Reactivity of fluorinated C_3-Olefins at Nickel (0)

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Abstract

This project is related broadly to the study of coördination chemistry, and more specifically to the study of fluoroörganometallic chemistry—that is, the study of interactions of fluorinated organic compounds with metals. The specific purpose of this project is to study the reactivity of three-carbon fluorinated olefins at zerovalent nickel with a variety of ligand systems. While the coordination chemistry of hexafluoropropene has been investigated previously, we were interested to investigate the possibility of C-F and/or C-O bond activation in trifluoromethyl trifluorovinyl ether (PFMVE) and 3,3,3-trifluoropropene (HFO-1243zf). The effects of electron-rich ligands, such as N-heterocyclic carbenes (NHCs) or trialkylphosphines on the formation of complexes were examined. To do this, NHC precursors, 1,3-substituted imidazolium salts, were synthesized in the fume hood. Due to the air-sensitivity of free carbenes and alkyl phosphines, the remaining preparative work was done in a nitrogen-filled glovebox. The fluoroölefin gases were injected into NMR tubes or vials using a syringe and reaction progress was analyzed by ^{19}F NMR spectroscopy. It was found that 1243zf reacts with Ni(cyclooctadiene)$_2$ and the NHC ligand, IAd, forming a 3-membered metallacycle (π-olefin complex) which can be precipitated by conducting the reaction in a nonpolar solvent. For the vinyl ether, unselective C–F bond activation products form, which we believe to arise from the three-membered metallacycle which could also be discerned in the NMR spectrum.

Background

N-heterocyclic carbenes have been used as ligands for nickel-adducts of various fluorinated olefins incl. tetrafluoroethylene and vinylidene difluoride. With the former, three-coördinate metallacyclopentanes formed[2], while with the latter, β-fluoride elimination from an intermediate metallacyclopentane has been observed[3].

References

1. Asthana, A. (2017, April 20). Introduction to Coordination Chemistry.
2. N. O. Andrella *et al. Chem. Sci.* **2015**, *6*, 6392-6397.
3. A. J. Sicard (unpublished work).

