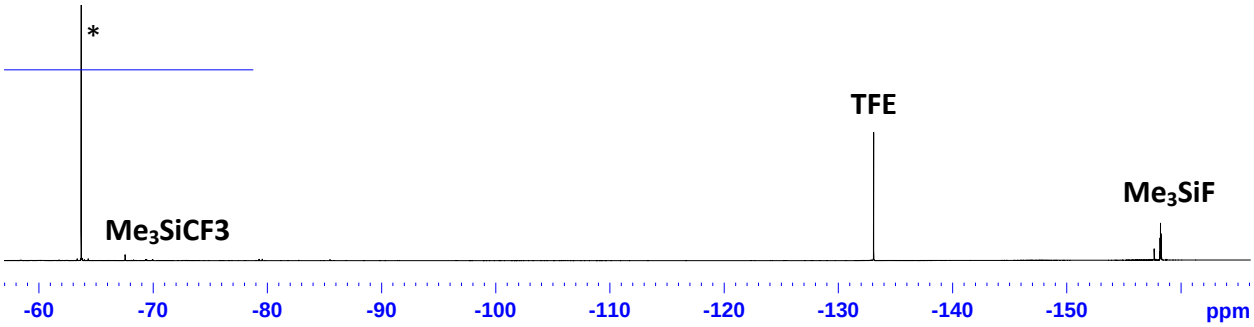

Figure S1. Crude ^{19}F NMR (282 MHz, THF) spectrum of reaction with Me_3SiCF_3 (25 mg, 0.173 mmol) and NaI (5 mg, 0.033 mmol) in THF, at 65 ^{o}C for 2 hours. The major products are TFE and Me_3SiF, while trace amounts of SiF_4 and CF_3H are also present (not shown in figure). BTB, labeled '*', was used as internal NMR standard.

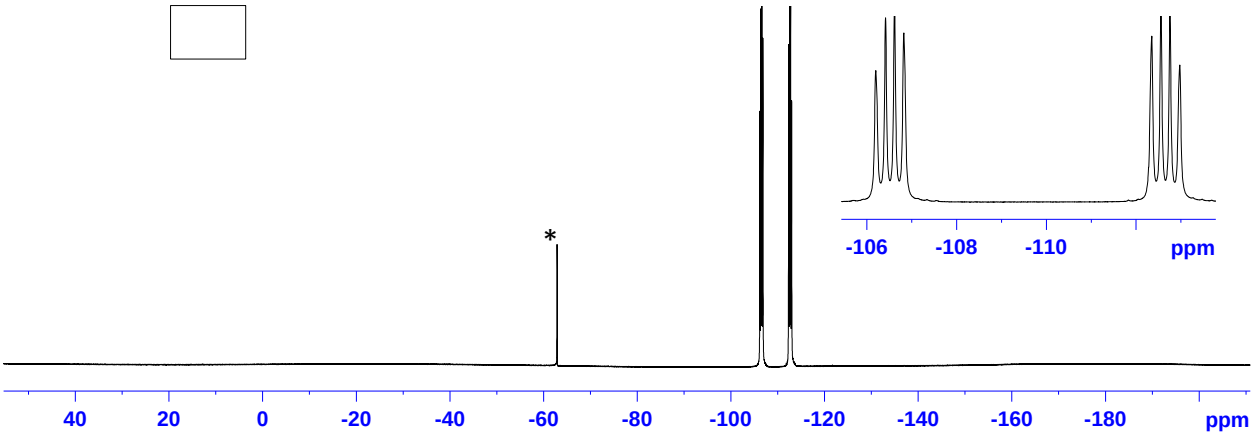

Figure S2. ^{19}F NMR (282 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(CO)$ (**3a**). BTB, labeled '*', was used as internal NMR standard.

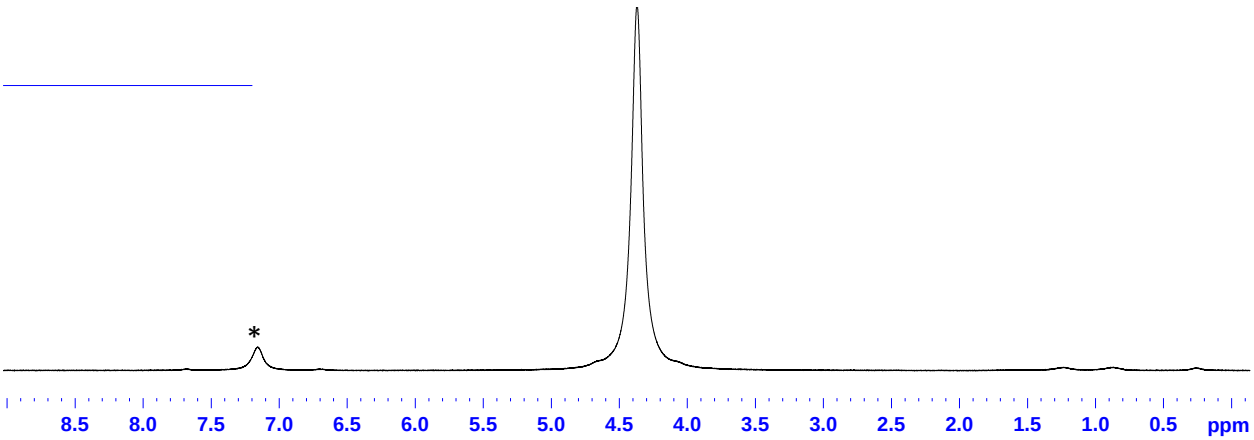

Figure S3. ^{1}H NMR (300 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(CO)$ (**3a**). Residual solvent peaks (C_6H_6) labelled as '*'.

