Copper-Catalyzed Hydrodefluorination of Fluoroalkenes

Nancy Xu, Nicholas O. Andrella and R. Tom Baker*, *Department of Chemistry and Biomolecular Sciences and CCRI, University of Ottawa, Ottawa, ON K1N 6N5*

Introduction

Fluorinated alkenes have various applications in the world of industrial chemistry, ranging from refrigerants and foam-blowing agents, to fluoro-polymers and even as components for pharmaceutical synthesis. With such wide applications, the demand for fluoroalkenes is high. However, current methods of synthesis are difficult and inefficient.

Established routes of synthesis for fluoroalkenes in the literature usually involve a combination of:

I. Halogen exchange reactions
II. Hydrogenation
III. Dehydrohalogenation

However, such reactions require harsh conditions in addition to producing hydrogen fluoride, a corrosive gas, as a major byproduct.

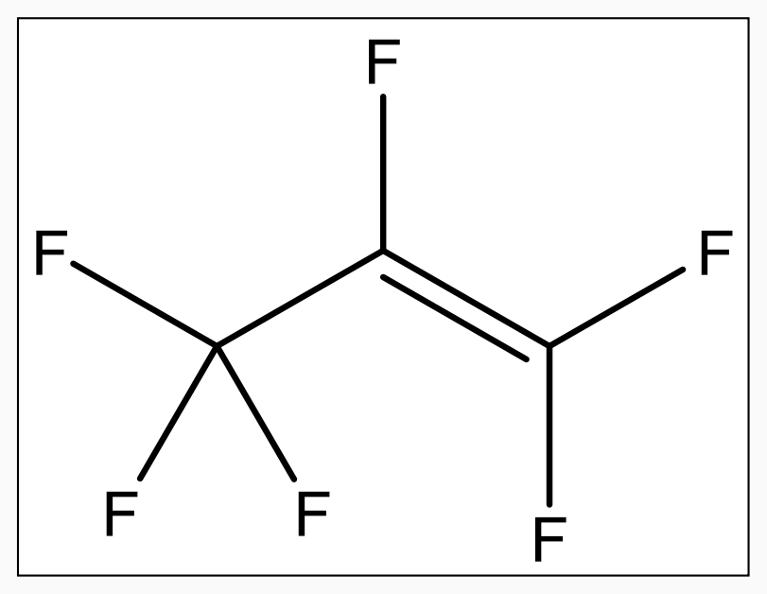


Figure 1. Chemical structure of hexafluoropropene

Our research goal is to create greener routes to these fluoroalkenes through hydrodefluorination. The approach is to use a source of copper hydride as catalyst and to vary the type of ligand in the reaction to selectively replace fluorine with hydrogen.

Methodology

Two types of reactions were run:

1. Ligand screening of the copper catalyzed hydrodefluorination of hexafluoropropene
2. Attempted hydrodefluorination of tetrafluoroethylene

Step 1

- **Method A**: Prepare ligand screen reactions in the glovebox (inert atmosphere) in an NMR tube for the hydrodefluorination reactions
- **Method B**: Reactions are prepared in a vial for scale-up and isolation of a copper tetrafluoroethyl complex, Cu-CF_2CF_2H, observed in the unsuccessful hydrodefluorination of tetrafluoroethylene.

Step 2

- Inject gas of choice, using an air-tight syringe, and let reaction run to completion.
- **Method A**: Hexafluoropropene is used, 3 mL.
- **Method B**: Tetrafluoroethylene is used, 20 mL

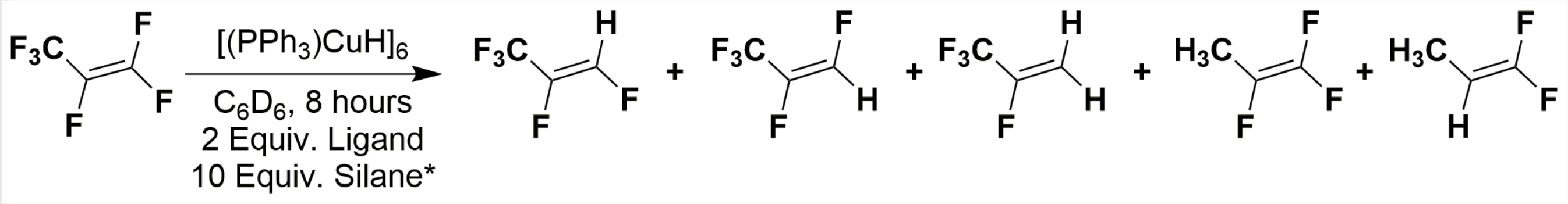
Step 3

- **Method A**: Analyze reaction products using ^{19}F, ^{1}H, ^{13}C, ^{31}P NMR, and gas-chromatography-mass spectrometry.
- **Method B**: Product is recrystallized from Et_2O at -30 °C for characterization. This provided satisfactory crystals for single crystal X-ray diffraction of the target copper complex.