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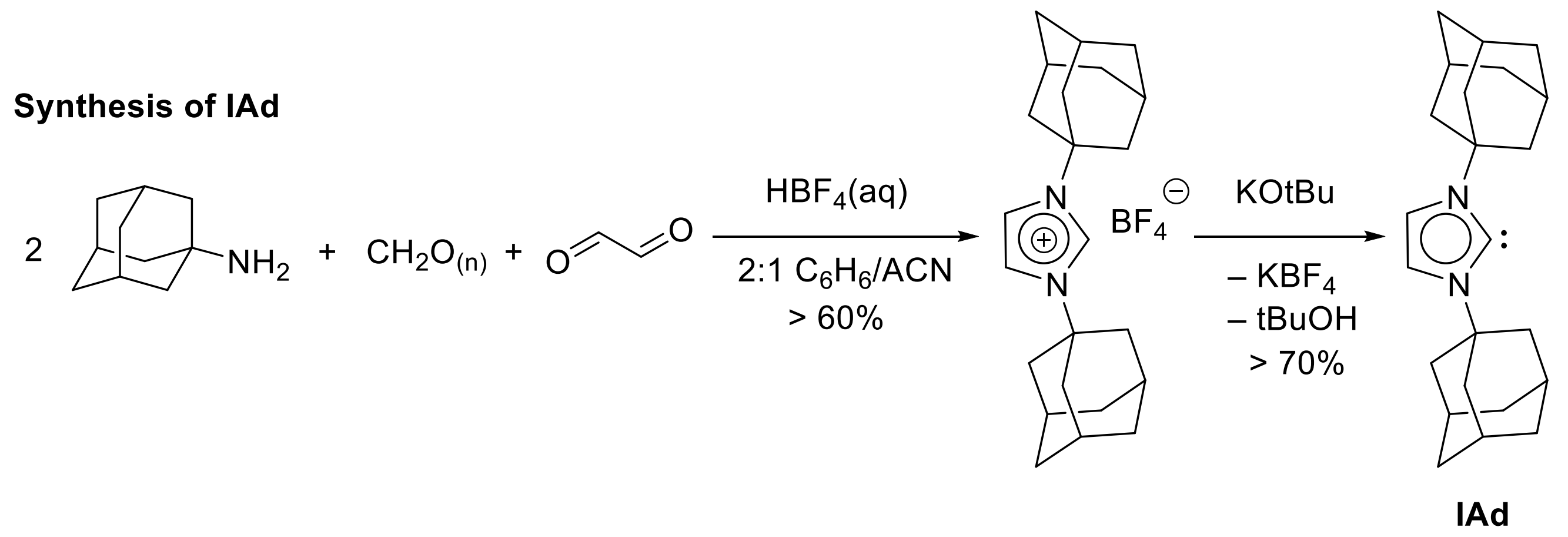
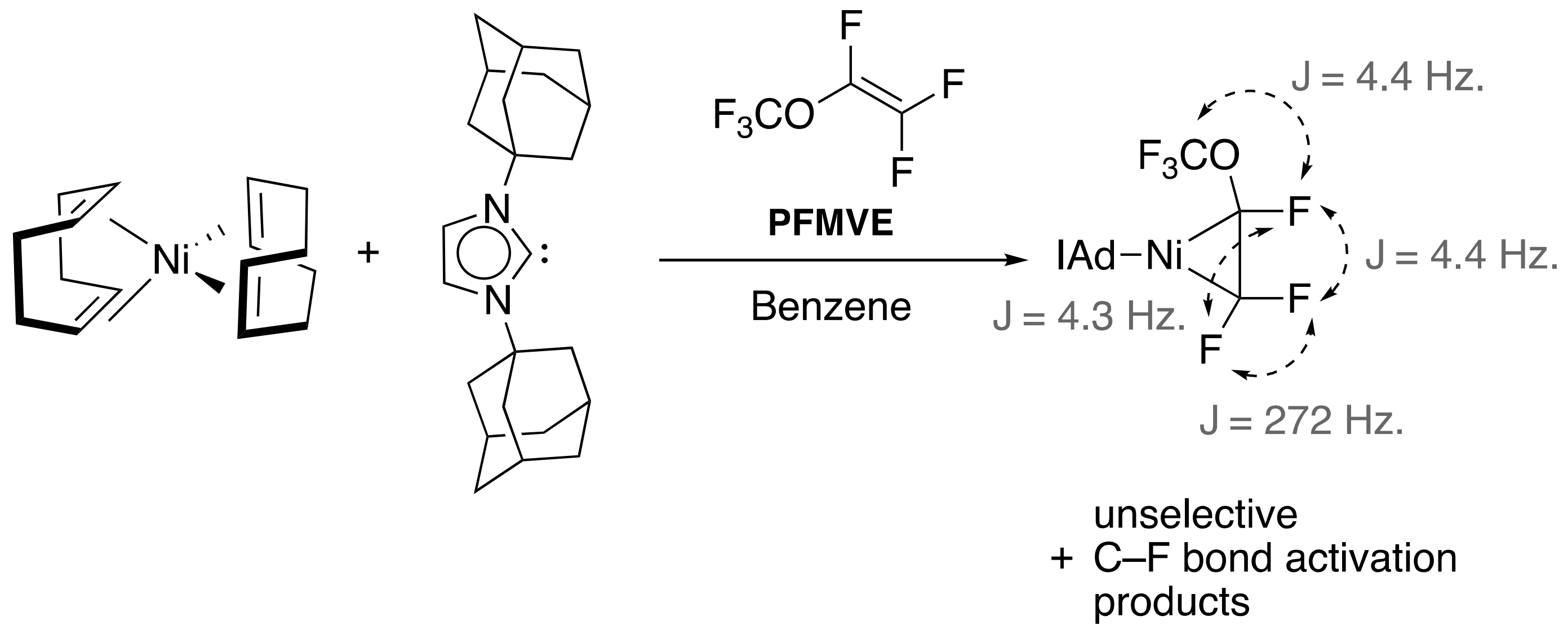
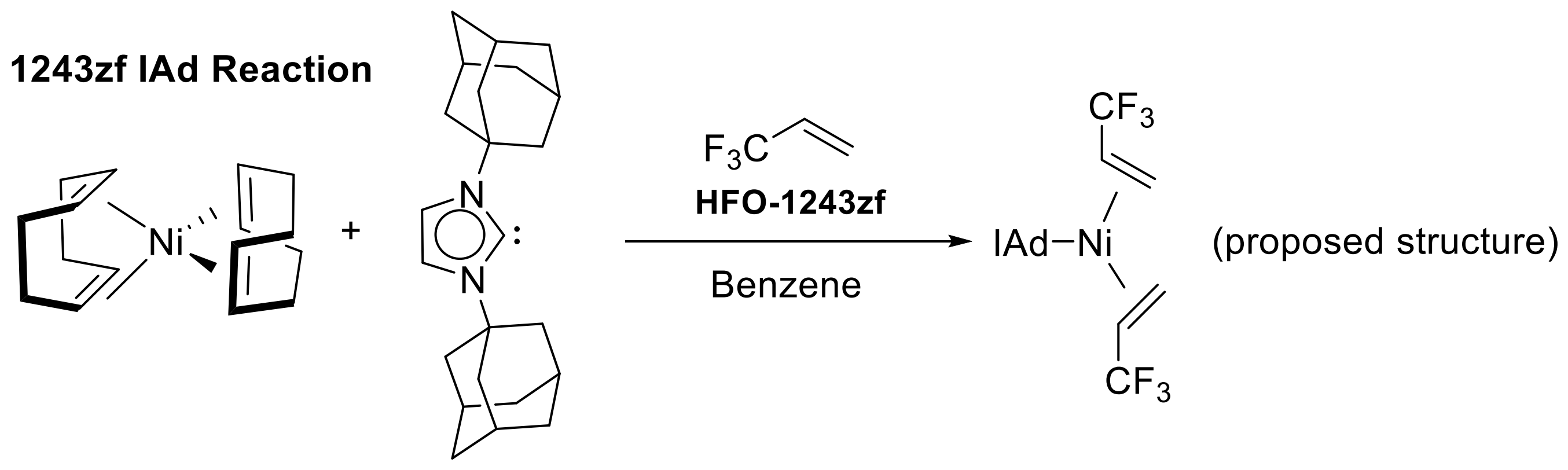
Methods

