

Supporting Information

Difluorocarbene transfer from a cobalt complex to an electron-deficient alkene

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1. Experimental

General procedures and Chemicals used

All manipulations were performed under an N₂ atmosphere by standard Schlenk techniques or in a glovebox. Methanol and acetonitrile were distilled under nitrogen from CaH₂. THF, toluene and pentane were distilled under nitrogen from Na wire. The *n*-butyl acrylate substrate was passed through a plug of basic alumina, deoxygenated by bubbling dinitrogen for at least an hour and stored at 4 °C in a Schlenk flask. [Co(TPP)] was purchased from STREM and used without further purification. [Co(TPPF₂₀)], ¹ [Co(TPP)Cl] ² and Co(salophen)³ (N,N'-bis(3,5-di-*tert*-butylsalicylidine)-1,2-benzenediamine(-2H)cobalt(II)) and PPh₃BrCF₂ ⁴ were synthesised according to published procedures. [Co(acac)₂], TMSCF₃, TBAT (Tetrabutylammonium difluorotriphenylsilicate), LiI, SCDA (Sodium chlorodifluoroacetate), MDFA (Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate), KI, TMSCl, K₂CO₃ Tetrabutyl ammonium bromide, CoCp*₂ Bis(pentamethylcyclopentadienyl)cobalt(II) and TMSCF₂Br was purchased from commercial sources and used without further purification. NaI was dried at 100 °C in a vacuum oven overnight prior to use. Fluorobenzene was purchased from Sigma-Aldrich, degassed prior to use and stored with molecular sieves.

All NMR spectra were recorded at room temperature.

¹H NMR: Bruker Avance 400 (400 MHz) or Mercury 300 (300 MHz), referenced internally to residual solvent resonance of CDCl₃ (δ = 7.26 ppm).

¹³C {¹H} NMR: Bruker Avance 400 (101 MHz), or Mercury 300 (75 MHz), referenced internally to residual solvent resonance of CDCl₃ (δ = 77.2 ppm) or THF-d₈ (67.21, 25.31).

Abbreviations used are: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

High Resolution Mass spectra were measured on an AccuTOF LC, JMS-T100LP Mass spectrometer (JEOL, Japan). FD/FI probe (FD/FI) is equipped with FD Emitter, Carbotec or Linden (Germany), FD 10 μm. Current rate 51.2 mA/min over 1.2 min FI Emitter, Carbotec or Linden (Germany), FI 10 μm. Flashing current 40 mA on every spectra of 30 ms. Typical measurement conditions are: Counter electrode -10kV, Ion source 37V.

2. Synthesis of compounds

2.1 Synthesis of [Co^{III}(TPP)(CF₃)]

113 mg of [Co(TPP)(Cl)] (0.16 mmol) and 1.5 mg of CsF (0.01 mmol) were dissolved in 3 mL of THF in a flame-dried Schlenk tube at room temperature. Subsequently 48 μL of TMSCF₃ (0.32 mmol) was added dropwise with a microsyringe. Subsequently, the reaction mixture was allowed to stir overnight. Evaporation of solvent led to formation of a red solid which was washed successively with water (5 mL) and pentane (5 mL) and dried in vacuo. Yield: 94 mg (80 %).

¹H NMR (300 MHz, Chloroform-*d*) δ 8.96 (s, 8H, belonging to pyrrolic protons from the porphyrin ring), 8.13 (s, br, 8H, *o*-protons from the phenyl rings in the porphyrin ring), 7.75 (m, br, 12H, *m*- and *p*- protons of the phenyl rings). **¹⁹F NMR** (CDCl₃) -19.08 ppm. **¹³C NMR** (75 MHz, THF-*d*₈) δ 142.64, 140.30, 131.90, 130.43, 125.68, 124.67, 118.38. (The CF₃ carbon was not detectible).

UV-vis spectrum in MeOH, λ_{max}/nm: 411, 540.

HRMS (FD): calculated for $C_{45}H_{28}Co_1F_3N_4$ (m/z) = 740.1598 (Da/e), found (m/z) 740.1624 (Da/e).

Elemental analysis- No reliable CHNF analysis could be obtained even after multiple trials due to incomplete combustion (which is more commonly observed for F-containing compounds).

