

Cobalt Fluorocarbenes: Cycloaddition Reactions with Tetrafluoroethylene and Reactivity of the Perfluorometallacyclic Products

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S Supporting Information

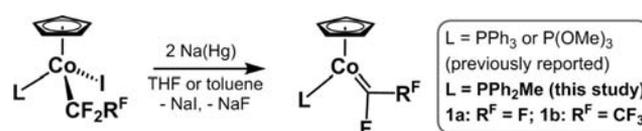
ABSTRACT: Cobalt fluorocarbene complexes $\text{CpCo}(\text{=CFR}^{\text{F}})(\text{PPh}_2\text{Me})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{R}^{\text{F}} = \text{F}$ or CF_3) react with tetrafluoroethylene to give the metallacyclobutanes $\text{CpCo}(\kappa^2\text{-CFR}^{\text{F}}\text{CF}_2\text{CF}_2\text{-})(\text{PPh}_2\text{Me})$ in the first examples of cycloaddition reactions between perfluoroalkenes and metal perfluorocarbenes. The metallacyclic products undergo a variety of reactions upon activation of the C–F bonds, including Brønsted acid-catalyzed C–F/Co–C scrambling. Implications for metal-catalyzed metathesis and polymerization of perfluoroalkenes are discussed.

Transition-metal alkylidenes ($[\text{M}]=\text{CRR}'$; R and R' = H, alkyl or aryl) are important intermediates in organometallic chemistry, most notably in catalytic alkene metathesis.¹ Metal carbenes ($[\text{M}]=\text{CRR}'$; R and/or R' = heteroatom donor group), including N-heterocyclic carbene complexes, are also implicated in a wide variety of catalytic and stoichiometric transformations.^{1–3} Metal fluorocarbenes ($[\text{M}]=\text{CFR}^{\text{F}}$; $\text{R}^{\text{F}} = \text{F}$ or perfluoroalkyl)⁴ have been studied in much less detail compared to metal alkylidenes and other types of metal carbenes and, so far, have not been utilized for catalysis. Terminal first-row metal fluorocarbenes are very rare, with only three examples reported prior to our work $\{[\text{CpFe}(\text{=CF}_2)(\text{CO})\text{L}]^+$; L = CO or PPh_3 ; Cp = $\eta^5\text{-C}_5\text{H}_5$ and $[\text{Mn}(\text{=CF}_2)(\text{CO})_5]^+\}$.⁵ These cationic complexes are potentially electrophilic at the carbene carbon atoms. Counting the carbene ligands as neutral two-electron donors, the metal atoms have formal d^6 electron configurations,⁶ and the metal-carbene π bonds are expected to be polarized toward the electron-deficient metal atoms.⁴ For potential catalytic applications based on electron-poor fluoroalkenes (e.g., metathesis or polymerization), we reasoned that more electron-rich/nucleophilic metal fluorocarbenes would be required.

We recently reported the first stable difluoro- and fluoro-(perfluoroalkyl)carbenes of cobalt.⁷ These complexes were synthesized by two-electron reduction of Co^{III} precursors (Scheme 1), following the method developed by Hughes et al. for making related iridium fluorocarbenes.⁸ The products have d^8 cobalt(I) centers, and the $[\text{Co}]=\text{CFR}^{\text{F}}$ bonds exhibited nucleophilic character in preliminary reactivity studies.⁷

For this study, we synthesized new derivatives with the more basic phosphine, PPh_2Me (Scheme 1), to obtain cobalt fluorocarbenes with enhanced nucleophilicity. Complexes **1a,b** were isolated in >70% yield (1–2 mmol scale), and their

Scheme 1



molecular structures are presented in Figure 1.⁹ Indeed, the PPh_2Me ligand renders **1a,b** more reactive (see below) than the PPh_3 and $\text{P}(\text{OMe})_3$ analogs disclosed previously.⁷