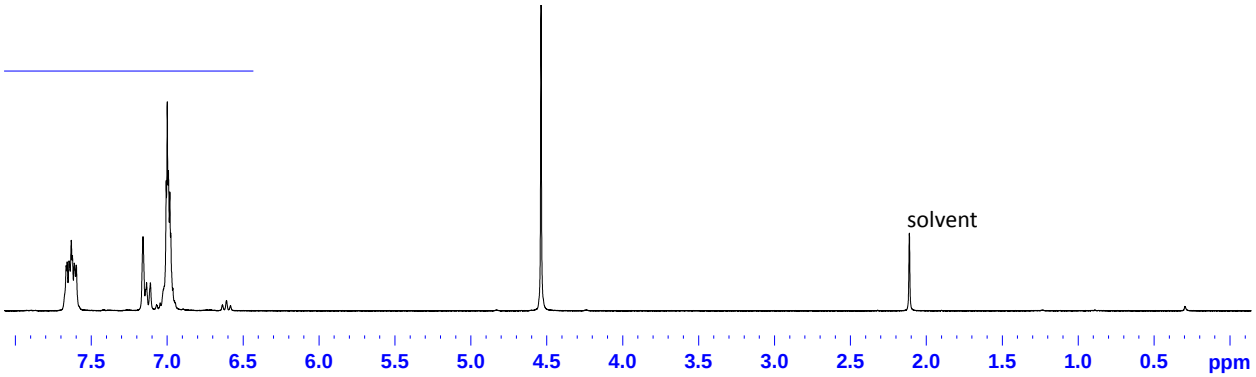

Figure S4. ^{1}H NMR (300 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(PPh_3)$ (**3b**).

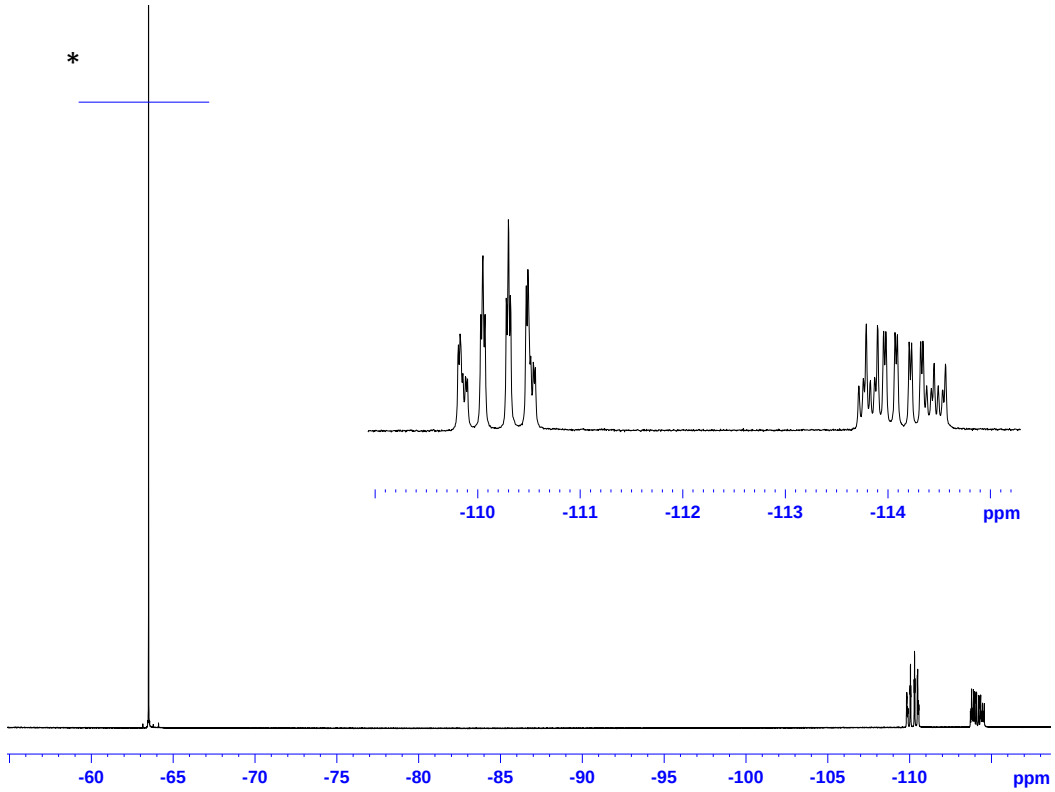

Figure S5. ^{19}F NMR (282 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(PPh_3)$ (**3b**). BTB, labeled '*', was used as internal NMR standard.

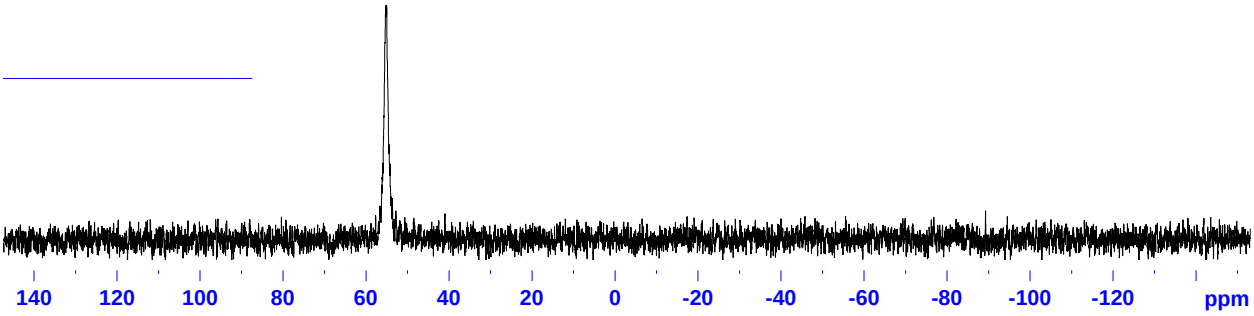

Figure S6. $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(PPh_3)$ (**3b**).