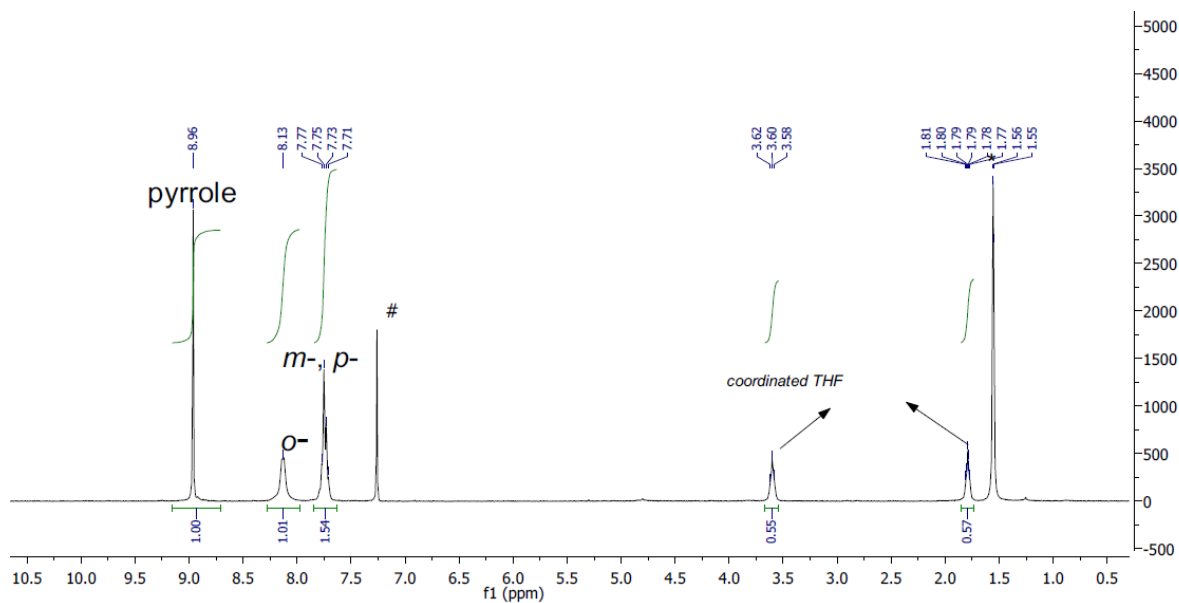


Figure S1. 1H NMR spectrum of $[Co^{III}(TPP)(CF_3)]$ in $CDCl_3$. # = solvent residual signal.

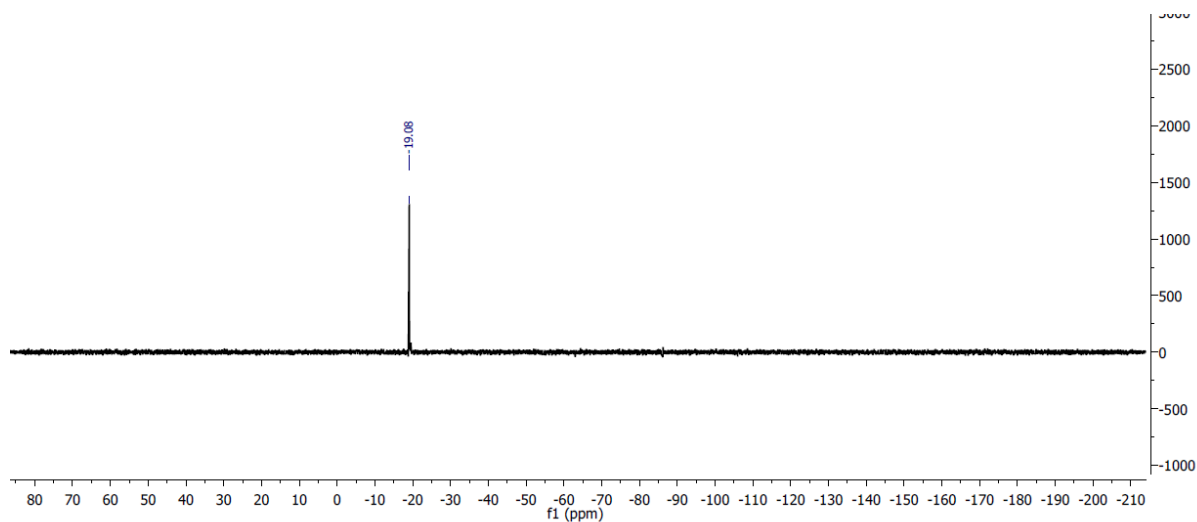


Figure S2. ^{19}F NMR spectrum of $[Co^{III}(TPP)(CF_3)]$ in $CDCl_3$

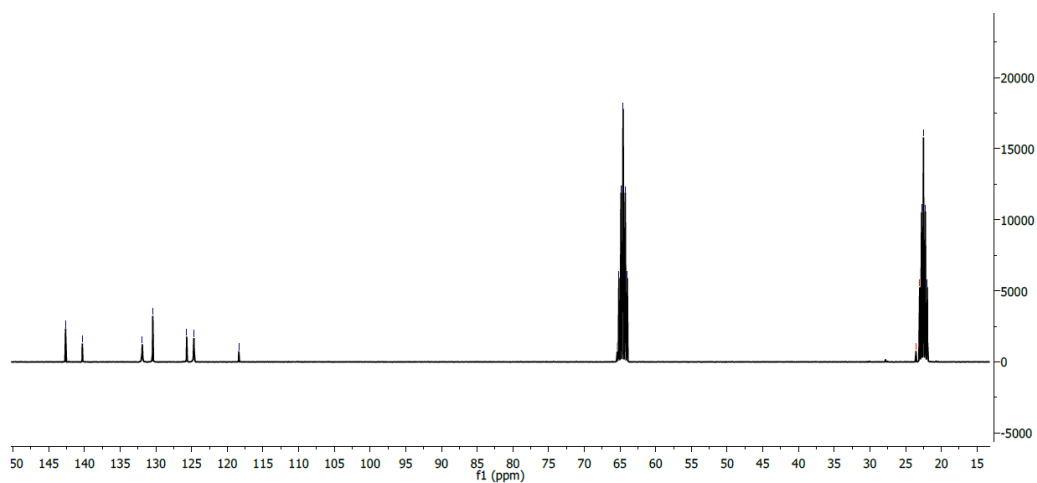


Figure S3. ^{13}C NMR spectrum of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ in THF-d_8

