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Stepwise addition of difluorocarbene to a transition metal centre†

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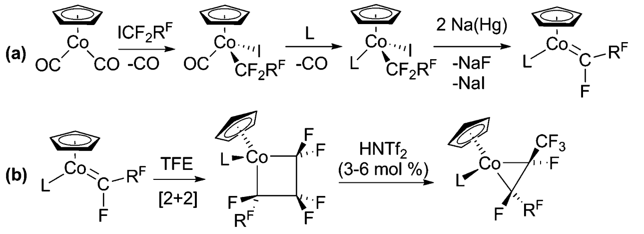
The Ruppert–Prakash reagent (Me_3SiCF_3) is used to introduce difluorocarbene (CF_2) and tetrafluoroethylene (TFE) ligands to cobalt(I) metal centres, whereby the TFE ligand is generated *via* [2+1] cycloaddition between [Co]$=$$CF_2$ and CF_2.

Among the most versatile tools for the synthesis of metal-fluoroalkyl complexes is the Ruppert–Prakash reagent (Me_3SiCF_3).[1] It has been used to prepare a variety of transition metal complexes with trifluoromethyl (CF_3) ligands, including examples of first-row (Ti, Ni, Cu), second-row (Ru, Rh, Pd) and third-row (Pt, Au) metals.[2] Recently, conditions were reported that render Me_3SiCF_3 an excellent source of difluorocarbene (CF_2) (eqn (1)), as applied to the synthesis of difluorocyclopropanes and difluorocyclopropenes,[3] as well as unusual fluorinated carbacycle motifs.[4] Iodide activates Me_3SiCF_3 to liberate the trifluoromethyl anion, which decomposes into CF_2 and F^-. The fluoride ion also reacts with Me_3SiCF_3 to release CF_3^-.[5]

$$\mathrm{Me_3SiCF_3} \xrightarrow[\text{THF}]{\text{NaI(initiator)}} \mathrm{Me_3SiF} + :\mathrm{CF_2} \qquad (1)$$

Here, we present a novel application of Me_3SiCF_3 for directly introducing the CF_2 group to transition metal compounds, providing new routes to metal difluorocarbene ([Co]$=$$CF_2$) and metal tetrafluoroethylene (TFE) complexes {[Co](η^2-C_2F_4)}. Such compounds are under investigation as intermediates in potential catalytic cycles utilizing perfluoroalkenes (*e.g.*, metathesis and polymerization).[6]

Examples of metal fluorocarbenes ([M]$=$$CFR^F$, R^F = F or CF_3) are rare and, relative to metal alkylidenes or other types of Fischer carbenes,[7] have been the subject of few reactivity studies.[8] Almost without exception, [M]$=$$CF_2$ complexes are prepared *via* fluoride abstraction/elimination from metal fluoroalkyl precursors.[9] Notably, Caulton and co-workers showed that Me_3SiCF_3 reacts with a ruthenium fluoride complex to give [Ru(CF_3)(H)(CO)(L_2)]; α fluoride migration from the CF_3 group to the metal centre yields [Ru($=$$CF_2$)(F)(H)(CO)($L_2$)].[2d] This difluorocarbene complex is electrophilic at the carbenoid carbon atom, demonstrated by hydride migration in the presence of coordinating solvent.[2d] Recently, we reported the synthesis of nucleophilic cobalt fluorocarbenes (Scheme 1a),[10] using a procedure adapted from Hughes and co-workers.[9] The [Co]$=$$CFR^F$ complexes undergo [2+2] cycloaddition reactions with tetrafluoroethylene (TFE) to give perfluorometallacyclobutanes.[6] The metallacyclobutane compounds exhibit rich reactivity upon activation of C_β–F bonds, including the catalytic isomerization to alkene complexes under acid catalysis (Scheme 1b).



Scheme 1 Previously reported synthesis (a), and reactivity (b) of cobalt fluorocarbenes. L = phosphine or phosphite, R^F = F or CF_3.