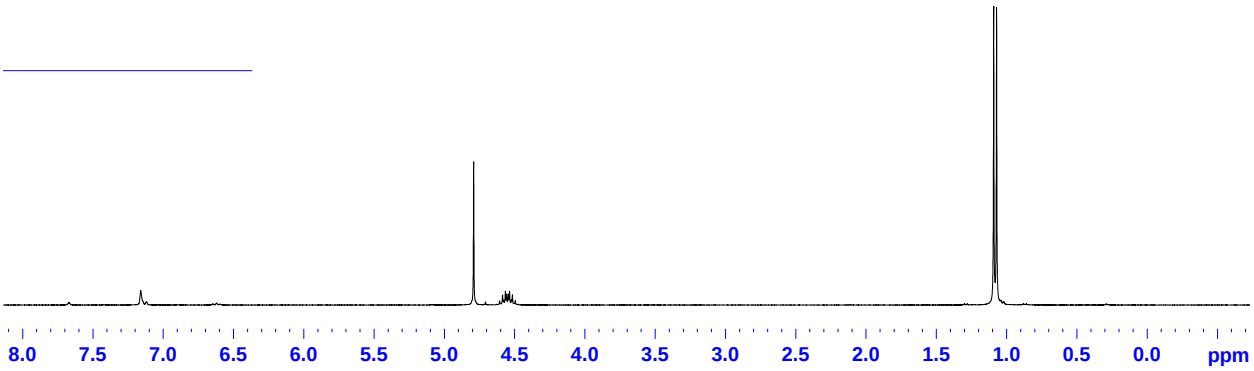

Figure S7. ^{1}H NMR (300 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(P(O^iPr)_3)$ (**3c**).

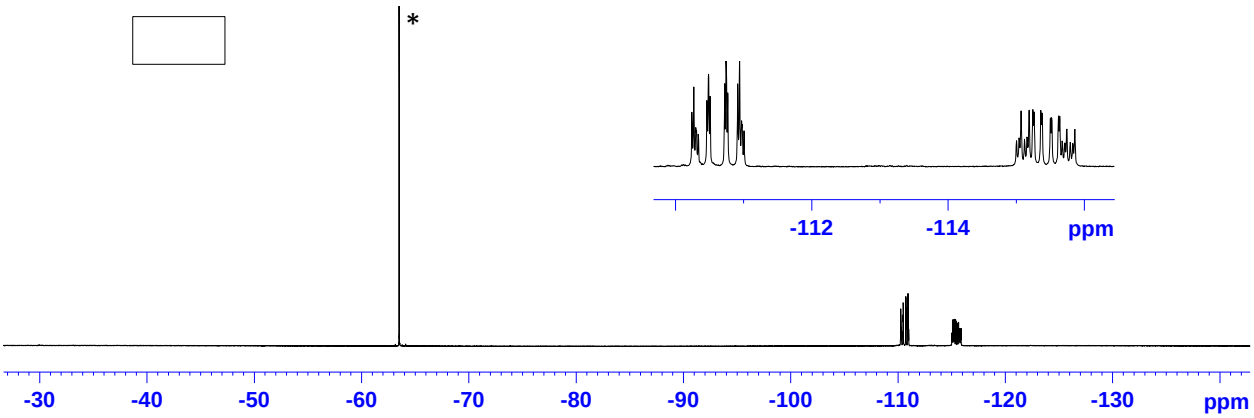

Figure S8. ^{19}F NMR (282 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(P(O^iPr)_3)$ (**3c**). BTB, labeled '*', was used as internal NMR standard.

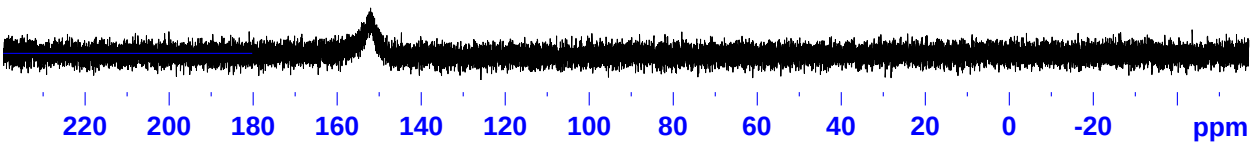

Figure S9. $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6) spectrum of $CpCo(\eta^2\text{-}C_2F_4)(P(O^iPr)_3)$ (**3c**).

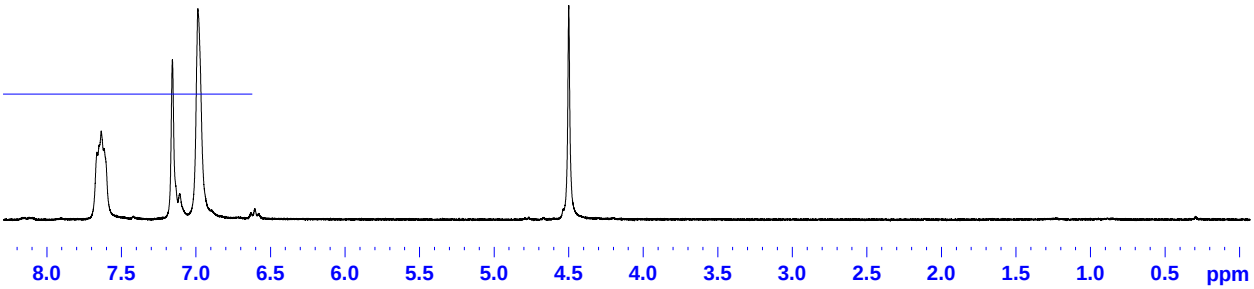

Figure S10. ^{1}H NMR (300 MHz, C_6D_6) spectrum of CpCo(η^2-$CF_2CF(CF_3)$)(PPh_3) (**5**).