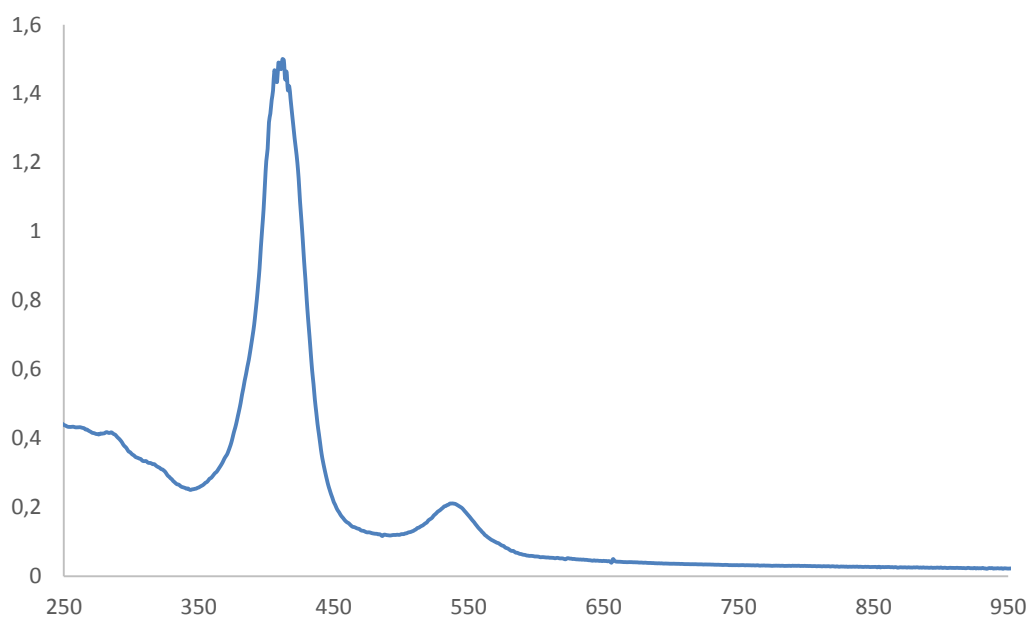


Figure S4. UV-Vis spectrum of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ in MeOH, $\lambda_{\text{max}}/\text{nm}$: 411, 540

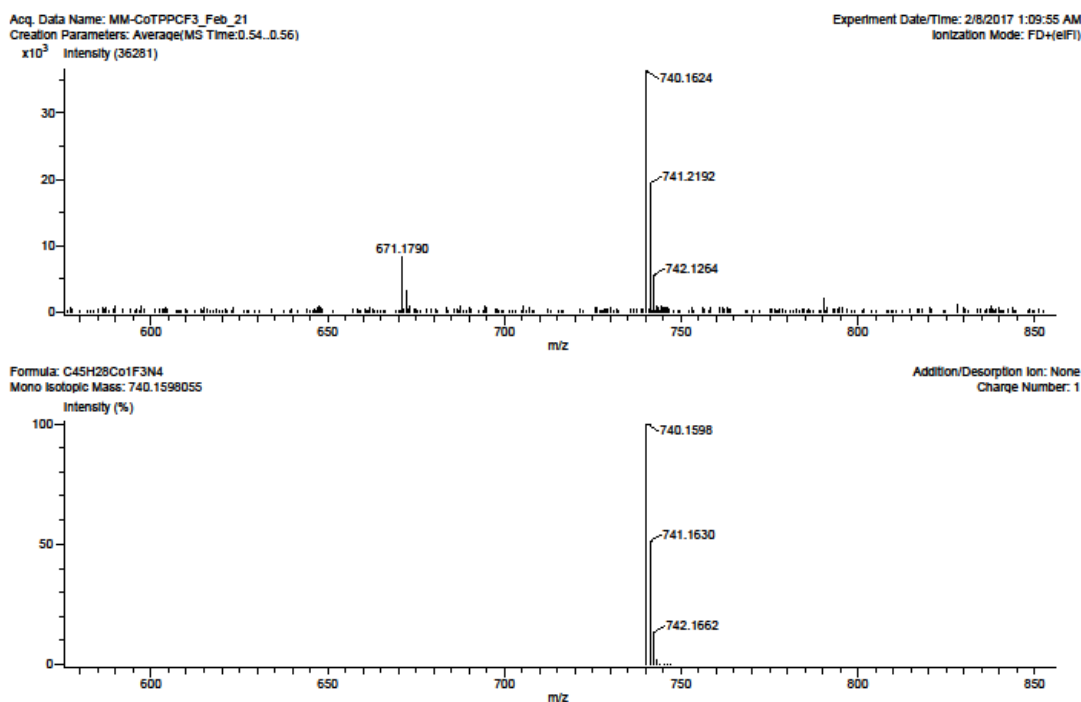


Figure S5. (top) HRMS (FD) of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ and (bottom) simulated spectra of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$. The experimental spectra also shows a peak at (m/z) 671.1790 (Da/e) which belongs to $[\text{Co}(\text{TPP})]$.

2.2 Gem-difluorocyclopropanation of *n*-butyl acrylate with $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$

Inside a glove-box, 37 mg (0.05 mmol) of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ and 8 μL (0.05 mmol) of *n*-butyl acrylate were dissolved in a Schlenk tube in 2 mL THF to give a dark red solution. Then, 16.5 mg (0.05 mmol) of CoCp_2^* and 9.4 μL of fluorobenzene (0.1 mmol) were added and the colour of the solution changed to dark green. The Schlenk tube was then taken out of the glovebox and heated at 65° C for 6 hours which resulted in formation of a dark brown solution. An aliquot of the reaction mixture was dissolved in CDCl_3 , filtered through a Teflon syringe filter and conversion to the product was determined using ^{19}F NMR. The corresponding ^{19}F NMR spectrum is shown in **Figure S6**.