For the present work, we investigated $CpCoL_2$ complexes [Cp = η^5-C_5H_5; **1a**, L = CO; **1b**, L = PPh_3; **1c**, L = P(O^iPr)$_3$] as potential CF_2 acceptors in reactions with the Ruppert–Prakash reagent. Compounds of type **1** were selected based on our previous work that demonstrated the [CpCoL] substructure can support the CF_2 fragment, making it an attractive platform for CF_2-transfer screening reactions.

Treatment of **1** with Me_3SiCF_3 (2 equivalents) and catalytic quantities of NaI in THF at 65 °C gave a mixture of the corresponding cobalt fluorocarbenes **2a–c**, and novel cobalt tetrafluoroethylene complexes **3a–c** (Scheme 2). The products were readily identified in solution by their distinct ^{19}F NMR signals.

Selectivity for products **2** *vs.* **3** depends on the nature of the ancillary ligands. When L = CO (*i.e.*, **1a**), the TFE complex **3a** is the major product, and only minor quantities of **2a** are observed. The ^{19}F NMR spectrum of **2a** displays two characteristically downfield resonances at δ = 112.5 ppm and 83.4 ppm ($^2J_{FF}$ = 152 Hz), consistent with data previously reported for [CpCo($=$$CF_2$)(L)] complexes.[6,10]

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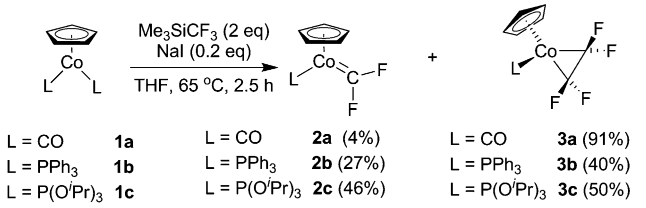


Scheme 2 Structures of cobalt fluorocarbenes **2**, and TFE complexes **3** (NMR determined yields)[11] from Co(I) complexes **1**.

Complex **3a** was isolated as a brown-yellow oil in 69% yield, whereas the carbene complex **2a** could only be observed spectroscopically. We previously reported that attempts to prepare **2a** *via* reduction of [CpCo(CO)I(CF$_3$)] were unsuccessful.[10] Complexes **1b** or **1c** (with PPh$_3$ or P(O^{i}Pr)$_3$ ligands) react under the same conditions to yield cobalt fluorocarbenes **2b** (reported previously)[10] or **2c**, respectively, as the minor products (although in much higher yields than **2a**), along with major products **3b** and **3c**. Using four equivalents of Me$_3$SiCF$_3$ increases the yield of alkene complexes **3b** and **3c** significantly, while carbenes **2b** and **2c** are no longer observed in solution. The crystal structures of **3b** and **3c** are presented in Fig. 1.

The ^{19}F NMR spectra of η^2-TFE complexes **3a–c** are highly characteristic. In THF or C$_6$D$_6$ at room temperature, the signals for the TFE ligand exhibit second order coupling indicative of either an AA′BB′ spin system for **3a**, or an AA′BB′X spin system for **3b** and **3c** (X = ^{31}P), and C_s symmetry for all three complexes. The observation of two resonances with well-resolved splitting patterns suggests the C$_2$F$_4$ fragment does not rotate with respect to the metal on the NMR timescale in solution, in contrast to related η^2-C$_2$F$_4$ complexes of Ni and Pd described by Ogoshi and co-workers,[12] or Ru and Ir complexes described by Hughes and co-workers.[13]