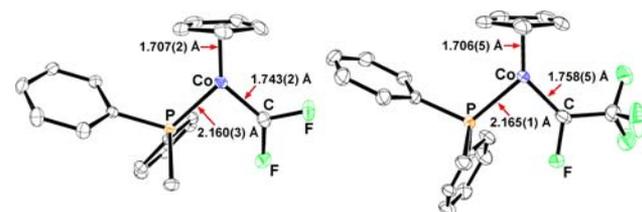
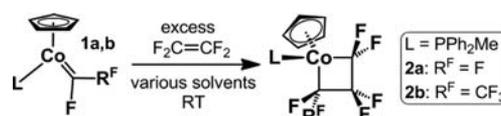


Figure 1. ORTEP representations of the molecular structures of **1a** (left) and **1b** (right) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity, and selected bond distances are indicated.⁹

Cobalt fluorocarbenes **1a** and **1b** react with TFE ($\text{CF}_2=\text{CF}_2$) to give the perfluorometallacyclobutanes **2a** and **2b**, via formal [2 + 2] cycloaddition (Scheme 2, Figure 2).⁹ The metallacycles

Scheme 2



were obtained in >75% isolated yields (¹⁹F NMR yields >85%) after 4 days at room temperature under 1.5–2 atm of TFE pressure. Compound **2b** is produced as a single diastereomer with the CF_3 group on the opposite face of the metallacycle relative to the phosphine (Figure 2). The only other reported transition-metal perfluorocyclobutane was produced by decarbonylation of an iron bis(acyl) complex.¹⁰

The mechanism of alkene addition is under investigation, but preliminary kinetic data reveal that the reaction between **1a** and

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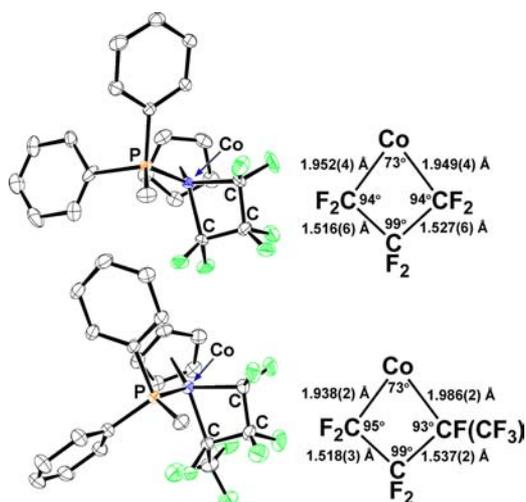
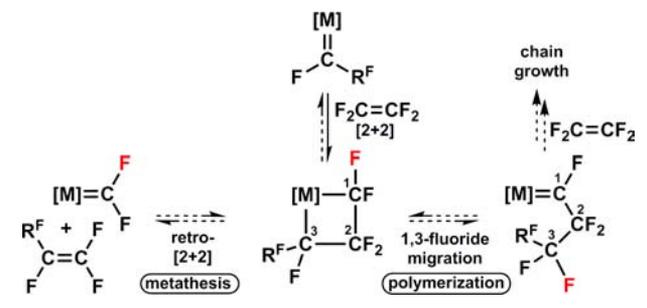


Figure 2. ORTEP representations of the molecular structures of **2a** (top) and **2b** (bottom) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances [Å]: **2a**: Co–Cp(centroid) = 1.724(5), Co–P = 2.209(1). **2b**: Co–Cp(centroid) = 1.723(2), Co–P = 2.226(6). For **2a**, one orientation is shown for the disordered F atoms on the central carbon atom.⁹

excess TFE is only marginally slower in the presence of 20 equiv of free PPh₂Me. Additionally, CpCo(=CF₂)[P(OMe)₃] undergoes TFE addition much slower than **1a** but slightly faster than the PPh₃ complex (SI). We therefore suggest that TFE addition proceeds without phosphine dissociation from the metal and small, Lewis-basic ligands appear to favor relatively rapid reactions.¹¹ Attempts to synthesize Co fluorocarbenes with L = PMe₃ or PMe₂Ph were unsuccessful using the reduction route (Scheme 1) or ligand substitution from the PPh₃ derivative under conditions similar to those used for the TFE cycloaddition reactions.