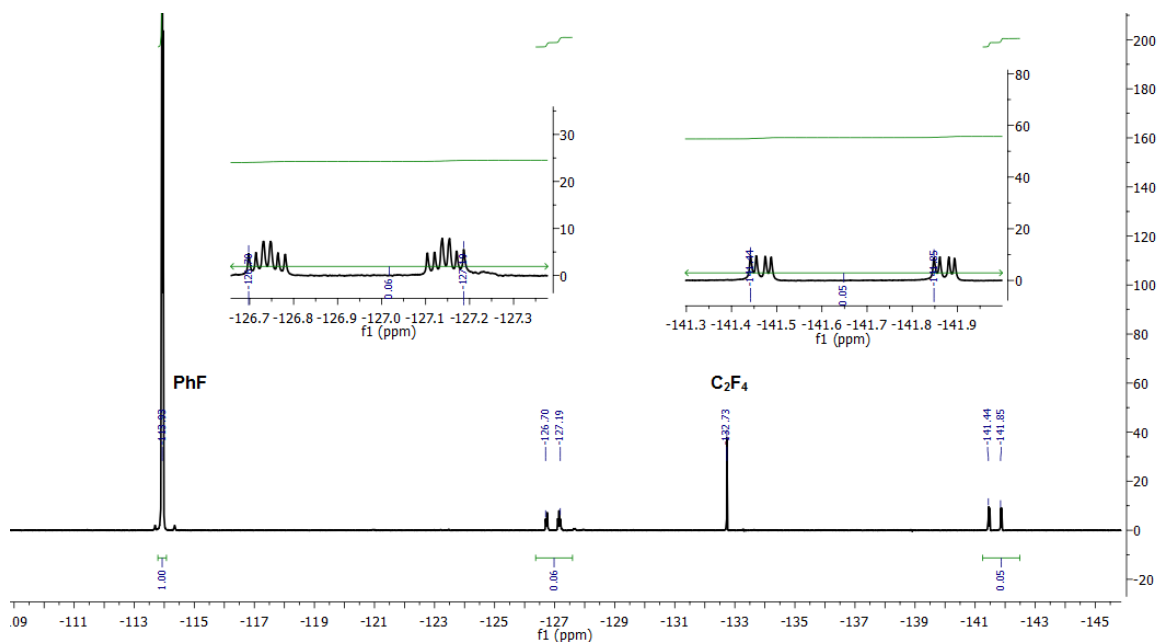


Figure S6. ^{19}F NMR spectrum of a reaction mixture of *gem*-difluorocyclopropanation of *n*-butyl acrylate with $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ and CoCp^*_2 . The inset shows the zoom for the signals that belong to the products.

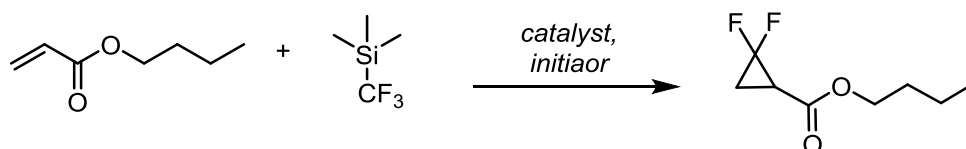
2.3 General procedure for catalytic *gem*-difluorocyclopropanation of *n*-butyl acrylate with TMSCF_3 and optimisation studies

0.025 mmol of the catalyst and 15 mg (0.1 mmol) of NaI was added to a flame dried Schlenk tube equipped with a stirring bar. Then 4 mL of THF was added followed by 72 μL (0.5 mmol) of *n*-butyl acrylate and 94 μL (1 mmol) of fluorobenzene internal standard. Finally 300 μL (~ 2 mmol) of TMSCF_3 was added. The dark red reaction mixture was then heated to a given temperature. At the end of the reaction (18h) an aliquot of the resulting dark brown reaction mixture was dissolved in CDCl_3 and the yield was determined by integration of the ^{19}F NMR signals of butyl 2,2-difluorocyclopropane-1-carboxylate and fluorobenzene. Analytical data matched those reported in literature.⁵

Optimisation studies

Various reaction conditions were evaluated for optimizing the yield of the *gem*-difluorocyclopropanation reaction of *n*-butyl acrylate. These are listed in **Table S1**. The variable that was altered is indicated in blue.

Table S1. Screening of reaction conditions for CF₂ transfer from Me₃SiCF₃ to *n*-butyl acrylate.



Entry	Catalyst	Solvent	TMSCF ₃ ^a (equiv)	Initiator ^a (equiv)	Temperature (°C)	Yield ^b
1	[Co(TPP)]	THF	4	NaI 0.2	50	12%
2	[Co(TPPF ₂₀)]	THF	4	NaI 0.2	50	24%
3	[Co(acac) ₂]	THF	4	NaI 0.2	50	0%
4	[Co(salophen)]	THF	4	NaI 0.2	50	0%
5	[Zn(TPP)]	THF	4	NaI 0.2	50	trace
6	none	THF	4	NaI 0.2	50	0%
7	[Co(TPPF ₂₀)]	DMF	4	NaI 0.2	50	0%
8	[Co(TPPF ₂₀)]	Toluene	4	NaI 0.2	60	0%
9	[Co(TPPF ₂₀)]	Toluene:THF (1:1)	4	NaI 0.2	50	0%
10	[Co(TPPF ₂₀)]	CH ₃ CN	4	NaI 0.2	50	0%
11	[Co(TPPF ₂₀)]	CH ₃ CN	4	NaI 0.2	70	20%
12	[Co(TPPF ₂₀)]	THF	4	LiI 0.2	50	0%
13	[Co(TPPF ₂₀)]	THF	4	TBAT 0.2	50	0%
14	[Co(TPPF ₂₀)]	THF	4	CsF 0.2	50	Mixture of many products
15	[Co(TPPF ₂₀)]	THF	4	NaBr 0.2	50	0% No activation of TMSCF ₃
16	[Co(TPPF ₂₀)] ^c	CH ₃ CN	8	NaI 0.2	70	40%
17	none ^d	CH ₃ CN	8	NaI 0.2	70	6%

Reactions performed with 0.5 mmol of alkene in 4 mL of solvent and 5 mol% catalyst, 18 h. ^a Equivalents w.r.t alkene. ^b Yields were determined with ¹⁹F NMR using fluorobenzene as internal standard. ^c 4 additional equivalents of TMSCF₃ were added after 4 hours of the reaction. ^d Control reaction for entry 16.

