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

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We report the synthesis of the trifluoromethyl cobalt(III)tetraphenylporphyrinato complex [Co(TPP)CF₃], which loses fluoride upon one-electron reduction and transfers a difluorocarbene moiety to *n*-butyl acrylate to produce the corresponding *gem*-difluorocyclopropane. Catalytic CF₂ transfer from Me₃SiCF₃ to *n*-butyl acrylate becomes possible when directly using the divalent cobalt(II) porphyrin catalysts in the presence of NaI.

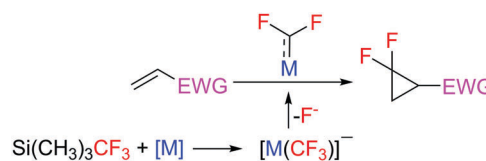
Metal-carbene complexes are key intermediates in many organic reactions *e.g.* olefin metathesis or cyclopropanation reactions.¹ Their rich chemistry is well understood and many recently developed catalytic transformations are based on the intriguing and diverse reactivity of these species. However, the chemistry of metallo-difluorocarbenes is thus far rather underdeveloped.² Only a handful of well-defined metal difluorocarbene complexes are reported that can mediate stoichiometric formation of new carbon-carbon bonds. Recently, the group of Baker disclosed some electron rich cobalt(I)³ and nickel(0)⁴ difluorocarbene complexes containing a nucleophilic M=CF₂ moiety. These species undergo cycloaddition reactions with tetrafluoroethylene (C₂F₄) or difluorocarbene producing perfluorinated metallacyclobutanes^{3b,4} and metallacyclopropanes,^{3c} respectively. A related electrophilic cobalt(III) complex mediated the insertion of difluorocarbene into a cobalt-perfluoroalkyl bond.⁵ However, the stability of the thus formed perfluoroalkyl metal complexes prohibited further reactivity.

Recently, the first example of catalytic olefin cross-metathesis of tetrafluoroethylene or other *gem*-difluoroolefins with enol ethers was reported.⁶ Despite the highly inert character of the Ru=CF₂ intermediate, turnover numbers of up to 13.4 could be reached. Palladium-difluorocarbene species were recently proposed as intermediates in palladium-catalysed difluoromethylation of arylboronic acids.^{7,8} Ichikawa and co-workers reported that the

yields of difluorocyclopropanation of electron rich silyl dienol ethers with free difluorocarbene were slightly improved in the presence of a nickel complex with a CNC-type pincer ligand.⁹ The same group reported catalytic cycloaddition of copper-difluorocarbene to silyl dienol ethers to form difluorocyclopentenes.¹⁰ However, to our best knowledge, no examples of catalytic CF₂ transfer to electron deficient alkenes have been reported, likely due to the electrophilic nature of the difluorocarbene moiety.

Traditional routes to *gem*-difluorocyclopropanes involve reacting the *in situ* generated free CF₂ carbene with an electron rich olefin.^{11,12} The scope of difluorocyclopropanation of electron deficient alkenes like acrylates is very limited, and rather harsh reaction conditions are required.¹³

We envisioned that by employing a transition metal centre that can render the difluorocarbene moiety more nucleophilic, the transfer of CF₂ to an electron deficient olefin would be facilitated (Scheme 1). Reaching this goal could enable catalytic *gem*-difluorocyclopropanation of electron deficient double bonds. Cobalt(II) porphyrin complexes are efficient catalysts for cyclopropanation of electron deficient alkenes using (stabilized) diazo esters as carbene precursors.¹⁴ This contrasts with the Fischer-type reactivity of the majority of cyclopropanation catalysts, which have a general preference for electron rich alkenes. The observed ‘umpolung’ of the reactivity of the cobalt-carbenoid species as compared to other metallo-carbenes is caused by the transfer a discrete unpaired electron to the coordinated (Fischer-type) carbene ligand. This renders the carbene moiety more nucleophilic and weakens the metal-carbon bond. We hypothesized



Scheme 1 Envisioned metal mediated difluorocarbene transfer to an electron deficient olefin.