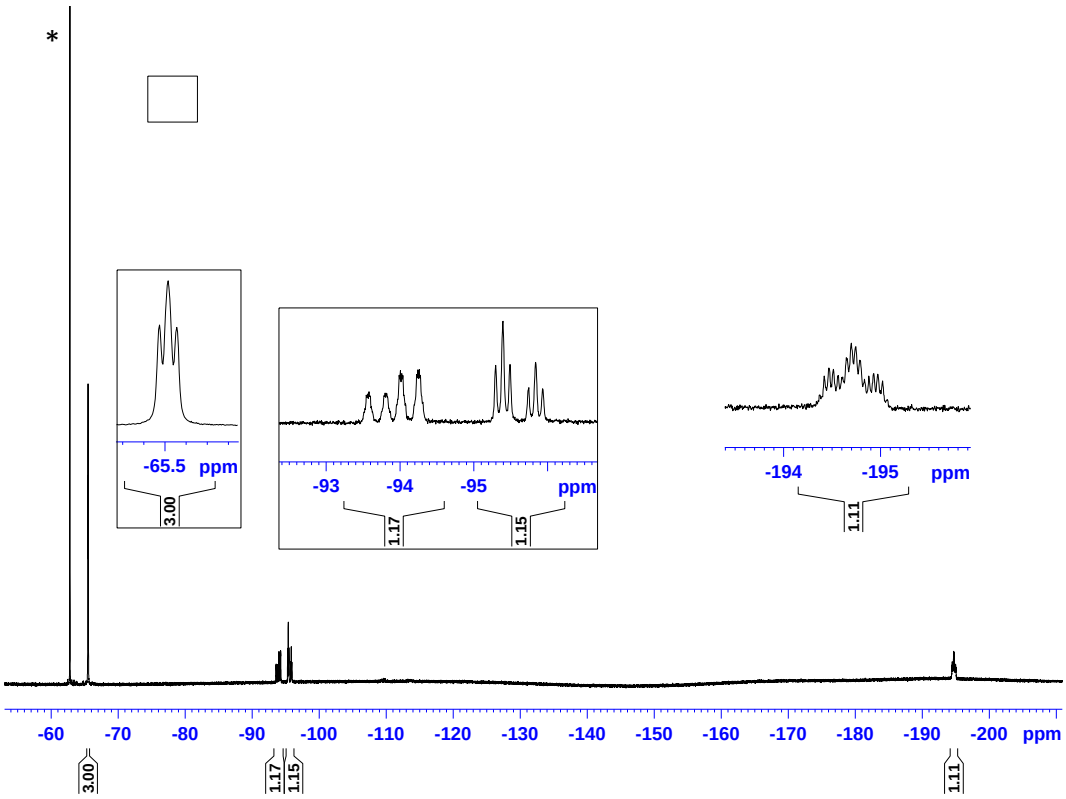

Figure S11. ^{19}F NMR (282 MHz, C_6D_6) spectrum of CpCo(η^2-$CF_2CF(CF_3)$)(PPh_3) (**5**). BTB, labeled '*', was used as internal NMR standard.

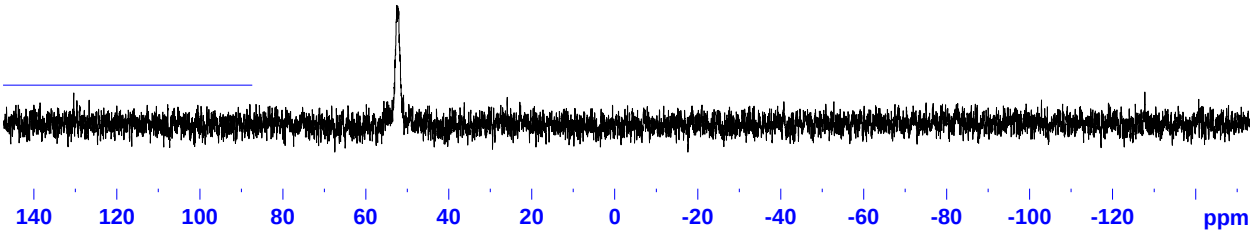

Figure S12. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) spectrum of CpCo(η^2-$CF_2CF(CF_3)$)(PPh_3) (**5**).

4. X-Ray Structure Data and Characterization

Table S1. Crystal Data and refinement for [CpCo(η^2-C_2F_4)(PPh_3)] (**3b**)

Identification code	tb092
Empirical formula	C28.50 H24 Co F4 P
Formula weight	532.38
Temperature	200(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.9032(3) A alpha = 98.010(2) deg.
	b = 9.6331(3) A beta = 95.934(2) deg.
	c = 15.0734(5) A gamma = 109.836(2) deg.
Volume	1188.35(7) A^3
Z, Calculated density	2, 1.488 Mg/m^3
Absorption coefficient	0.836 mm^-1
F(000)	546
Crystal size	0.17 x 0.12 x 0.05 mm
Theta range for data collection	2.46 to 28.23 deg
Limiting indices	-11<=h<=10, -12<=k<=12, -20<=l<=19
Reflections collected / unique	6984 / 5399 [R(int) = 0.0112]
Completeness to theta = 28.23	91.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9594 and 0.8709
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5399 / 0 / 296
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0503, wR2 = 0.1405
R indices (all data)	R1 = 0.0572, wR2 = 0.1474
Largest diff. peak and hole	1.348 and -0.606 e.A^-3

Table S2. Bond lengths [Å] and angles [°] for [CpCo(η^2-C_2F_4)(PPh_3)] (**3b**)