NaI is the initiator of choice for the decomposition of TMSCF_3 in THF at elevated temperatures.⁶ We believe that this is due to the optimal solubility of NaI in THF. Note that in entries 12-15 in SI Table 1 we report attempts to use other initiators that have different solubility in THF. These either gave no cyclopropane product (LiI, TBAT, NaBr) or gave a mixture of many products (CsF).

Furthermore, different difluorocarbene precursors were also tested in this transformation. These are listed in **Table S2**.

Table S2. Different CF_2 precursors tested for CF_2 transfer from TMSCF_3 to *n*-butyl acrylate catalysed by $[\text{Co}^{\text{II}}(\text{Por})]$ catalysts.

catalyst	CF_2 source	Initiator or another reagent	Temperature	Yield
$[\text{Co}(\text{TPP})]$ $[\text{Co}(\text{TPPF}_{20})]$	and $\text{PPh}_3\text{CF}_2\text{Br}$	none	80 °C	0%
$[\text{Co}(\text{TPP})]$ $[\text{Co}(\text{TPPF}_{20})]$	and MDFA	KI, TMSCl	60 °C	0%
$[\text{Co}(\text{TPP})]$ $[\text{Co}(\text{TPPF}_{20})]$	and SCDA	K_2CO_3 in DMF	60 °C	0%
$[\text{Co}(\text{TPP})]$ $[\text{Co}(\text{TPPF}_{20})]$	and TMSCF_2Br	Tetrabutyl ammonium bromide	60 °C	0% *

* TMSCF_2Br is not activated at this temperature.

3. CV studies

0.01 mmol (7.4 mg) of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ and 50 mg of tetrabutylammonium hexafluorophosphate (NBu_4PF_6) were dissolved in 4 mL of THF. The solution was placed in a gastight single-compartment three-electrode cell equipped with a glassy carbon working electrode, coiled platinum wire auxiliary, and silver wire pseudoreference electrodes. All redox potentials are reported against the ferrocene/ferrocenium (Fc/Fc^+) redox couple. Decamethylferrocene was used as an internal standard ($E = 0.427 \text{ V vs. Fc}/\text{Fc}^+$).⁷

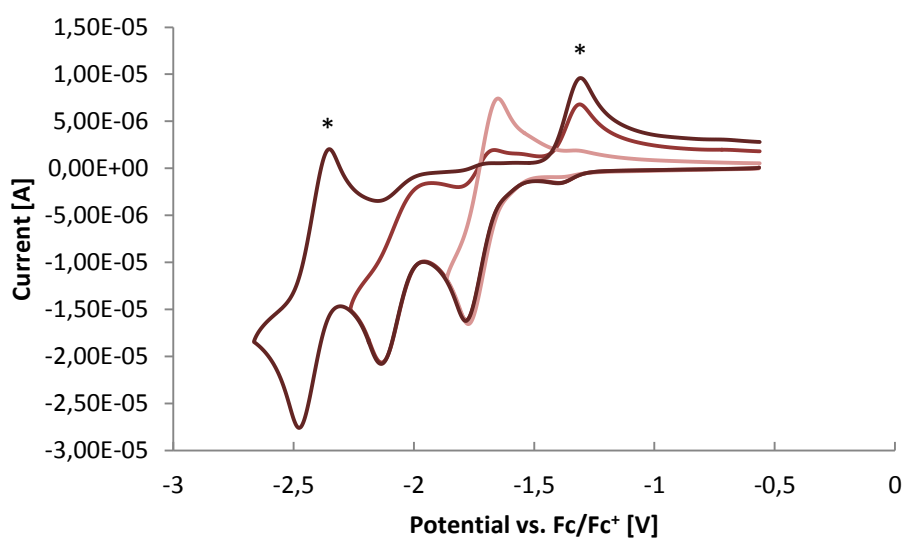


Figure S7. Subsequent electrochemical waves during reduction $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$. The waves of the $[\text{Co}(\text{TPP})]$ product formed as a result of the second reduction event are marked with an asterisk (*).

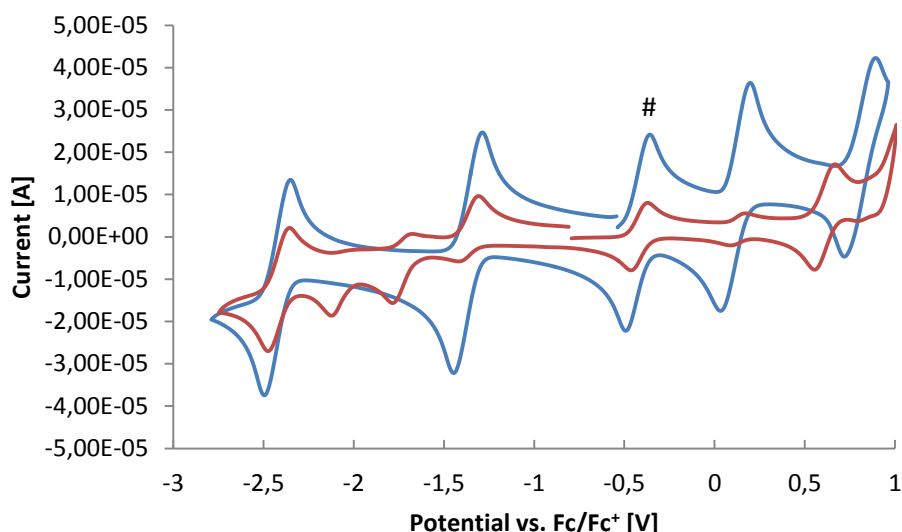


Figure S8. Overlay of cyclic voltammograms of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ (red) and $[\text{Co}(\text{TPP})]$ (blue) in the presence of decamethylferrocene (marked with a hash #).

