**Introduction**

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

Established routes of synthesis for fluoralkenes 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.

Our research goal is to create greener routes to these fluoralkenes 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-CF₃CF₂H, observed in the unsuccessful hydrodefluorination of tetrafluoroethylene.

### Step 2

- **Method A**: 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 ¹⁹F, ¹H, ¹³C, ¹⁹P NMR, and gas-chromatography-mass spectrometry.
- **Method B**: Product is recrystallized from Et₂O 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 fluoralkenes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Yields of dissolved gases vs. BCDB</th>
<th>int. std.</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ligand</td>
<td>22 % 16 %</td>
<td>21 %</td>
</tr>
<tr>
<td>P(PhH)₃</td>
<td>13 %</td>
<td>3 % 30 %</td>
</tr>
<tr>
<td>P(OEt)₃</td>
<td>24 % 14 %</td>
<td>20 %</td>
</tr>
<tr>
<td>P(o-tolyl)₃</td>
<td>15 %</td>
<td>33 % 3 %</td>
</tr>
<tr>
<td>dppf</td>
<td>12 % 16 %</td>
<td>16 %</td>
</tr>
<tr>
<td>Xantphos</td>
<td>12% 16%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

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

2. Synthesis and isolation of a copper tetrafluoroethyl complex.

   **Figure 3**: Crystals of [(PPh₃)₃Cu(CF₃H)]

   **Figure 4**: POV-ray representation of the preliminary molecular structure of [(PPh₃Me)₃Cu(CF₃H)] with phenyl fragments and hydrogens omitted for clarity

   **Figure 5**: Chemical structure of [(PPh₃Me)₃Cu(CF₃H)]. Highlighted in blue is the fluorinated fragment arising from tetrafluoroethylene (F,C=CF₂).

**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,2)-2,2,3,3,3-pentafluoropropene (PFPP).

B. Adding excess triphenylphosphine to the reaction immediately produces PFPP isomers and selectively converts (E)-PFPP 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 PFPP isomers but then stops functioning. DPFPE, DPPF, and Xantphos all convert HFP to tetrafluoroethylene and even difluoropropene. It is seen that bidentate ligands and the phosphite generate the most active catalysts.

**Using different sources of fluoralkenes:**

A. When reacting Cu-H with other fluoralkenes, 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 significantly 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 fluoralkene 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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