Co(1)-C(24)	1.883(3)	C(25)-Co(1)-C(2)	132.62(17)
Co(1)-C(25)	1.897(3)	C(1)-Co(1)-C(2)	39.42(17)
Co(1)-C(1)	2.069(3)	C(3)-Co(1)-C(2)	38.7(2)
Co(1)-C(3)	2.101(4)	C(24)-Co(1)-C(5)	125.35(15)
Co(1)-C(2)	2.115(4)	C(25)-Co(1)-C(5)	100.94(16)
Co(1)-C(5)	2.121(4)	C(1)-Co(1)-C(5)	38.79(15)
Co(1)-C(4)	2.123(4)	C(3)-Co(1)-C(5)	65.05(18)
Co(1)-P(1)	2.1930(6)	C(2)-Co(1)-C(5)	65.35(16)
P(1)-C(6)	1.837(2)	C(24)-Co(1)-C(4)	162.69(15)
P(1)-C(12)	1.834(2)	C(25)-Co(1)-C(4)	131.1(2)
P(1)-C(18)	1.845(2)	C(1)-Co(1)-C(4)	65.06(14)
F(1)-C(24)	1.357(3)	C(3)-Co(1)-C(4)	39.5(2)
F(2)-C(24)	1.362(4)	C(2)-Co(1)-C(4)	65.56(19)
F(3)-C(25)	1.361(4)	C(5)-Co(1)-C(4)	38.26(17)
F(4)-C(25)	1.347(4)	C(24)-Co(1)-P(1)	96.53(9)
C(1)-C(5)	1.392(5)	C(25)-Co(1)-P(1)	99.97(10)
C(1)-C(2)	1.412(6)	C(1)-Co(1)-P(1)	159.11(12)
C(2)-C(3)	1.397(7)	C(3)-Co(1)-P(1)	93.91(11)
C(3)-C(4)	1.428(8)	C(2)-Co(1)-P(1)	121.85(13)
C(4)-C(5)	1.391(6)	C(5)-Co(1)-P(1)	135.68(11)
C(6)-C(11)	1.400(4)	C(4)-Co(1)-P(1)	100.78(11)
C(6)-C(7)	1.393(4)	C(6)-P(1)-C(12)	106.06(11)
C(7)-C(8)	1.393(4)	C(6)-P(1)-C(18)	103.03(11)
C(8)-C(9)	1.382(5)	C(12)-P(1)-C(18)	100.33(11)
C(9)-C(10)	1.392(4)	C(6)-P(1)-Co(1)	110.51(8)
C(10)-C(11)	1.384(4)	C(12)-P(1)-Co(1)	113.20(8)
C(12)-C(13)	1.390(4)	C(18)-P(1)-Co(1)	122.11(8)
C(12)-C(17)	1.405(3)	C(5)-C(1)-C(2)	109.3(4)
C(13)-C(14)	1.383(4)	C(5)-C(1)-Co(1)	72.6(2)
C(14)-C(15)	1.391(4)	C(2)-C(1)-Co(1)	72.0(2)
C(15)-C(16)	1.391(5)	C(3)-C(2)-C(1)	106.5(4)
C(16)-C(17)	1.379(4)	C(3)-C(2)-Co(1)	70.1(2)
C(18)-C(23)	1.392(4)	C(1)-C(2)-Co(1)	68.5(2)
C(18)-C(19)	1.395(3)	C(2)-C(3)-C(4)	108.6(4)
C(19)-C(20)	1.386(4)	C(2)-C(3)-Co(1)	71.2(2)
C(20)-C(21)	1.383(4)	C(4)-C(3)-Co(1)	71.1(2)
C(21)-C(22)	1.382(4)	C(5)-C(4)-C(3)	107.3(4)
C(22)-C(23)	1.392(4)	C(5)-C(4)-Co(1)	70.8(2)
C(24)-C(25)	1.430(5)	C(3)-C(4)-Co(1)	69.4(2)
C(26)-C(27)	1.3900	C(4)-C(5)-C(1)	108.2(4)
C(26)-C(31)	1.3900	C(4)-C(5)-Co(1)	70.9(2)
C(26)-C(32)	1.64(2)	C(1)-C(5)-Co(1)	68.61(19)
C(27)-C(28)	1.3900	C(11)-C(6)-C(7)	118.8(2)
C(28)-C(29)	1.3900	C(11)-C(6)-P(1)	117.90(18)
C(29)-C(30)	1.3900	C(7)-C(6)-P(1)	123.27(19)
C(30)-C(31)	1.3900	C(8)-C(7)-C(6)	120.0(3)
		C(9)-C(8)-C(7)	120.8(3)
C(24)-Co(1)-C(25)	44.46(15)	C(8)-C(9)-C(10)	119.6(3)
C(24)-Co(1)-C(1)	98.18(14)	C(11)-C(10)-C(9)	119.8(3)
C(25)-Co(1)-C(1)	100.93(15)	C(10)-C(11)-C(6)	121.0(2)
C(24)-Co(1)-C(3)	139.1(2)	C(13)-C(12)-C(17)	118.7(2)
C(25)-Co(1)-C(3)	165.17(15)	C(13)-C(12)-P(1)	119.75(19)
C(1)-Co(1)-C(3)	65.31(16)	C(17)-C(12)-P(1)	121.34(19)
C(24)-Co(1)-C(2)	104.74(17)	C(14)-C(13)-C(12)	120.8(3)

C(13)-C(14)-C(15)	120.1(3)	F(2)-C(24)-Co(1)	122.5(2)
C(14)-C(15)-C(16)	119.5(3)	C(25)-C(24)-Co(1)	68.26(17)
C(17)-C(16)-C(15)	120.5(3)	F(4)-C(25)-F(3)	107.0(3)
C(16)-C(17)-C(12)	120.3(3)	F(4)-C(25)-C(24)	119.1(3)
C(23)-C(18)-C(19)	118.6(2)	F(3)-C(25)-C(24)	116.5(3)
C(23)-C(18)-P(1)	121.75(19)	F(4)-C(25)-Co(1)	125.5(2)
C(19)-C(18)-P(1)	119.60(19)	F(3)-C(25)-Co(1)	117.2(2)
C(20)-C(19)-C(18)	120.9(3)	C(24)-C(25)-Co(1)	67.28(17)
C(21)-C(20)-C(19)	119.9(3)	C(27)-C(26)-C(31)	120.0
C(22)-C(21)-C(20)	119.8(3)	C(27)-C(26)-C(32)	108.8(8)
C(21)-C(22)-C(23)	120.4(3)	C(31)-C(26)-C(32)	131.2(8)
C(22)-C(23)-C(18)	120.2(3)	C(28)-C(27)-C(26)	120.0
F(1)-C(24)-F(2)	105.9(2)	C(27)-C(28)-C(29)	120.0
F(1)-C(24)-C(25)	118.7(3)	C(30)-C(29)-C(28)	120.0
F(2)-C(24)-C(25)	118.6(3)	C(29)-C(30)-C(31)	120.0
F(1)-C(24)-Co(1)	119.7(2)	C(30)-C(31)-C(26)	120.0

