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AFRL

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LEAD | DISCOVER | DEVELOP | DELIVER



Synthesis and Reactivity of Backfluorinated NHC Carbene Complexes

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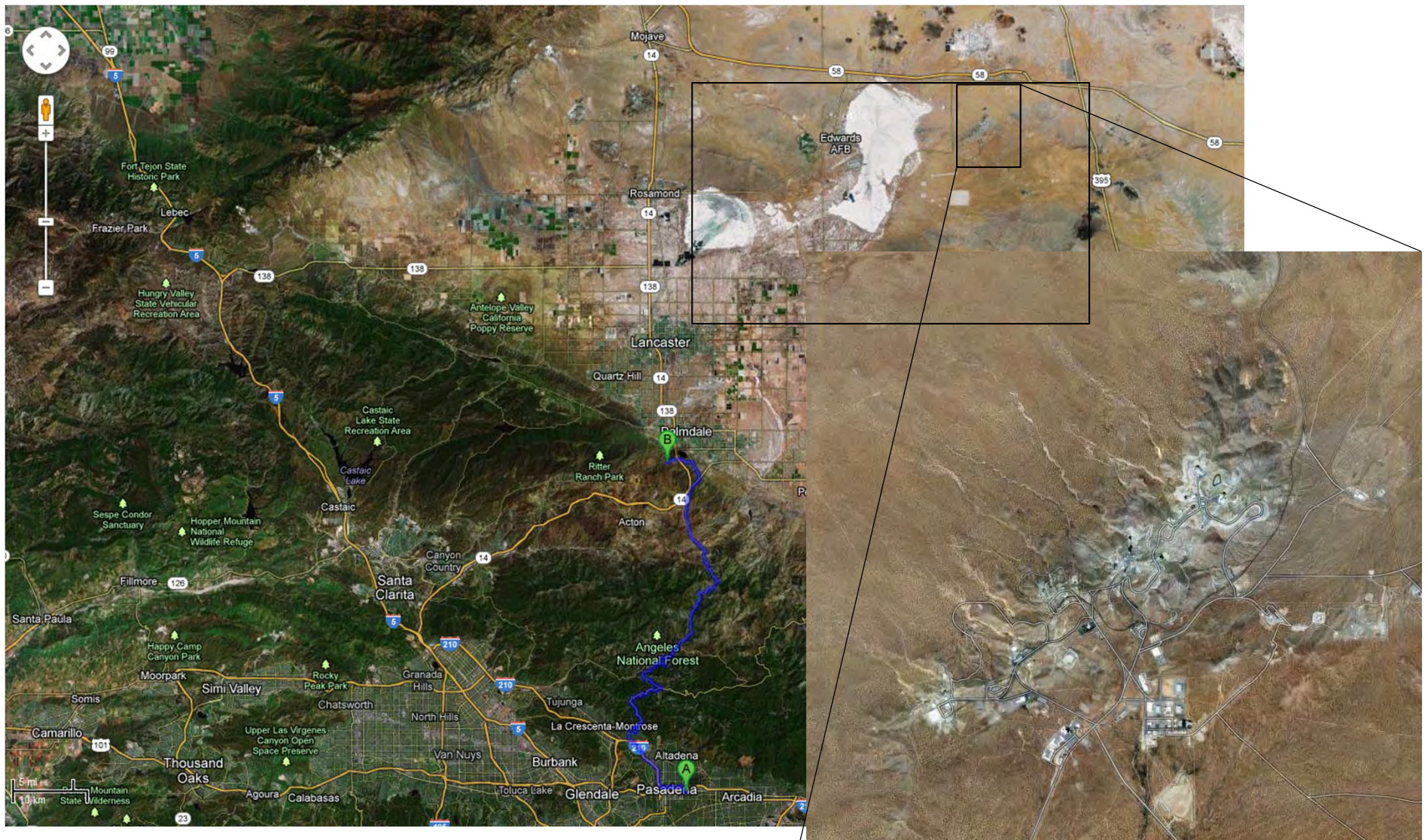
Introduction



- **Introduction**
- **Proposed Research Overview**
- **Synthesis of Backfluorinated NHC Carbene Precursors**
 - **Synthesis of Ir complexes**
 - **IR study of Ir dicarbonyl complexes**
 - **Synthesis of Ru complexes**
 - **Reactivity of Ru complexes**
- **Conclusions and Future Directions**



Edwards AFB – AFRL Rocket Propulsion Research





Palmdale to AFRL: 53 miles Located in the Middle of Nowhere





Edwards AFB



- **History**

- Originally known as Muroc Army Air Corps Base
- Test flights of the YB-42 (first American Jet) in the early '40s
- Location where Chuck Yeager broke the Sound Barrier in the Bell X-1 (Original craft at the Smithsonian)
- X-15 sub-orbital flights in the '60s (Armstrong)

- **AFRL**

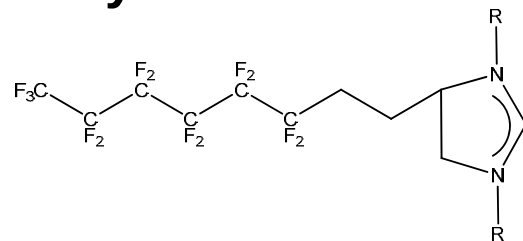
- Tenant of Edwards AFB since late '50s
- Full scale testing of the Atlas rockets (Gemini missions)
- Initial testing of the F-1 engine (Apollo missions) performed on site in the mid '60s
- Large scale testing of solid rocket motors (Titan IV)
- “Iranian nuclear facility” destroyed by the Transformers in “Transformers: The Dark side of the Moon”