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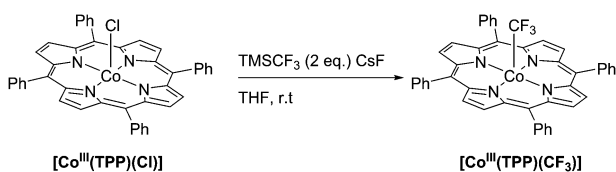
that this feature might also promote the formation of difluorocyclopropanes from related cobalt difluorocarbene intermediates. In this perspective the use of trimethyl(trifluoromethyl)silane (Me_3SiCF_3) as the difluorocarbene source is attractive, as it can operate at mild temperatures.¹²

To evaluate the feasibility of difluorocarbene transfer from cobalt to an olefin we first decided to investigate whether a difluorocarbene cobalt(II) complex can be formed by one-electron reduction of the novel trifluoromethyl cobalt(III) complex $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ (TPP = *meso*-tetraphenyl-porphyrinato). Formation of a cobalt difluorocarbene complex by reduction and subsequent dissociation of fluoride from a cobalt trifluoromethyl complex has been reported by Baker and co-workers.^{3a} Thus, we anticipated that the release of F^- from the anionic $[\text{Co}^{\text{II}}(\text{TPP})(\text{CF}_3)]^-$ complex could lead to formation of a $[\text{Co}^{\text{II}}(\text{TPP})(\text{CF}_2)]$ species, potentially capable of CF_2 transfer to acrylates under mild reaction conditions.

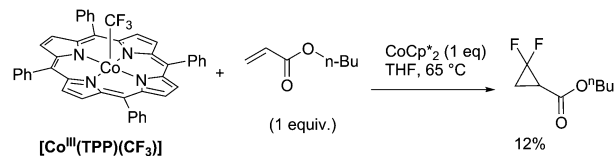
The trifluoromethyl cobalt(III) porphyrin complex $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ required for these studies was obtained in 80% yield (see ESI† for characterisation) by reacting $[\text{Co}^{\text{III}}(\text{TPP})(\text{Cl})]$ with Me_3SiCF_3 and CsF as an initiator (Scheme 2).

To evaluate the potential of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ to form a difluorocarbene complex we investigated its electrochemistry under reductive conditions. The cyclic voltammogram (CV) of complex $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ in THF reveals a reversible reduction wave at -1.71 V, followed by an irreversible one with the peak wave at -2.13 V. *vs.* Fc/Fc^+ (See ESI,† Fig. S7). The first wave can be attributed to the one-electron reduction of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ to form the anionic complex $[\text{Co}^{\text{II}}(\text{TPP})(\text{CF}_3)]^-$. The subsequent irreversible reduction leads to clean formation of $[\text{Co}^{\text{I}}(\text{TPP})]^-$ as evidenced by an independent measurement of an original $[\text{Co}^{\text{II}}(\text{TPP})]$ sample (See ESI,† Fig. S8). These results show that one-electron reduction of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ leads to formation of the anionic complex $[\text{Co}^{\text{II}}(\text{TPP})(\text{CF}_3)]^-$, which is stable on the CV timescale (scan rate 100 mV s^{-1}). The second reduction step leads to rapid (net) loss of the CF_3^- anion from the cobalt centre.

Knowing that $[\text{Co}^{\text{II}}(\text{TPP})(\text{CF}_3)]^-$ can be selectively accessed using reductants with a reduction potential in the -1.8 – 2.0 V range (*vs.* Fc/Fc^+), we next investigated its propensity to generate a metallodifluorocarbene species on an extended timescale and at elevated temperatures. Interestingly, the intended reduction of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ with one equivalent of dcamethylcobaltocene (CoCp^*_2 , $E^0 = -1.91$ *vs.* Fc/Fc^+) in the presence of *n*-butyl acrylate at 65 °C indeed led to the formation of the desired *gem*-difluorocyclopropanated acrylate in 12% yield as determined by ^{19}F NMR (Scheme 3). Additionally, C_2F_4 was formed as a side product. In the absence of CoCp^*_2 no reaction took place.



Scheme 2 Synthesis of $[\text{Co}(\text{TPP})(\text{CF}_3)]$.



Scheme 3 Reaction of $[\text{Co}(\text{TPP})(\text{CF}_3)]$ with *n*-butyl acrylate upon one-electron reduction.