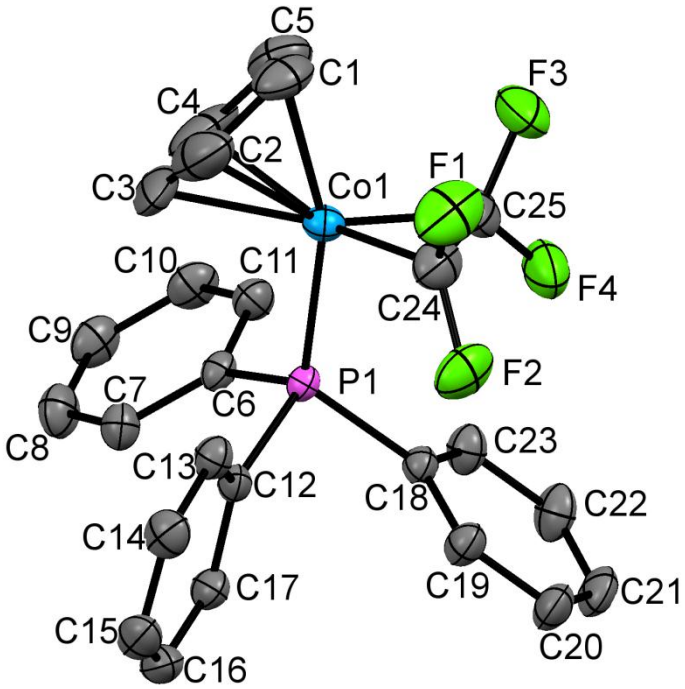

Figure S13. ORTEP drawing and labelling scheme of complex **3b** with thermal ellipsoids set to 50% probability. Hydrogen atoms and crystallization toluene solvent molecules omitted for clarity.

Table S3. Crystal data and structure refinement for [CpCo(η^2-C_2F_4)(P(O^iPr)$_3$)] (**3c**)

Identification code	tb113a	
Empirical formula	C16 H26 Co F4 O3 P	
Formula weight	432.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.0497(5) Å	a= 90°.
	b = 16.2106(6) Å	b= 94.782(2)°.
	c = 9.5283(3) Å	g = 90°.
Volume	2008.63(12) Å^3	
Z	4	
Density (calculated)	1.429 Mg/m^3	
Absorption coefficient	0.981 mm^{-1}	
F(000)	896	
Crystal size	0.450 x 0.220 x 0.170 mm^3	
Theta range for data collection	2.008 to 30.572°.	
Index ranges	-17<=h<=13, -17<=k<=23, -13<=l<=12	
Reflections collected	10214	
Independent reflections	5463 [R(int) = 0.0249]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6713	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5463 / 0 / 226	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0833	
R indices (all data)	R1 = 0.0661, wR2 = 0.0948	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.280 and -0.261 e.Å^{-3}	

Table S4. Bond lengths [Å] and angles [°] for [CpCo(η^2-C_2F_4)(P(O^iPr)$_3$)] (**3c**)

Co(1)-C(6)	1.880(2)	C(6)-Co(1)-P(1)	96.99(7)
Co(1)-C(7)	1.895(2)	C(7)-Co(1)-P(1)	100.10(7)
Co(1)-C(5)	2.047(2)	C(5)-Co(1)-P(1)	160.09(7)
Co(1)-C(1)	2.085(2)	C(1)-Co(1)-P(1)	124.16(7)
Co(1)-C(2)	2.088(2)	C(2)-Co(1)-P(1)	94.05(6)
Co(1)-C(4)	2.101(2)	C(4)-Co(1)-P(1)	131.24(7)
Co(1)-C(3)	2.110(2)	C(3)-Co(1)-P(1)	97.91(7)
Co(1)-P(1)	2.1479(5)	O(2)-P(1)-O(3)	100.27(8)
P(1)-O(2)	1.5826(13)	O(2)-P(1)-O(1)	99.98(7)
P(1)-O(3)	1.5881(14)	O(3)-P(1)-O(1)	105.99(8)
P(1)-O(1)	1.5903(14)	O(2)-P(1)-Co(1)	122.49(6)
F(1)-C(6)	1.372(2)	O(3)-P(1)-Co(1)	108.51(6)
F(2)-C(6)	1.376(3)	O(1)-P(1)-Co(1)	117.36(6)
F(3)-C(7)	1.370(2)	C(8)-O(1)-P(1)	125.10(13)
F(4)-C(7)	1.356(2)	C(11)-O(2)-P(1)	129.05(12)
O(1)-C(8)	1.455(2)	C(14)-O(3)-P(1)	123.82(14)
O(2)-C(11)	1.460(2)	C(2)-C(1)-C(5)	107.0(2)
O(3)-C(14)	1.464(3)	C(2)-C(1)-Co(1)	70.64(12)
C(1)-C(2)	1.393(3)	C(5)-C(1)-Co(1)	68.55(12)
C(1)-C(5)	1.415(3)	C(1)-C(2)-C(3)	108.6(2)
C(2)-C(3)	1.421(3)	C(1)-C(2)-Co(1)	70.36(13)
C(3)-C(4)	1.375(3)	C(3)-C(2)-Co(1)	71.05(12)
C(4)-C(5)	1.414(3)	C(4)-C(3)-C(2)	108.1(2)
C(6)-C(7)	1.412(3)	C(4)-C(3)-Co(1)	70.56(14)
C(8)-C(9)	1.494(4)	C(2)-C(3)-Co(1)	69.40(12)
C(8)-C(10)	1.499(4)	C(3)-C(4)-C(5)	108.2(2)
C(11)-C(13)	1.494(3)	C(3)-C(4)-Co(1)	71.31(13)
C(11)-C(12)	1.495(3)	C(5)-C(4)-Co(1)	68.04(13)
C(14)-C(16)	1.491(4)	C(1)-C(5)-C(4)	108.2(2)
C(14)-C(15)	1.497(4)	C(1)-C(5)-Co(1)	71.41(13)
		C(4)-C(5)-Co(1)	72.12(13)
C(6)-Co(1)-C(7)	43.92(11)	F(1)-C(6)-F(2)	105.16(18)
C(6)-Co(1)-C(5)	99.68(10)	F(1)-C(6)-C(7)	118.3(2)
C(7)-Co(1)-C(5)	99.45(9)	F(2)-C(6)-C(7)	118.0(2)
C(6)-Co(1)-C(1)	105.57(10)	F(1)-C(6)-Co(1)	120.62(17)
C(7)-Co(1)-C(1)	131.28(10)	F(2)-C(6)-Co(1)	123.21(15)
C(5)-Co(1)-C(1)	40.04(9)	C(7)-C(6)-Co(1)	68.61(13)
C(6)-Co(1)-C(2)	139.44(10)	F(4)-C(7)-F(3)	105.64(17)
C(7)-Co(1)-C(2)	164.92(9)	F(4)-C(7)-C(6)	118.9(2)
C(5)-Co(1)-C(2)	66.14(9)	F(3)-C(7)-C(6)	117.9(2)
C(1)-Co(1)-C(2)	39.00(9)	F(4)-C(7)-Co(1)	124.93(14)
C(6)-Co(1)-C(4)	127.95(10)	F(3)-C(7)-Co(1)	118.60(16)
C(7)-Co(1)-C(4)	100.89(10)	C(6)-C(7)-Co(1)	67.47(13)
C(5)-Co(1)-C(4)	39.83(9)	O(1)-C(8)-C(9)	109.2(2)
C(1)-Co(1)-C(4)	66.36(9)	O(1)-C(8)-C(10)	106.9(2)
C(2)-Co(1)-C(4)	65.40(9)	C(9)-C(8)-C(10)	112.5(3)
C(6)-Co(1)-C(3)	165.09(10)	O(2)-C(11)-C(13)	109.68(19)
C(7)-Co(1)-C(3)	131.87(10)	O(2)-C(11)-C(12)	106.83(19)
C(5)-Co(1)-C(3)	65.80(10)	C(13)-C(11)-C(12)	111.0(2)
C(1)-Co(1)-C(3)	65.99(9)	O(3)-C(14)-C(16)	106.3(2)
C(2)-Co(1)-C(3)	39.55(9)	O(3)-C(14)-C(15)	108.6(2)
C(4)-Co(1)-C(3)	38.13(9)	C(16)-C(14)-C(15)	112.2(3)