Under the reaction conditions outlined in Scheme 2, we envision two likely pathways for formation of TFE complexes **3a–c**, as illustrated in Scheme 3. In pathway A, tetrafluoroethylene, formed *in situ* from two equivalents of CF$_2$,[14] reacts directly with complexes **1a–c**. ^{19}F NMR analysis of a mixture of only Me$_3$SiCF$_3$ and NaI in THF confirms that TFE is formed cleanly as the major product upon heating, with concomitant formation of Me$_3$SiF (Fig. S1, ESI†). In order to probe the feasibility of path A, complexes **1a–c** were treated with TFE (1.7 atm) in THF at 65 °C. Complexes **1a** and **1c** did not react under these conditions, and the addition of NaI also had no effect. Small amounts of **3a** were observed in a complex mixture when a THF solution of **1a** was photolyzed (medium-pressure Hg lamp) in the presence of TFE (1.7 atm), presumably through photolytically-generated [CpCo(CO)].[15] Interestingly, Stone and co-workers reported in 1961 that **1a** reacts with excess TFE in cyclohexane at high temperatures (160 °C) to produce the perfluorocyclopentane complex [CpCo(CF$_2$)$_4$(CO)] in 11% yield.[16] While **3a** is likely an intermediate in this process, we did not observe the 5-membered ring product under the conditions we explored.

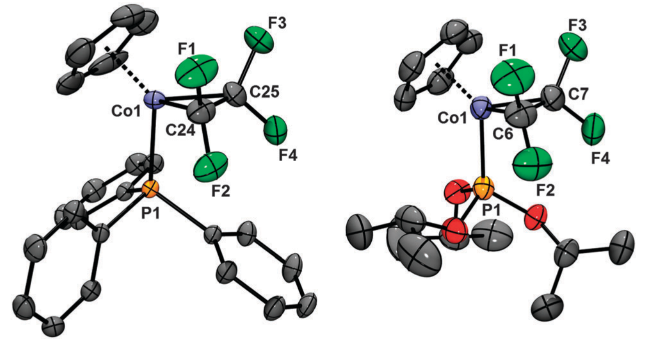
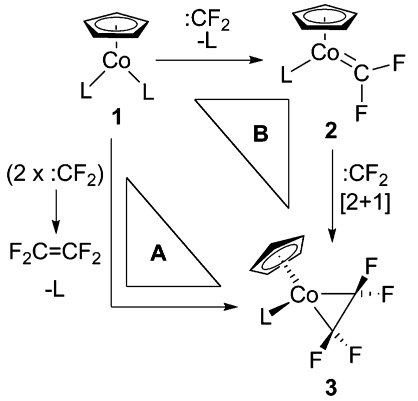


Fig. 1 Molecular structures of **3b** (left) and **3c** (right). The ellipsoids are set to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): **3b**: Co1–C24 1.884(3), Co1–C25 1.897(3), Co1–P1 2.1930(7), Co1–Cp(centroid) 1.735(6), C24–F1 1.357(5), C24–F2 1.361(4), C25–F3 1.362(4), C25–F4 1.347(5), C24–Co1–C25 44.49, Co1–C25–C24 67.27, C25–C24–Co1 68.24. **3c**: Co1–C6 1.880(2), Co1–C7 1.896(2), Co1–P1 2.1478(6), Co1–Cp(centroid) 1.711(2), C6–F1 1.372(3), C6–F2 1.376(3), C7–F3 1.370(2), C7–F4 1.356(3), C6–Co1–C7 43.92, Co1–C7–C6 67.45, C7–C6–Co1 68.62.

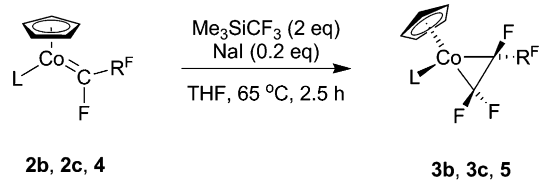


Scheme 3 Proposed pathways for generation of **3**. Path A involves direct addition of TFE to **1**, while path B is comprised of the stepwise addition of CF$_2$, with **2** formed as a stable intermediate.