Results

1. Effects of changing the ligand on the copper-catalyzed hydrodefluorination reaction.

Figure 2. Table describing the various effects of ligands on the conversion of hexafluoropropene (HFP) to other fluoroalkenes.



Ligand	Yields of	dissolved	gases vs.	BCDB	int. std.
No ligand	22 %	16 %			
PPh_3	13 %		21 %		
$P(OEt)_3$				3 %	30 %
P(*o*-tolyl)$_3$	24 %	14 %	4 %		
t-BuXphos	15 %		20 %		
dppe			33 %		3 %
dppf			12 %		16 %
Xantphos			12%		16%
IPr			*N/A*		

***Silane was 1,1,3,3-tetramethyldisiloxane (TMDSO)**

2. Synthesis and isolation of a copper tetrafluoroethyl complex.

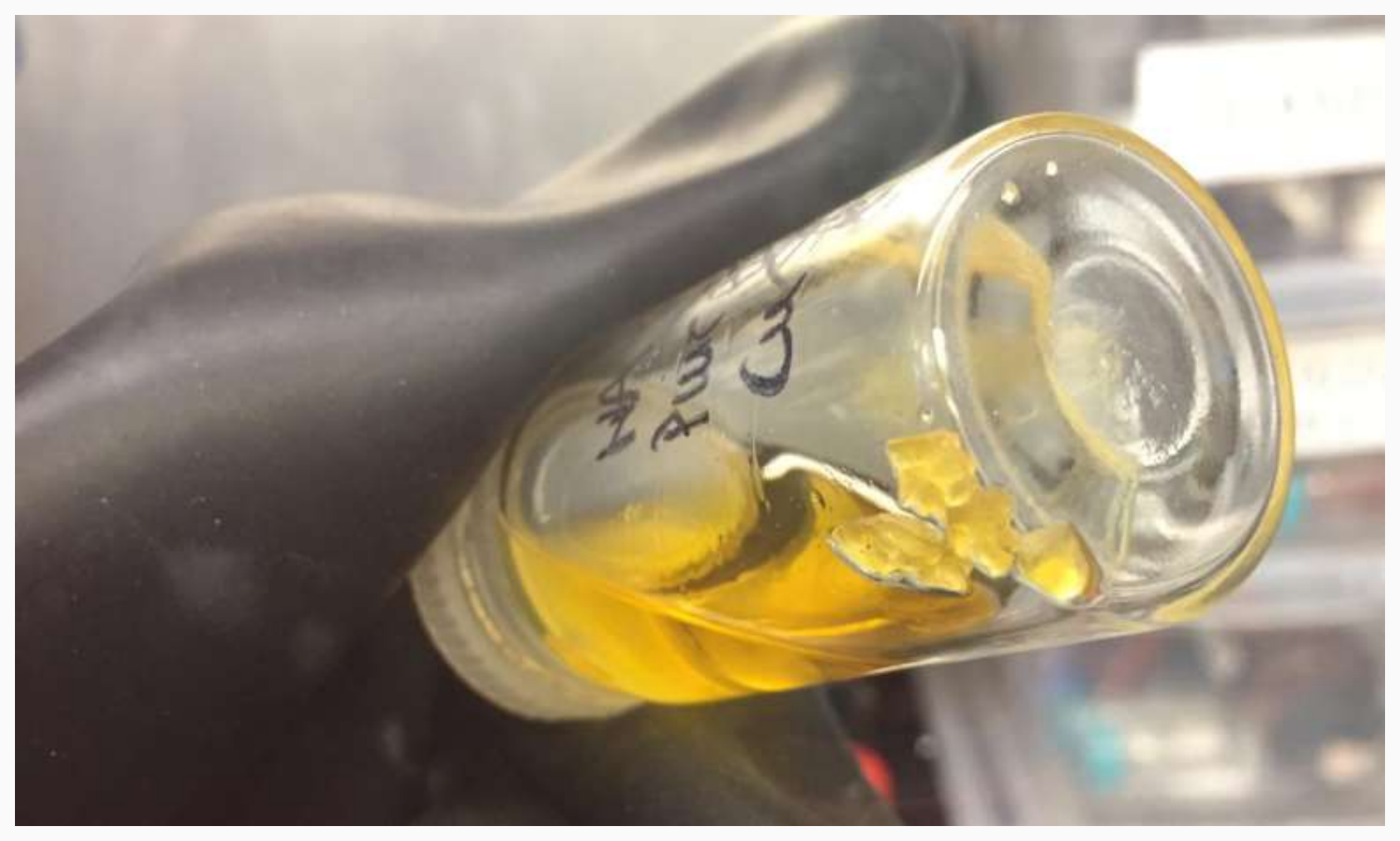


Figure 3. Crystals of $[(PPh_2Me)_3Cu(C_2F_4H)]$

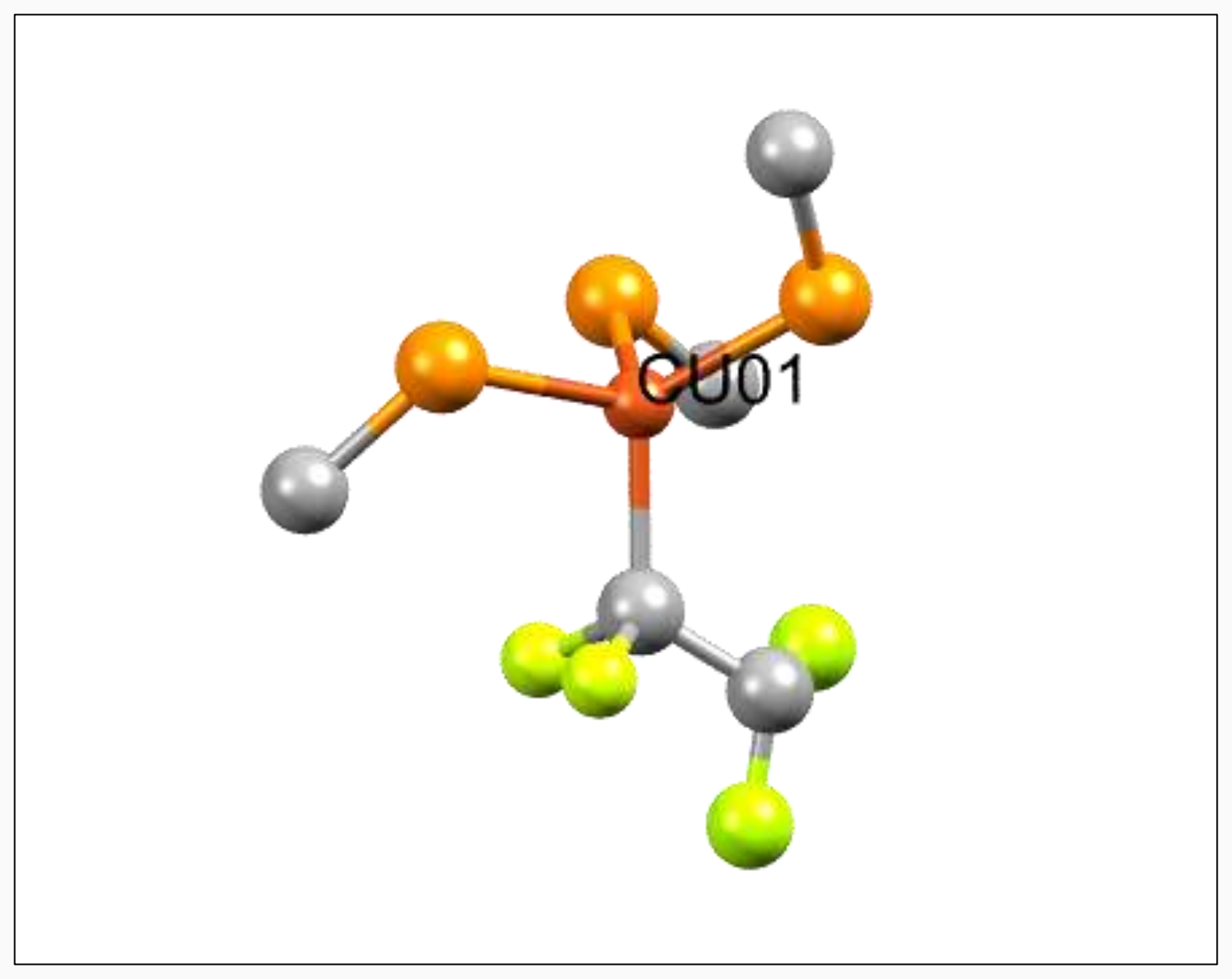


Figure 4. POV-ray representation of the preliminary molecular structure of $[(PPh_2Me)_3Cu(C_2F_4H)]$ with phenyl fragments and hydrogens omitted for clarity

