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Stepwise addition of difluorocarbene to a transition metal centre†

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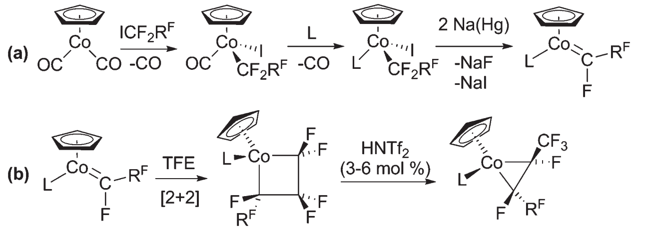
The Ruppert–Prakash reagent (Me_3SiCF_3) is used to introduce difluorocarbene (CF_2) and tetrafluoroethylene (η^2-C_2F_4) ligands to cobalt(I) metal centres, whereby the TFE ligand is generated *via* [2+1] cycloaddition between [Co]═CF_2 and CF_2.

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 successfully 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]

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

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 processes).[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.

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

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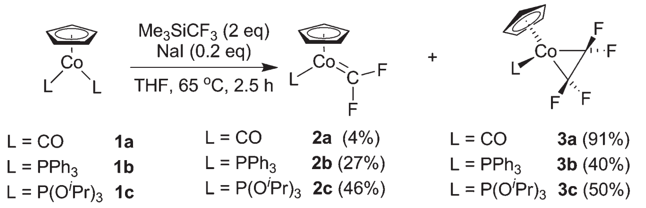


Scheme 2 Structures of cobalt fluorocarbenes **2**, and TFE complexes **3** (NMR determined yields)[11] from Co(I) complexes **1**.

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 (${}^{2}J_{FF}$ = 152 Hz), consistent with data previously reported for $[CpCo({=}CF_2)(L)]$ complexes.[6,10] 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 $P(O^iPr)_3$ 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_3SiCF_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_6D_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_2F_4 fragment does not rotate with respect to the metal on the NMR timescale in solution, in contrast to related η^2-C_2F_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]

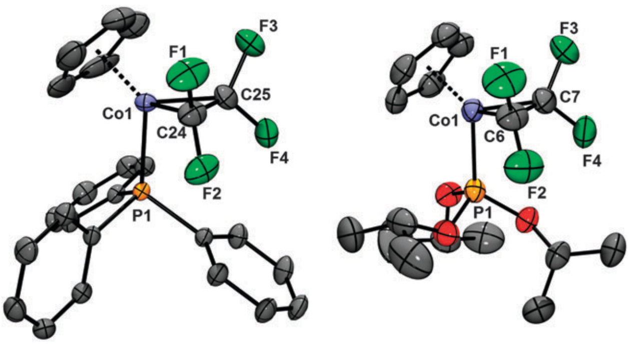
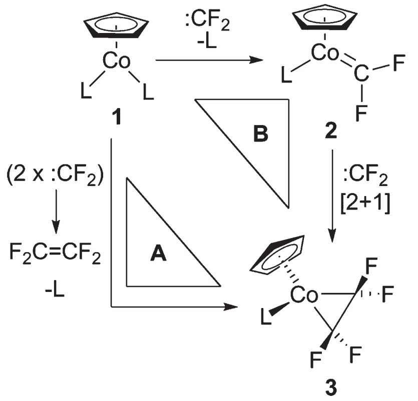


Fig. 1 Molecular structures of **3b** (left) and **3c** (right). The ellipsoids are set to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): **3b**: Co1–C24 1.884(3), Co1–C25 1.897(3), Co1–P1 2.1930(7), Co1–Cp(centroid) 1.735(6), C24–F1 1.357(5), 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.

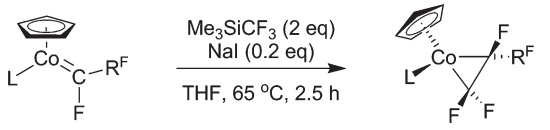


Scheme 3 Proposed pathways for generation of **3**. Path A involves direct addition of TFE to **1**, while path B is comprised of the stepwise addition of CF_2, with **2** formed as a stable intermediate.

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_3SiCF_3 and NaI in THF confirms that TFE is formed cleanly as the major product upon heating, with concomitant formation of Me_3SiF (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 any of the 5-membered ring product under the conditions we explored.

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 $P(O^iPr)_3$, 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_3SiCF_3/NaI, producing **3b** and **3c**, respectively, in high yield (>90% by ${}^{19}F$ NMR). Similarly, the fluoro(trifluoromethyl) carbene complex **4** (reported previously)[9] 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.



2b, **2c**, **4** **3b**, **3c**, **5**

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.

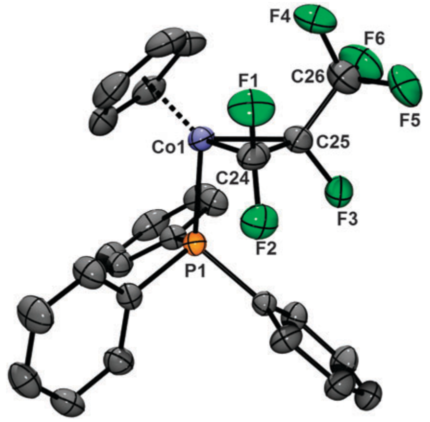


Fig. 2 Molecular structure of **5**. The ellipsoids are set to 50% probability, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Co1–C24 1.902(3), Co1–C25 1.943(2), Co1–P1 2.2267(6), Co1–Cp(centroid) 1.718(3), C24–F1 1.373(3), C24–F2 1.351(3), C25–F3 1.388(3), C24–Co1–C25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

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.

The Co=C bonds of cobalt(I) fluorocarbene complexes, CpCo(=CFR^F)L [R^F = F, CF_3; L = PPh_3, $P(OMe)_3$] were previously shown to react with electrophiles such as H^+ and Me^+, while being inert to water.[10] 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. 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. These reactions provide the first examples of using the Ruppert–Prakash reagent as a source of CF_2 for making transition metal difluorocarbene complexes. The first [2+1] cycloaddition reactions between metal fluorocarbenes and CF_2 were also presented. Finally, we 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 with potential relevance to catalytic processes involving fluorocarbon substrates.

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