The formation of the desired difluorocyclopropane suggests that upon reduction of $[\text{Co}^{\text{III}}(\text{TPP})(\text{CF}_3)]$ a cobalt-difluorocarbene complex is formed, which is apparently nucleophilic enough to facilitate CF_2 transfer to the electrophilic $\text{C}=\text{C}$ bond of the acrylate. The $[\text{Co}^{\text{II}}(\text{TPP})(\text{CF}_2)]$ intermediate could not be observed with EPR spectroscopy though (see ESI† for details).

The feasibility of the stoichiometric reaction shown in Scheme 3 triggered us to evaluate whether catalytic CF_2 transfer from Me_3SiCF_3 to *n*-butyl acrylate is possible when directly using a divalent cobalt(II) porphyrin catalyst in the presence of NaI as the activator. Indeed, with 5 mol% of $[\text{Co}^{\text{II}}(\text{TPP})]$ in THF catalytic formation (TON = 2.4) of the desired *gem*-difluorocyclopropanated acrylate was observed (Table 1, entry 1), albeit in low yield (12%). Besides the desired cyclopropane, the only other ^{19}F -NMR detected fluorine containing side product was C_2F_4 , presumably formed by free carbene dimerization. The $\text{TMSCF}_3/\text{NaI}$ combination can transfer CF_2 to electron rich alkenes¹² and metals.^{3c} Control experiments show that in the absence of cobalt (Table 1, entry 2) no *gem*-difluorocyclopropane product was formed, which makes it unlikely that the cyclopropanation proceeds *via* free CF_2 or the free CF_3^- anion.

The low turnover numbers obtained using $[\text{Co}(\text{TPP})]$ as the catalyst suggests that the catalyst quickly deactivates under the applied reaction conditions. Hence, in an attempt to increase the TONs we explored a few additional catalysts (Table 1). The complexes $[\text{Co}^{\text{II}}(\text{acac})_2]$ and $[\text{Co}^{\text{II}}(\text{salophen})]$ proved inactive (entries 3–4), but the perfluorinated porphyrin complex $[\text{Co}(\text{TPPF}_{20})]$ (TPPF₂₀ = *meso*-tetra(pentafluorophenyl)-porphyrinato) indeed proved to be a somewhat more robust catalyst (entry 5) than $[\text{Co}(\text{TPP})]$, producing the desired *gem*-difluorocyclopropanated

Table 1 Catalyst screening for CF_2 transfer from Me_3SiCF_3 to *n*-butyl acrylate (for further screening, see Table S1 in the ESI)

#	Catalyst	Solvent	T (°C)	Yield ^a (%)	TON ^b
1	$[\text{Co}^{\text{II}}(\text{TPP})]$	THF	50	12	2.4
2	None	THF	50	0	—
3	$[\text{Co}^{\text{II}}(\text{acac})_2]$	THF	50	0	—
4	$[\text{Co}^{\text{II}}(\text{salophen})]$	THF	50	0	—
5	$[\text{Co}^{\text{II}}(\text{TPPF}_{20})]$	THF	50	24	4.8
6	$[\text{Co}(\text{TPPF}_{20})]^c$	THF	50	40	8

Reaction conditions: 0.5 mmol of *n*-butyl acrylate; 2 mL of solvent; 5 mol% catalyst and 4 equiv. of TMSCF_3 , 18 h.^a With respect to *n*-butyl acrylate using ^{19}F NMR spectroscopy and fluorobenzene as an internal standard. ^b Turnover numbers. ^c A second batch of 4 equiv. of Me_3SiCF_3 was added after 4 hours.

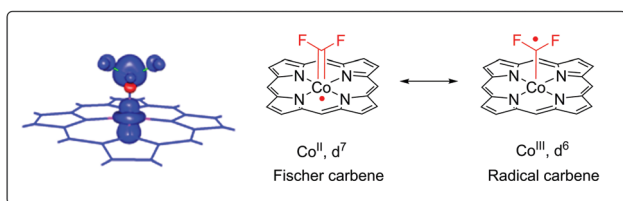
acrylate in 24% yield (TON = 4.8). Changing the initiator, solvent and the amount of Me_3SiCF_3 did not improve the yield of the difluorinated cyclopropane (see ESI,† Table S1). However, when an additional batch of 4 equivalents of Me_3SiCF_3 was added after 4 hours (Table 1, entry 6), the yield increased to 40% (TON = 8). Any further addition of Me_3SiCF_3 did not lead to an increased yield.