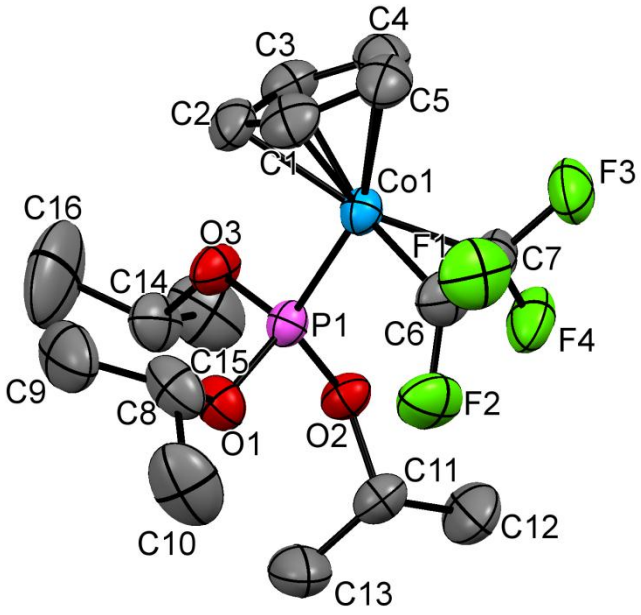

Figure S14. ORTEP drawing and labelling scheme of complex **3c** with thermal ellipsoids set to 50% probability. Hydrogen atoms omitted for clarity.

Table S5. Crystal Data and refinement for [CpCo(η^2-$CF_2CF(CF_3)$)(PPh_3)] (**5**)

Identification code	tb104	
Empirical formula	C26 H20 Co F6 P	
Formula weight	536.32	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.9397(4) Å	a= 90°.
	b = 10.3337(3) Å	b= 90.5376(17)°.
	c = 18.4688(6) Å	g = 90°.
Volume	2278.60(13) $Å^3$	
Z	4	
Density (calculated)	1.563 Mg/m^3	
Absorption coefficient	0.885 mm^{-1}	
F(000)	1088	
Crystal size	0.230 x 0.160 x 0.090 mm^3	
Theta range for data collection	1.706 to 30.493°.	
Index ranges	-16<=h<=16, -13<=k<=14, -26<=l<=26	
Reflections collected	50536	
Independent reflections	6769 [R(int) = 0.0372]	
Completeness to theta = 25.242°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6769 / 0 / 307	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1317	
R indices (all data)	R1 = 0.0784, wR2 = 0.1549	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.156 and -0.470 $e.Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for [CpCo(η^2-$CF_2CF(CF_3)$)(PPh_3)] (**5**)