Metallacycles and metal carbenes/alkylidenes are key intermediates in numerous stoichiometric and catalytic processes,^{1–3} and we are interested in harnessing perfluoroalkene metathesis (e.g., Scheme 3, left) as a powerful technique for

Scheme 3



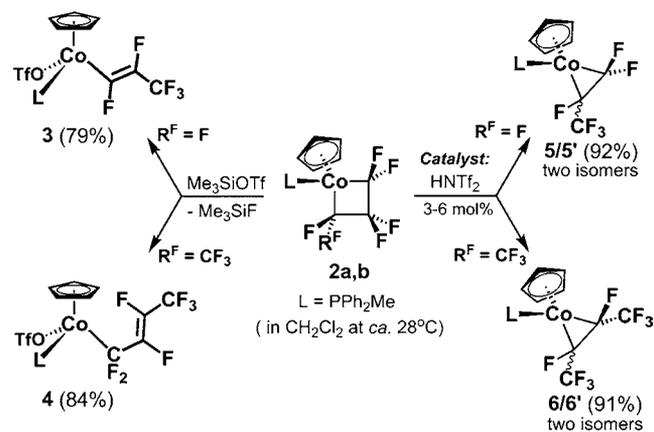
organofluorine chemistry. We are also considering metal fluorocarbenes as potential initiators for the polymerization of tetrafluoroethylene (TFE) and other fluorinated alkenes. The controlled polymerization of perfluoroalkenes in a metal coordination sphere has not been achieved,¹² despite being an attractive alternative to the currently used radical polymerization methods which require environmentally persistent fluorosurfactants.¹³

To avoid the problem of alkene insertion into inert [M]–R^F bonds,^{14a} as required by the Cossee–Arlman mechanism,¹⁵ we

are investigating a fluoro-variant of the Green–Rooney mechanism¹⁶ as a potential route to fluoropolymers. The proposed cycle is initiated by formal [2 + 2] fluoroalkene addition to a metal fluorocarbene to give a perfluorometallacyclobutane intermediate, identical to the first step of the alkene metathesis sequence. Ideally, activation of one of the C_α–F bonds,^{4,8b,14} accompanied by 1,3-fluoride migration and opening of the strained metallacycle, generates a new metal fluorocarbene with a growing perfluoroalkyl chain (Scheme 3, right).

Compounds **2a,b** are thermally stable, with or without TFE present, and do not decompose or react further upon heating for >24 h at 60 °C in C₆D₆. However, when **2a,b** are treated with Me₃SiOTf (Tf = SO₂CF₃), fluoride abstraction yields perfluoro-*trans*-vinyl (**3**)¹⁷ or perfluoro-*trans*-allyl (**4**) products (Scheme 4,

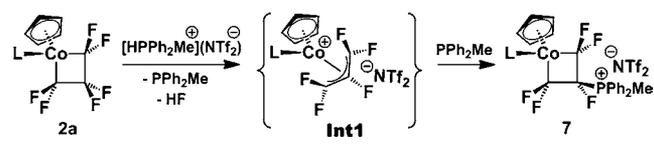
Scheme 4



left; yields from ¹⁹F NMR).¹⁸ Moreover, catalytic quantities of HNTf₂ induce clean isomerization/ring-contraction reactions, affording cobalt hexafluoropropene (**5/5'**, R^F = F) or perfluoro-2-butene (**6/6'**, R^F = CF₃) complexes (Scheme 4, right). Brønsted and Lewis acids have been shown to activate C_α–F bonds in metal perfluoroalkyls,^{4,8b,14} but previous examples have used stoichiometric quantities of acid and the fluoride ion was lost irreversibly.