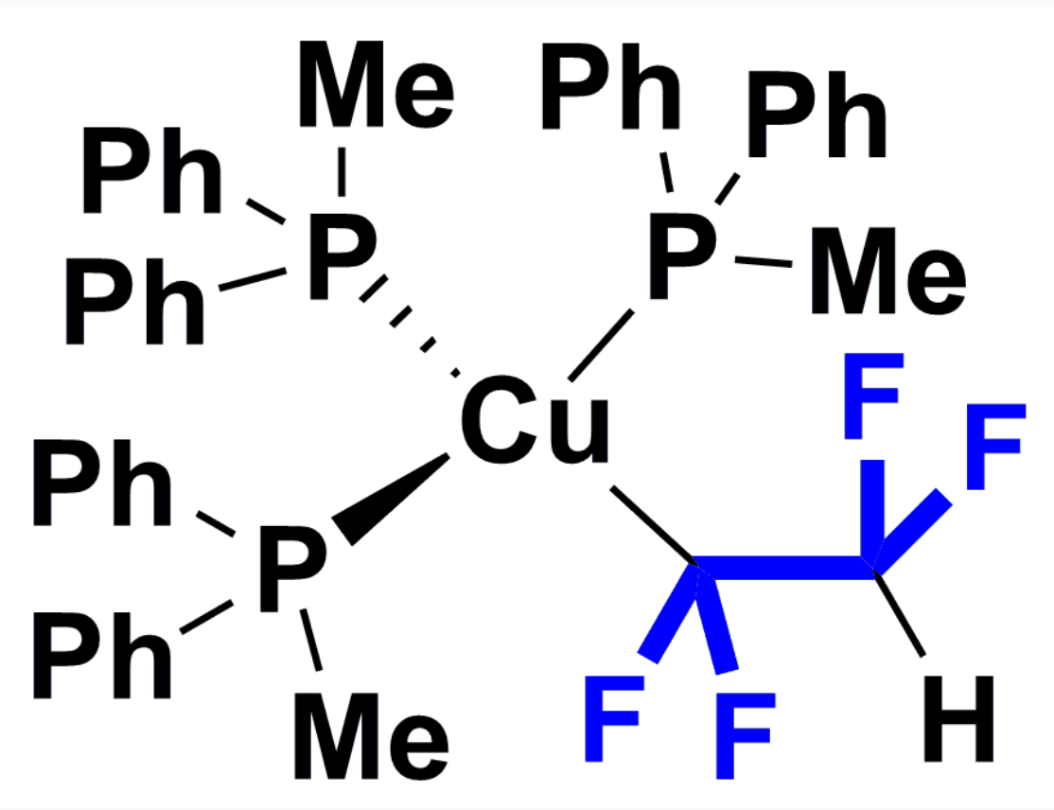


Figure 5. Chemical structure of $[(PPh_2Me)_3Cu(C_2F_4H)]$. **Highlighted in blue** is the fluorinated fragment arising from tetrafluoroethylene ($F_2C=CF_2$).

Discussion

Effects of changing the ligand (**Figure 2**):

A. When no excess ligand is added, the reaction fully converts hexafluoropropene (HFP) to an isomeric mixture of (E,Z)-1,2,3,3,3-pentafluoropropene (PFP).

B. Adding excess triphenylphosphine to the reaction immediately produces PFP isomers and selectively converts (E)-PFP to 2,3,3,3-tetrafluoropropene after a few hours. This is similarly seen when using an electron-rich and bulky ligand (i.e. tBuXphos).

C. When a bulky aromatic phosphine is used, the reaction rapidly converts HFP to PFP isomers but then stops functioning. DPPE, DPPF and Xantphos all convert HFP to tetrafluoropropene and even difluoropropene. It is seen that bidentate ligands and the phosphite generate the most active catalysts.

Using different sources of fluoroalkenes:

A. When reacting Cu-H with other fluoroalkenes, there was formation of hydrodefluorination products but conditions require further optimization.

B. When Cu-H is reacted with tetrafluoroethylene (TFE), there is formation of a stable copper tetrafluoroethyl complex (**Figures 3-5**) that is thermally robust. To achieve hydrodefluorination of TFE, a Lewis acid can be added.

Conclusions

A. When hexafluoropropene was reacted with a silane (as a source of hydride) and a catalytic amount of copper, successful hydrodefluorination was achieved.

I. The reaction is highly dependent on the stoichiometry of the silane that is used.
II. With a more electron-rich olefin hydrodefluorination is significanty slower. As such, ***mono***-hydrodefluorination is preferred over ***di***-hydrodefluorination and ***tri***-hydrodefluorination
III. Of note for 1,2,3,3,3-pentafluoropropene, the rate of substitution of the *E* isomer is significantly faster than *Z.*

B. With judicious choice of the ligand we could achieve selective hydrodefluorination to the fluoroalkene of choice.

C. The stable and easily isolated copper tetrafluoroethyl complex will be explored for use in cross-coupling reactions.

References

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2. Hu J.Y., Zhang J.L. (2015) *Hydrodefluorination Reactions Catalyzed by Transition-Metal Complexes*. in: Braun T., Hughes R. (Eds) Organometallic Fluorine Chemistry. Topics in Organometallic Chemistry, vol 52. Springer.

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