Co(1)-C(24)	1.902(3)	C(25)-Co(1)-C(2)	103.81(11)
Co(1)-C(25)	1.943(2)	C(3)-Co(1)-C(2)	39.35(13)
Co(1)-C(3)	2.055(2)	C(4)-Co(1)-C(2)	66.07(12)
Co(1)-C(4)	2.076(3)	C(5)-Co(1)-C(2)	65.88(11)
Co(1)-C(5)	2.090(3)	C(24)-Co(1)-C(1)	161.88(10)
Co(1)-C(2)	2.112(2)	C(25)-Co(1)-C(1)	132.52(11)
Co(1)-C(1)	2.138(2)	C(3)-Co(1)-C(1)	65.39(11)
Co(1)-P(1)	2.2266(6)	C(4)-Co(1)-C(1)	65.51(11)
P(1)-C(6)	1.829(2)	C(5)-Co(1)-C(1)	39.20(11)
P(1)-C(12)	1.829(2)	C(2)-Co(1)-C(1)	38.55(11)
P(1)-C(18)	1.851(2)	C(24)-Co(1)-P(1)	98.47(7)
F(1)-C(24)	1.372(3)	C(25)-Co(1)-P(1)	97.96(7)
F(2)-C(24)	1.351(3)	C(3)-Co(1)-P(1)	156.57(10)
F(3)-C(25)	1.388(3)	C(4)-Co(1)-P(1)	118.58(10)
F(4)-C(26)	1.344(3)	C(5)-Co(1)-P(1)	90.50(8)
F(5)-C(26)	1.347(4)	C(2)-Co(1)-P(1)	135.43(8)
F(6)-C(26)	1.330(4)	C(1)-Co(1)-P(1)	99.64(7)
C(1)-C(2)	1.403(4)	C(6)-P(1)-C(12)	106.35(10)
C(1)-C(5)	1.419(4)	C(6)-P(1)-C(18)	99.65(10)
C(2)-C(3)	1.404(5)	C(12)-P(1)-C(18)	101.62(10)
C(3)-C(4)	1.406(5)	C(6)-P(1)-Co(1)	113.90(8)
C(4)-C(5)	1.405(5)	C(12)-P(1)-Co(1)	108.49(7)
C(6)-C(7)	1.388(3)	C(18)-P(1)-Co(1)	124.96(7)
C(6)-C(11)	1.389(3)	C(2)-C(1)-C(5)	108.1(3)
C(7)-C(8)	1.388(4)	C(2)-C(1)-Co(1)	69.72(14)
C(8)-C(9)	1.373(4)	C(5)-C(1)-Co(1)	68.58(14)
C(9)-C(10)	1.378(4)	C(1)-C(2)-C(3)	107.7(3)
C(10)-C(11)	1.391(4)	C(1)-C(2)-Co(1)	71.73(14)
C(12)-C(13)	1.392(3)	C(3)-C(2)-Co(1)	68.14(14)
C(12)-C(17)	1.397(3)	C(4)-C(3)-C(2)	108.7(3)
C(13)-C(14)	1.395(4)	C(4)-C(3)-Co(1)	70.91(15)
C(14)-C(15)	1.373(5)	C(2)-C(3)-Co(1)	72.51(14)
C(15)-C(16)	1.380(5)	C(5)-C(4)-C(3)	107.7(3)
C(16)-C(17)	1.391(4)	C(5)-C(4)-Co(1)	70.83(15)
C(18)-C(19)	1.390(3)	C(3)-C(4)-Co(1)	69.30(16)
C(18)-C(23)	1.396(3)	C(4)-C(5)-C(1)	107.7(3)
C(19)-C(20)	1.389(3)	C(4)-C(5)-Co(1)	69.74(15)
C(20)-C(21)	1.367(4)	C(1)-C(5)-Co(1)	72.22(15)
C(21)-C(22)	1.388(4)	C(7)-C(6)-C(11)	118.8(2)
C(22)-C(23)	1.386(3)	C(7)-C(6)-P(1)	120.10(18)
C(24)-C(25)	1.444(4)	C(11)-C(6)-P(1)	121.01(18)
C(25)-C(26)	1.503(4)	C(6)-C(7)-C(8)	120.4(2)
		C(9)-C(8)-C(7)	120.1(2)
C(24)-Co(1)-C(25)	44.09(11)	C(10)-C(9)-C(8)	120.2(2)
C(24)-Co(1)-C(3)	97.29(11)	C(9)-C(10)-C(11)	119.8(2)
C(25)-Co(1)-C(3)	105.43(11)	C(10)-C(11)-C(6)	120.5(2)
C(24)-Co(1)-C(4)	105.12(12)	C(13)-C(12)-C(17)	119.2(2)
C(25)-Co(1)-C(4)	137.25(12)	C(13)-C(12)-P(1)	124.02(18)
C(3)-Co(1)-C(4)	39.79(13)	C(17)-C(12)-P(1)	116.81(17)
C(24)-Co(1)-C(5)	140.50(12)	C(12)-C(13)-C(14)	119.7(2)
C(25)-Co(1)-C(5)	169.66(10)	C(15)-C(14)-C(13)	120.5(3)
C(3)-Co(1)-C(5)	66.42(12)	C(16)-C(15)-C(14)	120.4(2)
C(4)-Co(1)-C(5)	39.43(13)	C(15)-C(16)-C(17)	119.7(3)
C(24)-Co(1)-C(2)	124.12(11)	C(16)-C(17)-C(12)	120.5(2)

C(19)-C(18)-C(23)	118.4(2)	C(25)-C(24)-Co(1)	69.43(14)
C(19)-C(18)-P(1)	122.28(16)	F(3)-C(25)-C(24)	116.2(2)
C(23)-C(18)-P(1)	119.31(16)	F(3)-C(25)-C(26)	104.2(2)
C(18)-C(19)-C(20)	120.7(2)	C(24)-C(25)-C(26)	123.5(2)
C(21)-C(20)-C(19)	120.6(2)	F(3)-C(25)-Co(1)	119.55(15)
C(20)-C(21)-C(22)	119.5(2)	C(24)-C(25)-Co(1)	66.48(13)
C(21)-C(22)-C(23)	120.4(2)	C(26)-C(25)-Co(1)	124.16(19)
C(22)-C(23)-C(18)	120.4(2)	F(6)-C(26)-F(4)	107.7(2)
F(2)-C(24)-F(1)	105.6(2)	F(6)-C(26)-F(5)	106.6(3)
F(2)-C(24)-C(25)	118.2(2)	F(4)-C(26)-F(5)	105.4(2)
F(1)-C(24)-C(25)	117.8(2)	F(6)-C(26)-C(25)	112.5(3)
F(2)-C(24)-Co(1)	122.79(16)	F(4)-C(26)-C(25)	113.1(2)
F(1)-C(24)-Co(1)	120.11(16)	F(5)-C(26)-C(25)	111.0(2)

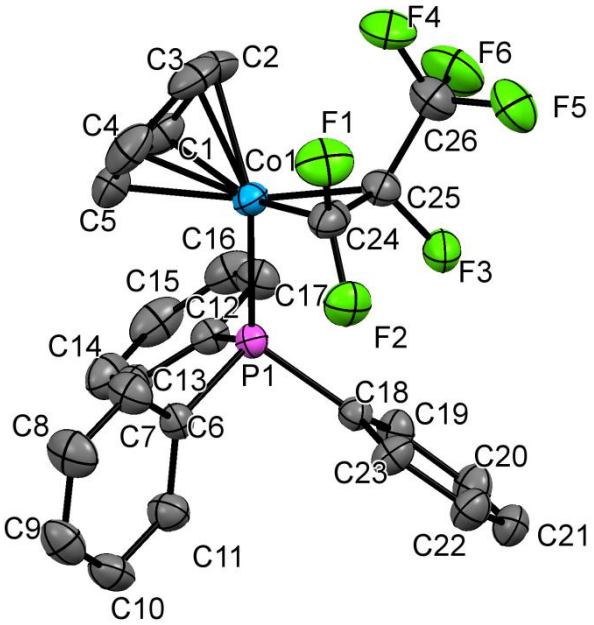

Figure S15. ORTEP drawing and labelling scheme of complex **5** with thermal ellipsoids set to 50% probability. Hydrogen atoms omitted for clarity.