Stepwise addition of difluorocarbene to a transition metal centre†

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The Ruppert–Prakash reagent (Me3SiCF3) is used to introduce difluorocarbene (CF2) and tetrafluoroethylene (η2-C2F4) ligands to cobalt(II) metal centres, whereby the TFE ligand is generated via [2+1] cycloaddition between [Co]=CF2 and CF2.

Among the most versatile tools for the synthesis of metal-fluoroalkyl complexes is the Ruppert–Prakash reagent (Me3SiCF3).1 It has been used to successfully prepare a variety of transition metal complexes with trifluoromethyl (CF3) 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 Me3SiCF3 an excellent source of difluorocarbene (CF2) [eqn (1)], as applied to the synthesis of difluorocyclopropanes and difluorocyclopropenes,3 as well as unusual fluorinated carbacycle motifs.4 Iodide activates Me3SiCF3 to liberate the trifluoromethyl anion, which decomposes into CF3 and F‾. The fluoride ion also reacts with Me3SiCF3 to release CF3–.5

Here, we present a novel application of Me3SiCF3 for directly introducing the CF2 group to transition metal compounds, providing new routes to metal difluorocarbene ([Co]=CF2) and metal tetrafluoroethylene (TFE) complexes \{[Co]η2-C2F4\}. 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, R=F or CF3] are rare and, relative to metal alkylidene or other types of Fischer carbenes,7 have been the subject of few reactivity studies.8 Almost without exception, [M]=CF2 complexes are prepared via fluoride abstraction/elimination from metal fluoroalkyl precursors.9 Notably,

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\text{Me3SiCF3} + \text{Na(THF)} \rightarrow \text{Me3SiF} + \cdot \text{CF2} \quad \text{(1)}
\]

Caulston and co-workers showed that Me3SiCF3 reacts with a ruthenium fluoride complex to give [Ru(CF3)(H)(CO)(L2)];2 fluoride migration from the CF3 group to the metal centre yields [Ru(=CF2)(F)(H)(CO)(L2)].10 This difluorocarbene complex is electrophilic at the carbenoid carbon atom, demonstrated by fluoride 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]=CF2 complexes undergo [2+2] cycloaddition reactions with tetrafluoroethylene (TFE) to give perfluorometallacyclobutanes.6 The metallacyclobutane compounds exhibit rich reactivity upon activation of Cp–F bonds, including the catalytic isomerization to alkene complexes under acid catalysis (Scheme 1b).

For the present work, we investigated CpCoL2 complexes [Cp = η5-C5H5; 1a, L = CO; 1b, L = PPh3; 1c, L = P(OiPr)3] as potential CF2 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 CF2 fragment, making it an attractive platform for CF2-transfer screening reactions.

Treatment of 1 with Me3SiCF3 (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 19F 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
$^1$H NMR spectrum of 2a displays two characteristically downfield
resonances at $\delta = 112.5$ ppm and $83.4$ ppm ($J_{HF} = 152$ Hz),
consistent with data previously reported for $[\text{CpCo}(\equiv \text{CF}_2\beta\beta\beta\beta)(\text{L})]$ com-
plexes.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 $[\text{CpCo}(\equiv \text{CF}_2\beta\beta\beta\beta)]$ complexes were unsuccessful.10
Complexes 1b or 1c (with PPh$_3$ or P(OPh)$_3$ ligands) react under the same
conditions to yield cobalt fluorocarbenes 2b (reported previously$^{14}$)
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 $^1$F NMR spectra of $\eta^2$-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 $C_2$ symmetry for all three complexes. The observa-
tion 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 $\eta^1$-C$_2$F$_3$ 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 ($^\circ$): 3b: Co1–C24 1.884(3), Co1–C25 1.897(3), Co1–
P1 2.1930(7), Co1–Cp centroid 1.735(6), C23–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.

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.13 $^1$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, ES$^+$). 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 $[\text{CpCo}(\equiv \text{CF}_2\beta\beta\beta\beta)]^{15}$ Interestingly, Stone and co-
workers reported in 1961 that 1a reacts with excess TFE in cyclohex-
ane at high temperatures (160 °C) to produce the perfluorocyclo-
pentane complex $[\text{CpCo}(\text{CF}_3)]$ 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 99% yield by $^1$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 $\pi$-accepting CO and P(OPh)$_3$ allowing generation
of 16e$^-$ complex $[\text{CpCo}(\text{P} \text{Ph}_3)]$ 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 fluorocarbenyl 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 $^1$F
NMR). Similarly, the fluoro(trifluoromethyl) carbene complex 4
(reported previously$^9$) is converted to the corresponding fluoroalk-
ene 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.

The Co–C bonds of cobalt(i) fluorocarbenes, CpCo(CF3)2, and 2 were formally oxidized to Co(n). The Co–C (TFE) bonds in 3b (Co–C 1.884 Å; Co–C 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 (Co–C 1.902 Å; Co–C 1.943 Å) relative to the Co–C bond of 1 (1.751 Å).

In conclusion, we have demonstrated that cobalt difluorocarbenes and perfluoroalkene transition metal complexes with potential relevance to catalytic processes involving fluorocarbon substrates.

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Notes and references


5 For investigations of reactive species associated with Me5SiCF3/NaI complexes, via [2+1] cycloaddition.
7 (a) McCall, T. R., boron trifluoride (BF3) is used as a convenient precursor for generating Me3SiCF3. Future work will extend the methods described here to synthesize new difluorocarbene complexes. For complexes 4 and 5, L = PPh3, R' = CF3.
18 While this work was in progress, Ozerov et al. reported obtaining a mixture of [M]=CF₂ and [M][µ²-C₂F₄] products from the reaction of a [PNP]Rh alkene complex with a mixture of Me₃SiCF₃ and CsF in C₆D₆ at 70 °C: Canadian Society of Chemistry Abstract. INOR 163, May 27, 2013.