4. EPR studies

In order to trap any reactive intermediates formed during the reaction of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ with CoCp^*_2 we attempted the following reaction:

Inside a glove box, 1.7 mg (0.005 mmol) of CoCp^*_2 was dissolved in 2 mL of 2-MeTHF. This solution was added to 3.7 mg (0.005 mmol) of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ in a Schlenk tube. The Schlenk tube was sealed and taken out of the glove-box. To this, 7 μL of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was added at -78°C under an N_2 atmosphere and allowed to stir for 10 minutes. The Schlenk tube was then reintroduced to the glove-box and 0.2 mL aliquot was transferred to an EPR tube. This sample was then measured at 20K. The corresponding spectrum is shown in Figure S9.

Consequently we also measured the EPR spectrum of the parent $[\text{Co}^{\text{II}}(\text{TPP})]$ complex in 2-MeTHF. This gave the same spectrum as observed previously on adding $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to the reduced $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ complex. This means that no intermediates were observed under these reaction conditions and the reduced complex underwent follow-up reactions to give the $[\text{Co}^{\text{II}}(\text{TPP})]$. Adding acrylate to this reaction mixture did not lead to a different EPR spectrum.

An EPR spectrum was also measured directly after adding the CoCp^*_2 (1.7 mg, 0.005 mmol) reductant to the $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ (3.7 mg, 0.005 mmol) complex in 2 mL 2-MeTHF. This time a distinctly different spectrum was obtained pointing to the formation of the anionic, paramagnetic $[\text{Co}^{\text{II}}(\text{TPP})(\text{CF}_3)]^-$ complex (**Error! Reference source not found.**). Addition of acrylate to this mixture led to rapid loss of intensity of the signal, and apparently any other intermediates involved in the difluorocyclopropanation reaction of the n-butyl acrylate are too short-lived to detect with EPR spectroscopy.

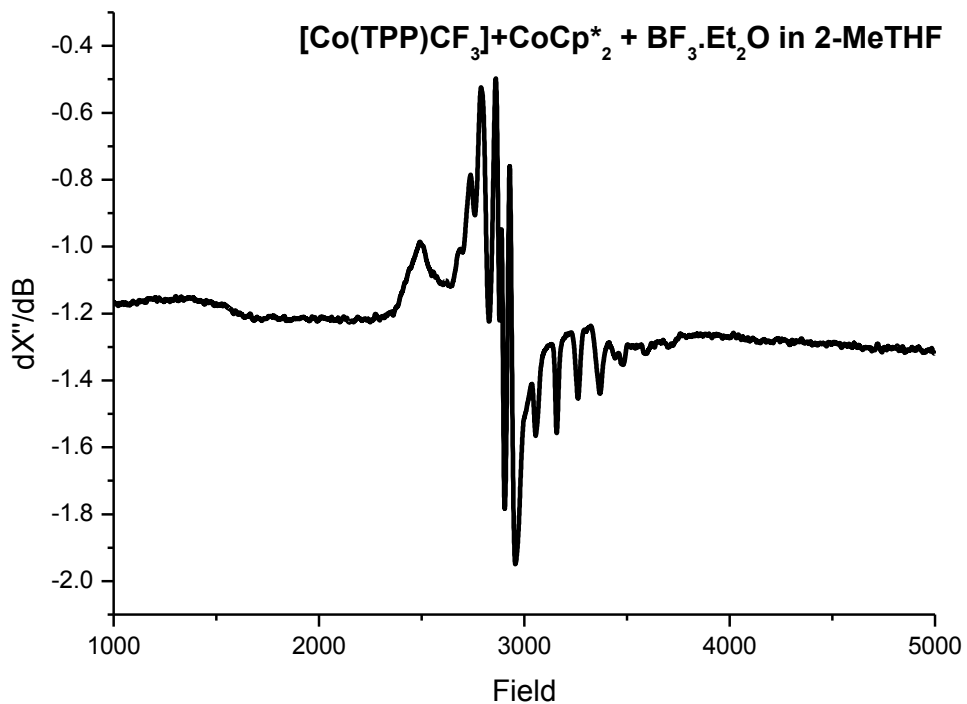


Figure S9. EPR spectrum (20 K) of a mixture of [Co^{III}(TPP)(CF₃)], CoCp*₂ and BF₃·Et₂O in 2-MeTHF