The reactions reported in Table 1 serve as a proof-of-principle, clearly showing the feasibility of cobalt-catalysed CF_2 transfer from Me_3SiCF_3 to electron-deficient alkenes. However, the currently applied catalysts do not seem to be robust enough to obtain the cyclopropane product in high yields exceeding 40%. Hence, additional catalyst screening is clearly a subject of follow-up research.

Due to the redox non-innocent behaviour of carbenes,¹⁵ the electronic structure of oxidation state +II group 9 transition metal carbene complexes is best described as metal(III) ‘carbene radical’ species in which the unpaired electron resides mainly in the p-orbital of the carbene moiety (the SOMO being the metal d – carbene p antibonding π^* molecular orbital, which is strongly polarized to carbon). This phenomenon has been reported for various transition metal carbene complexes, and can lead to unique reactivity of the carbene moiety.^{15,16} A similar behaviour has been reported for group 9 nitrene complexes.¹⁷ However, as pointed out by Woodcock and co-workers, cobalt porphyrinato difluorocarbene complexes actually might not behave as so-called ‘carbene radicals’.¹⁸ According to their NBO analysis (DFT, M06-L functional) the spin density is mainly located on the metal (71%) rather than on the carbon atom (28%) and thus $[\text{Co}(\text{por})(\text{CF}_2)]$ should have a substantial Fischer-type carbene character. Hence, unlike all other reported carbene adducts of cobalt(II) porphyrins,^{15,16,18} the CF_2 adduct might not behave as a genuine ‘carbene radical’. Thus, we wondered if the CF_2 carbene adduct reacts with alkenes *via* a stepwise (typical for ‘carbene radicals’) or a concerted (typical for Fischer carbenes) mechanism. Therefore we performed additional DFT calculations to shed light on the mechanistic details concerning the observed CF_2 transfer reactions from the $[\text{Co}(\text{por})(\text{CF}_2)]$ complex to the electron deficient acrylate.

In agreement with the results reported by Woodcock,¹⁸ the DFT (BP86, def2-TZVP) calculated NBO spin populations of $[\text{Co}(\text{por})(\text{CF}_2)]$, which is a simplified model of the experimental porphyrin complexes without meso-substituents, are 65% for cobalt and only 23% for the carbene carbon atom (Scheme 4).

However, despite the dominant metalloradical character of the $[\text{Co}(\text{por})(\text{CF}_2)]$ species, the computed carbene transfer to



Scheme 4 Spin density plot and resonance structures of $[\text{Co}(\text{por})(\text{CF}_2)]$.

methylacrylate does proceed *via* a stepwise radical process, just like other cobalt(II) porphyrin catalysed carbene and nitrene transfer reactions. All attempts to find the transition state for a concerted addition of acrylate failed and converged to the stepwise pathway. Addition of the difluorocarbene species **A** to the olefin proceeds *via* a relatively low energy transition state (**TS1**, $\Delta G_{298\text{K}}^\ddagger = +14.4$ kcal mol⁻¹), generating the $[\text{Co}(\text{por})(\text{CF}_2\text{-CH}_2\text{-CH-COOMe})]$ species **B**, which has its unpaired electron primarily localized at the γ -carbon of the ‘alkyl’ moiety. Hence, despite its significant Fischer-type character in the ground state, the reactivity of $[\text{Co}(\text{por})(\text{CF}_2)]$ follows the characteristics of a ‘carbene radical’ species. The transition state **TS2** for ring closure leading to formation of the cyclopropane product involves simultaneous C–C bond formation and homolytic cleavage of the Co–C bond. The barrier for this process is higher ($\Delta G_{298\text{K}}^\ddagger = +20.7$ kcal mol⁻¹) and seems to be the rate limiting step of the overall reaction (Fig. 1).

We also investigated an alternative pathway in which the difluorocarbene generated on the cobalt centre dissociates to react with the acrylate outside the metal coordination sphere. The release of free difluorocarbene from cobalt is energetically uphill ($\Delta G_{298\text{K}}^\circ = +16.3$ kcal mol⁻¹) and the reverse reaction is barrierless (see ESI,† Fig. S9). This energy is comparable to the energy barrier for coupling of the cobaltocarbene with methyl acrylate. Formation of free CF_2 in this manner, as well as the coupling of two $[\text{Co}(\text{por})(\text{CF}_2)]$ species, could be responsible for the observed formation of C_2F_4 as a side product in the reaction. However, free CF_2 carbene formation is unlikely associated with formation of the cyclopropane product, as the addition of free difluorocarbene to methyl acrylate has a much higher barrier ($\Delta G_{298\text{K}}^\ddagger = +28.0$ kcal mol⁻¹) than those associated with the metal-mediated pathway (**TS1** and **TS2** in Fig. 1). Lewis-acid activation of the acrylate also seems unlikely, as in a separate control experiment with $[\text{Zn}(\text{TPP})]$ only traces (<1%) of the *gem*-difluorocyclopropane product was formed (see ESI,† Table S1).