Synthesis of IAd





1243zf IAd Reaction



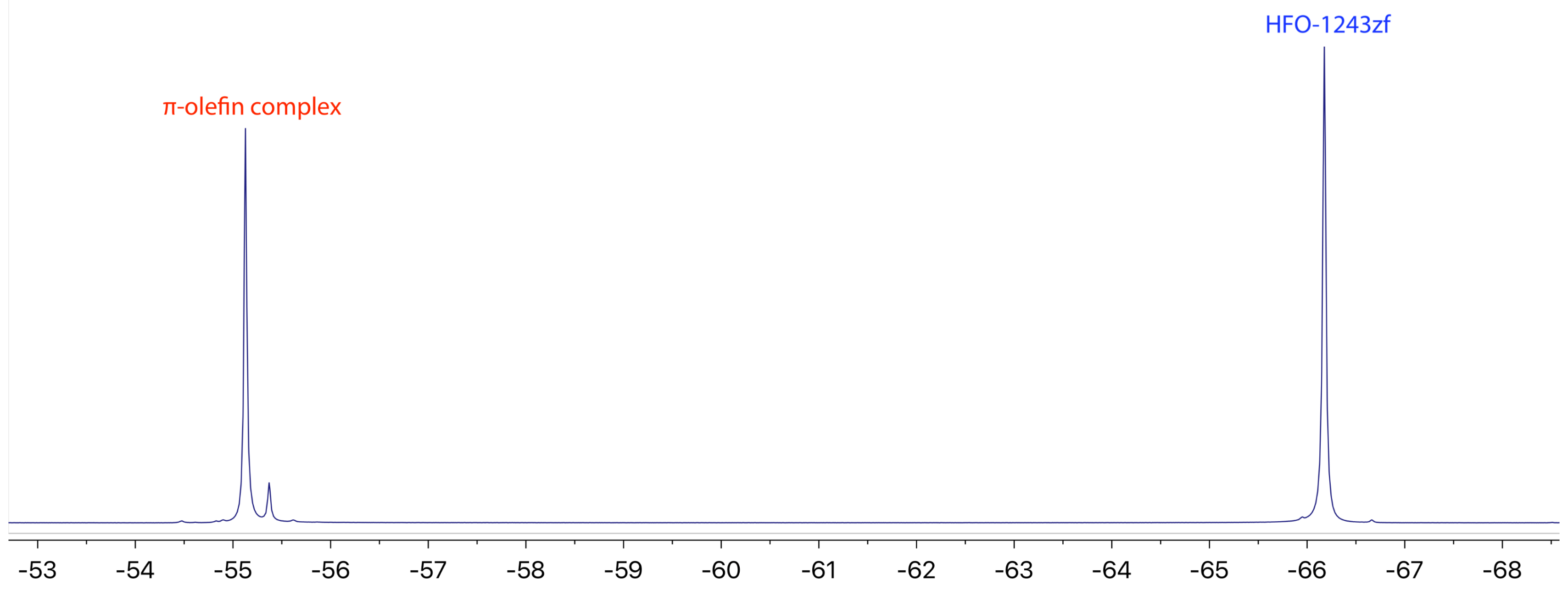
- Organic reactions were performed to synthesize 1,3-dialkylimidazolium salts (NHC precursors) in the fume hood.
- This process involved multi-component one-pot reactions (all done in a flask), extractions (to separate unwanted compounds or impurities from the phase containing the desired product) and recrystallizations (to obtain a pure product).
- The neutral NHC, IAd, was prepared in a nitrogen-filled glovebox by deprotonating its precursor salt using potassium tert-butylate.
- Air-sensitive ligands were chelated to the nickel compound by adding the reactants to an NMR tube in the glovebox, along with 550 µL of deuterated benzene (or in a small vial with a bonded-septum cap containing approximately 5 mL of proteo-solvent)
- To insert the olefin, the gas was withdrawn from its lecture bottle with a syringe through a septum and injected into the NMR tube or vial through a gas-tight septum.
- Results were monitored by ^{19}F NMR and possible product structures were determined

Results

The ^{19}F NMR of the HFO-1243zf reaction with IAd and Ni(cod)$_2$ is shown on the right.

A sharp peak around -55 ppm represents the π-olefin complex (three-membered metallacycle), while the peak at -66 ppm is simply some unreacted HFO-1243zf (the olefin).

It is proposed that the bis(olefin) adduct is forming and that the small peak to the right is a different, less favored isomer (possibly with the CF_3 oriented in the opposite direction).



Conclusions

- HFO1243zf reacts with the nickel/IAd complex to produce a three-membered metallacycle (right reaction scheme)
- Further studies are being done to observe the effects of PFMVE on the nickel complex (left reaction scheme)
- Perhaps another bulkier ligand will be used in the future to control the reaction with Ni(0) and PFMVE and improve the selectivity.