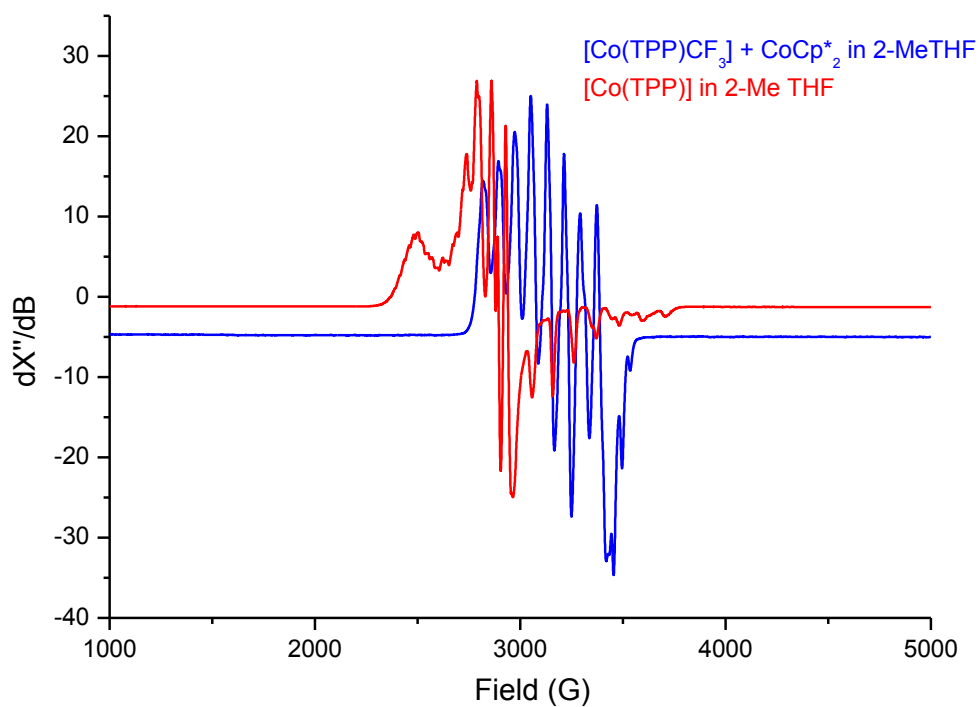


Figure S9. (red) EPR spectrum of [Co^{II}(TPP)] complex in 2-MeTHF (20K). (blue) EPR spectrum of reduced [Co^{III}(TPP)CF₃] complex under the same conditions.

5. DFT studies

Computational Methods. Geometry optimizations were carried out using the TURBOMOLE 6.5 program package⁸ coupled with the PQS Baker optimizer⁹ via the BOpt package¹⁰ using the BP86 functional,¹¹ def2-TZVP basis set¹² and the resolution-of-identity method.¹³ All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by numerical calculation of the Hessian matrix. Zero point energy and gas phase thermal corrections (enthalpy and entropy, 298K, 1 bar) were calculated. Estimated condensed phase (1 L mol⁻¹) free energies were obtained from these data by neglecting the enthalpy RT term and subsequent correction of the condensed phase (CP) reference volume [$S_{CP} = S_{GP} + R \ln(1/24.5)$] for all steps involving a change in the number of species.

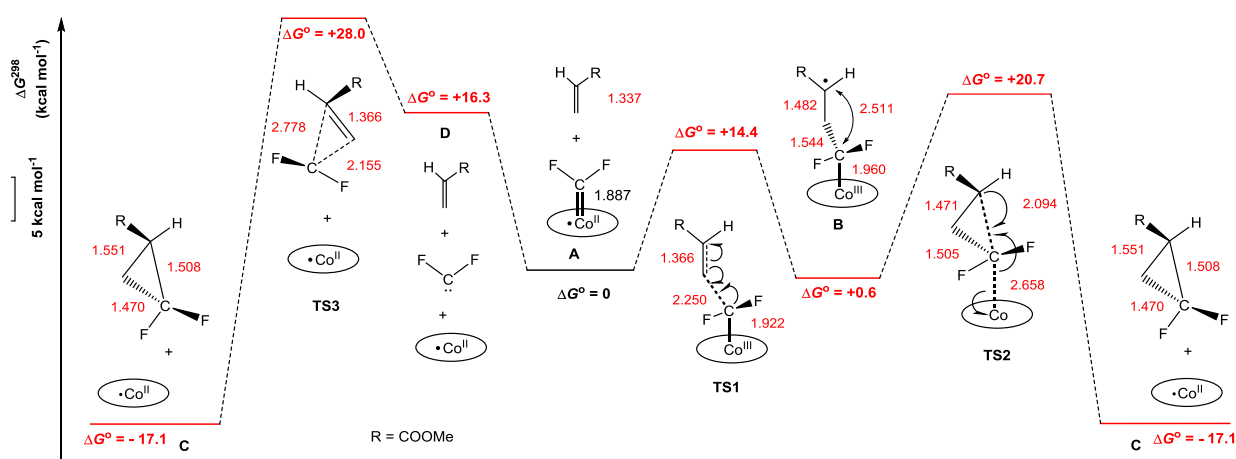


Figure S10. Two possible pathways for cyclopropanation of methyl acrylate mediated by $[\text{Co}(\text{por})(\text{CF}_2)]$. Free energies in kcal mol⁻¹. Selected bond distances (Å) are presented as well.

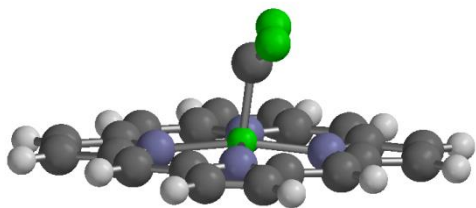
Table S3. Absolute calculated SCF energies (E_{SCF}), zero point corrections (ZPE), thermal corrections (ZPE+RT+TRV), entropy contribution (TS), zero point energies (E_{ZPE}), enthalpies (H) and free energies (G^{298}).

	E_{SCF} /hartree	ZPE /hartree	ZPE+RT+TRV /hartree	TS /hartree	E_{ZPE} /hartree	H /hartree	G^{298} /hartree
CF ₂	-237.8190788	0.00651	0.01048	0.0274	-237.813	-237.809	-237.836
Methylacrylate (MA)	-306.6104266	0.0921	0.09983	0.03833	-306.518	-306.511	-306.549
TS3	-544.4259534	0.10064	0.1116	0.04788	-544.325	-544.314	-544.362
Cyclopropane	-544.5041566	0.10485	0.11487	0.04479	-544.399	-544.389	-544.434
Co(por)	-2371.924224	0.26691	0.28559	0.06188	-2371.66	-2371.64	-2371.7
Co(por)CF ₂	-2609.78417	0.27591	0.29839	0.07267	-2609.51	-2609.49	-2609.56
TS1	-2916.388542	0.36903	0.39901	0.09089	-2916.02	-2915.99	-2916.08
B	-2916.41412	0.37122	0.40082	0.08919	-2916.04	-2916.01	-2916.1
TS2	-2916.379734	0.3703	0.40021	0.09097	-2916.01	-2915.98	-2916.07