The mechanistic details of the reactions of **2a,b** are currently being explored by computational methods. However, the reaction between **2a** and [HPPH₂Me](NTf₂) produces the β-phosphonium metallacycle **7** (40 °C, 22 h in CH₂Cl₂, 81% isolated yield), strongly suggesting that fluoride-abstraction occurs at the β position.¹⁹ We propose that C_β–F activation yields HF and an electrophilic π perfluoroallyl complex (**Int1** in Scheme 5), and the latter is trapped by the phosphine.

Scheme 5

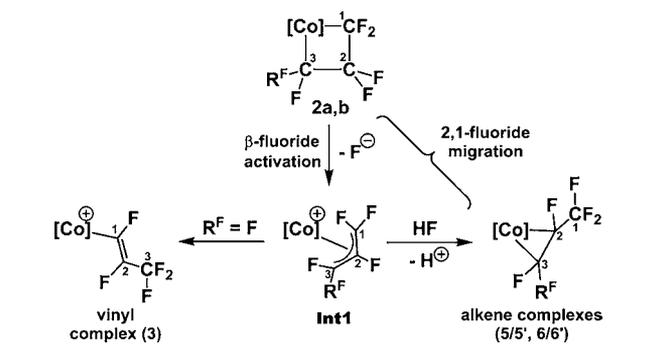


Nucleophilic attack of PMe₃ and F[–] at the β position of a related η³-perfluoroallyl iron complex has been documented, providing support for **Int1**.²⁰ Thus, the ring-opening and catalytic ring-contraction reactions likely proceed via a unique C_β–F activation pathway and probable allyl intermediates (**Int1**), rather than the expected C_α–F activation mechanism

observed previously for metal fluoroalkyls and fluorometallacyclopentanes.^{4,8b,14}

For $R^F = CF_3$, the σ allyl species was observed directly (4, above). In the case of $R^F = F$, an allyl complex is likely formed upon fluoride abstraction but undergoes isomerization to the CF_3 -substituted vinyl species (3) (Scheme 6, left), unless the

Scheme 6



intermediate is trapped by a nucleophile. The rearrangement of unsubstituted (i.e., C_3F_5) perfluoroallyl ligands to vinyl groups has been noted previously.²¹ When C–F activation is effected with catalytic $HNTf_2$, **Int1** is again a probable intermediate: we propose fluoride addition to the C_α position (C1 in Scheme 6, right) of the π allyl intermediate gives the observed perfluoroalkene complexes, with HF serving as the fluoride carrier. Hydrogen fluoride was observed by ^{19}F NMR in stoichiometric reactions between **2a** and $HNTf_2$, and the catalytic isomerization reactions were inhibited by the HF-scavenger CsF (SI).

In summary, we have made electron-rich cobalt fluorocarbenes, which react with TFE to form perfluorometallacyclobutanes. The cycloaddition of a perfluoroalkene to a metal fluorocarbene had not been demonstrated prior to this work.²² The metallacyclic products react with Lewis and Brønsted acids through an unusual β -fluoride activation mechanism. Under Brønsted acid catalysis, the metallacyclobutanes rearrange via 2,1-fluoride migration to alkene complexes (Scheme 6, right), instead of the desired metathesis or chain growth products (Scheme 3). Nonetheless, we conclude that the reactivity described here is promising for metal-catalyzed metathesis and polymerization of perfluoroalkenes. New ligand/metal motifs will likely be required to achieve these unprecedented processes. In a combined experimental and computational effort, we are seeking new systems to address (i) the slow reactions with TFE and (ii) the preference for perfluoroalkene complex formation over metal fluorocarbenes upon C–F activation.

ASSOCIATED CONTENT

Supporting Information

Experimental details and data. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(19) Reaction of **2a** with the alternative Lewis acid AgBF_4 produces **7** as its BF_4^- salt, along with other products apparently resulting from β -fluoride activation. See the SI.

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