In contrast to **1a** and **1c**, complex **1b** reacts with TFE to produce **3b** in 89% yield by ^{19}F NMR. These results indicate that under the conditions explored, path A does not likely contribute to the formation of **3a** and **3c**, but *can* contribute to the formation of **3b**, if TFE is formed in appreciable quantities. The increased reactivity toward TFE of **1b** *vs.* **1a,c** is apparently due to the increased lability of PPh$_3$ relative to π-accepting CO and P(O^{i}Pr)$_3$, allowing generation of 16e$^-$ complex [CpCo(PPh$_3$)] in solution. These results suggest a dissociative mechanism for pathway A.

Pathway B represents a new synthetic route to metal fluoroalkene complexes. In this scheme, a metal fluorocarbene intermediate **2** is formed initially, which undergoes [2+1] cycloaddition reaction with a second equivalent of CF$_2$ to yield perfluoroalkene complexes **3**. Indeed, independently-synthesized **2b** and **2c** react with Me$_3$SiCF$_3$/NaI, producing **3b** and **3c**, respectively, in high yield (>90% by ^{19}F NMR). Similarly, the fluoro(trifluoromethyl) carbene complex **4** (reported previously)[10] is converted to the corresponding fluoroalkene complex **5** in high yield under the same conditions. These reactions are summarized in Scheme 4, and the crystal structure of **5** is presented in Fig. 2.

From these results, it can be reasoned that path B likely contributes, along with path A, to the formation of **3b**. In the case of **3a** and **3c**, B appears to be the dominant pathway. The detailed mechanism of pathway B, (difluorocarbene addition to complexes **1** and **2**) is under further investigation using DFT calculations.



Scheme 4 Synthesis of fluoroalkene complexes *via* [2+1] cycloaddition between CF_2 and pre-isolated cobalt fluorocarbenes. For complexes **4** and **5**, L = PPh_3, R^F = CF_3.

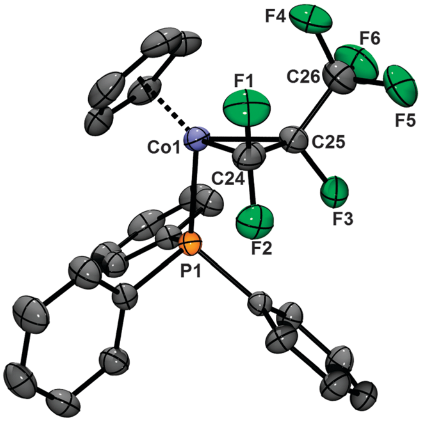


Fig. 2 Molecular structure of **5**. The ellipsoids are set to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Co1–C24 1.902(3), Co1–C25 1.943(2), Co1–P1 2.2267(6), Co1–Cp(centroid) 1.718(3), C24–F1 1.373(3), C24–F2 1.351(3), C25–F3 1.388(3), C24–Co1–C25 44.08, Co1–C25–C24 66.47, C25–C24–Co1 69.45.

The unique [2+1] reactions described here, involving highly electrophilic difluorocarbene,[17] are consistent with the nucleophilic character of the Co=C bond of the Co(I) fluorocarbene complexes.[6,10] Upon addition of CF_2, the Co(I) metal centre of carbenes **2** are formally oxidized to Co(III). The Co–C (TFE) bonds in **3b** (Co1–C24 1.884 Å; Co1–C25 1.897 Å) are significantly longer than the Co=C bond of **2b** (1.7395 Å), and the same is true for the analogous Co–C (TFE) bonds of **5** (Co1–C24 1.902 Å; Co1–C25 1.943 Å) relative to the Co=C bond of **4** (1.751 Å).

In conclusion, we have demonstrated that cobalt difluorocarbenes and η^2-TFE complexes are generated *via* sequential addition of CF_2, generated from Me_3SiCF_3 and catalytic NaI, to $CpCoL_2$ complexes. We also note that Me_3SiCF_3/NaI can be used as a safe and convenient precursor for generating tetrafluoroethylene. Future work will extend the methods described here to synthesize new difluorocarbene and perfluoroalkene transition metal complexes[18] with potential relevance to catalytic processes involving fluorocarbon substrates.

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