Based on the above considerations we propose a mechanism in which the CF_3^- anion (generated by the reaction of Me_3SiCF_3

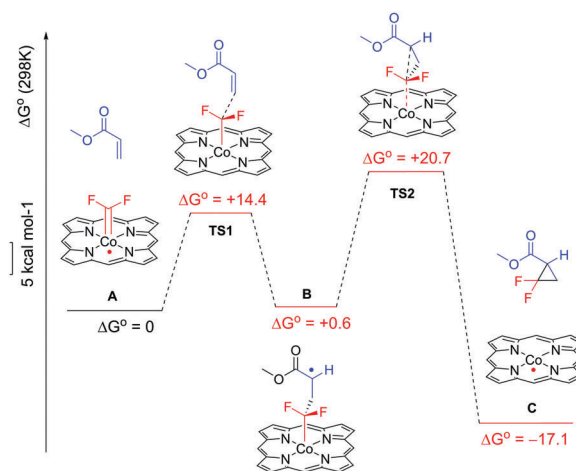
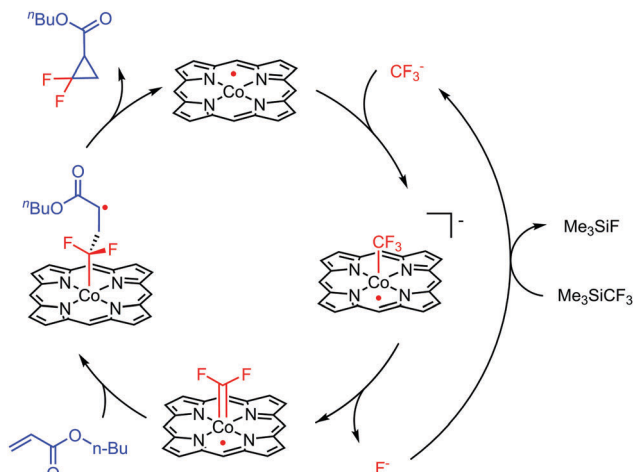


Fig. 1 DFT calculated pathway for difluorocyclopropanation of methyl acrylate by a cobalt(II) porphyrinato complex.



Scheme 5 Proposed catalytic cycle for the difluorocyclopropanation of *n*-butyl acrylate catalysed by a cobalt(II) porphyrinato complex.

and NaI) coordinates to [Co(TPP)] to form the anionic complex [Co(TPP)(CF₃)][−], which produces the neutral carbene adduct [Co(TPP)(CF₂)] upon loss of a fluoride anion (Scheme 5). The cobalt difluorocarbene complex subsequently undergoes a stepwise radical-type addition to the acrylate double bond, forming an alkylcobalt(III) intermediate with the unpaired electron residing at the γ -carbon atom of the alkyl chain. Subsequent (and likely rate limiting) ring closure with concerted Co–C bond cleavage furnishes the difluorocyclopropane and regenerates the [Co(TPP)] catalyst.

In conclusion, cobalt(II)-porphyrinato complexes catalyse difluorocarbene transfer from the trifluoromethyl anion to *n*-butyl acrylate forming a *gem*-difluorocyclopropane. The reactions reported here serve as a proof-of-principle, clearly showing the feasibility of cobalt-catalysed CF₂ transfer from Me₃SiCF₃ to electron-deficient alkenes. The data further show that the current cobalt(II) porphyrin catalysts quickly deactivate under the applied reaction conditions (maximum TON = 8), thus suggesting that future investigations aimed at the development of efficient protocols for catalytic CF₂ transfer reactions using Me₃SiCF₃ as the carbene source should focus on using catalysts that are more stable in the presence of the reactive, free CF₂ and CF₃[−] intermediates generated under the applied reaction conditions.

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