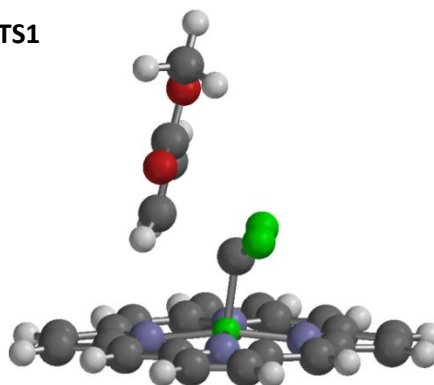
Table S4. Relative calculated SCF energies (ΔE_{SCF}), zero point energies (ΔE_{ZPE}), enthalpies (ΔH) entropy contributions (TS), and free energies in gas (ΔG^{298}) and solution phase ($\Delta G_{\text{sol}}^{298}$).

	ΔE_{SCF}	ΔE_{ZPE}	ΔH	ΔS	ΔG^{298}	$\Delta G_{\text{sol}}^{298}$
[Co(por)CF ₂]+ MA	0	0	0	0	0	0
[Co(por) + CF ₂]+ MA	25.64459	24.08209	24.18877	-10.4212	13.76757	16.25357
TS3 + [Co(por)]	27.87356	27.5849	27.22722	-0.04788	28.01205	28.01205
[Co(por)] + Methylacrylate cyclopropane	-21.1997	-18.8466	-19.7941	2.71958	-17.0745	-17.0745
TS1	3.799287	4.439347	4.29502	12.62265	16.91767	14.43167
B	-12.251	-10.2367	-10.6195	13.68802	3.068524	0.582524
TS2	9.326865	10.76386	10.57561	12.57323	23.14884	20.66284

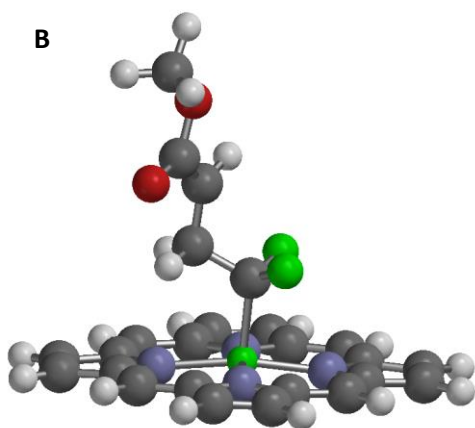
[Co(por)(CF₂)]



TS1



B



TS2

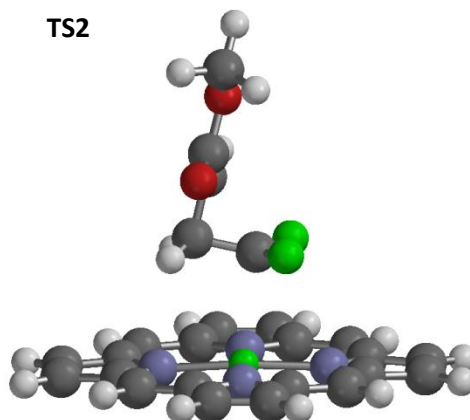


Figure S11. Calculated structure of [Co(por)CF₂], and of the stationary points along the stepwise addition of methyl acrylate to Co(Por)CF₂: TS1; intermediate B; and TS2

5. Single crystal X-ray diffraction studies

Despite numerous attempts of crystallization of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ using various solvent combinations, the obtained crystals were always diffracted very poorly or were of bad quality. The best data could be obtained from the material obtained by slow evaporation of a chloroform solution of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ in dark. This resulted in formation of clustered crystals of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ chloroform solvate which despite twinning and overall poor data quality, have shown the expected connectivity between atoms.

Apparent crystal data: $\text{C}_{45}\text{H}_{28}\text{CoF}_3\text{N}_4 \cdot \text{CHCl}_3$ Fw = 860.01, red rough fragment, 0.32 x 0.21 x 0.20 mm, monoclinic, P 21/n (no. 14), $a = 13.4359(9)$, $b = 18.2392(13)$, $c = 15.6674(11)$ Å, $\beta = 90.312(4)$, $V = 3839.4(5)$ Å³, $Z = 4$, R1/wR2: 0.1221/0.3091. $S = 2.081$.

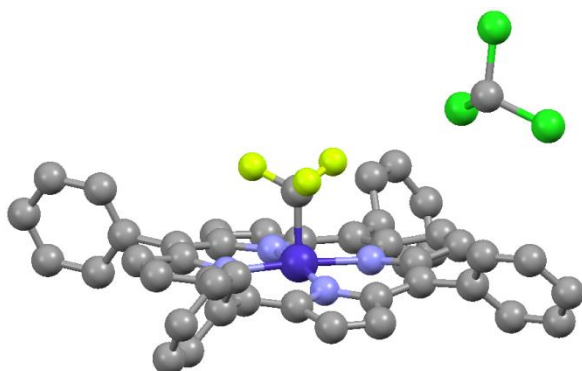


Figure S12. Connectivity of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ as determined by single crystal X-ray diffraction. The CHCl_3 solvate molecule is shown.

X-ray Single Crystal Determination. Data was collected on a Bruker D8 Quest Eco diffractometer, equipped with a TRIUMPH monochromator and a CMOS PHOTON 50 detector, using Mo-K α radiation ($\lambda = 0.71073$ Å). Data collection was conducted at 150(2) K. The intensity data were integrated with the Bruker APEX2 software.¹⁴ Absorption correction and scaling was performed with SADABS.¹⁵ The structures were solved with SHELXS-97.¹⁶ Least-squares refinement was performed with SHELXL-2013¹⁶ against F^2 of all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located at calculated positions using a riding model.

6. References

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