Edwards AFB – AFRL Projects



- **The Air Force has an interest in NHC carbene precursors for a variety applications**
 - Ionic liquid propellants and additives
 - Ligands for Supercritical Chemical Fluid Deposition (SCFD)
- **The Air Force also has an interest in fluorinated NHC carbenes**
 - perfluoroalkyl chains generally known to improve solubility of systems in supercritical fluids
 - “Backfluorinated” NHC carbenes to improve solubility in supercritical fluids and perhaps maintain ligand stability
 - Surprisingly, the backfluorinated systems have never been reported





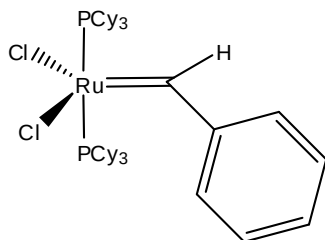
Potential for Collaboration Backfluorinated NHC-Ru Catalysts



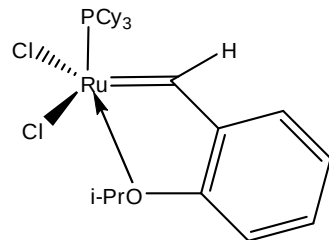
- It was an easy leap to see that this technology should be applicable to other research areas
 - Hydrogenation in fluorinated solvents
 - Organic transformations in fluorinated solvents
 - Olefin metathesis in fluorinated solvents
 - Perhaps improved olefin metathesis of fluorinated olefins
- Questions
 - How does the addition of a perfluoroalkyl chain to the back of an imidazolinyldene ligand affect its electronic properties?
 - How does the addition of a perfluoroalkyl chain to the back of an imidazolinyldene ligand affect the catalytic properties of the ruthenium alkylidene complexes?
 - Does the addition of perfluoroalkyl chains improve the solubility of Ru alkylidene complexes in fluorinated solvents?



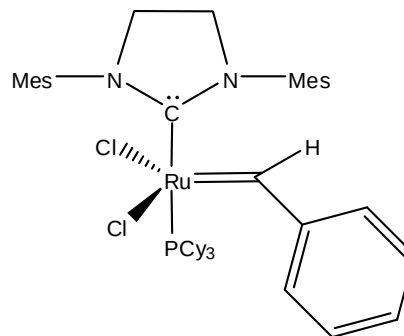
Fluoroalkene Metathesis



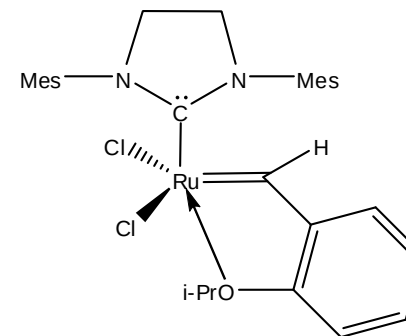
1st Generation Grubbs' Catalyst



1st Gen Grubbs-Hoveyda Catalyst



2nd Generation Grubbs' Catalyst

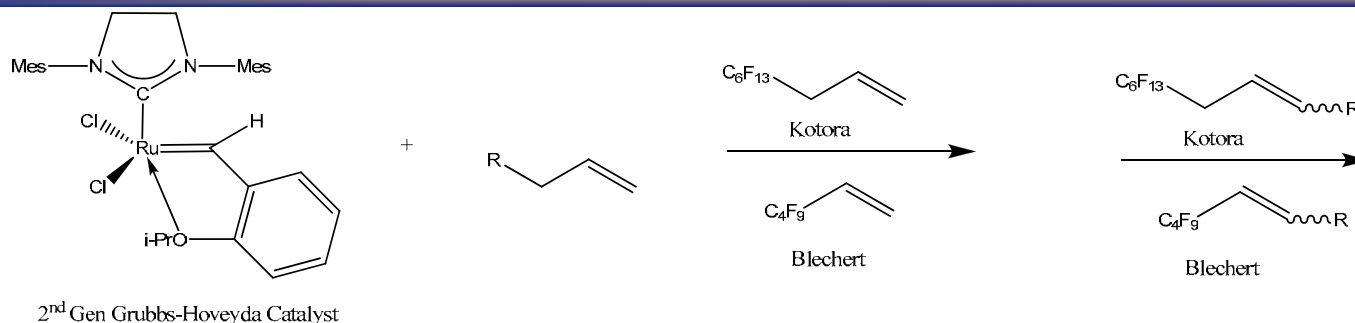


2nd Gen Grubbs-Hoveyda Catalyst

- **Fluoroalkene metathesis first reported by Blechert in 2001**
- **1st generation systems not effective**
- **2nd generation systems are effective**
 - **2nd Generation Grubbs-Hoveyda most effective**



Fluoroalkene Metathesis



- Blechert (2001) found that cross metathesis of perfluorobutyl(ethene) and various allylics required 10 mol% of catalyst with generally good yields (7-95+%)
- Kotora (2010) found that the cross metathesis of perfluorohexyl(propene) and various allylics was effective for several systems but the yields varied considerably (11-70% yield)
- Also, when the perfluoroalkyl chain is longer (perfluorooctyl-, perfluorodecyl-), personal research suggests that the catalyst has solubility issues



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SPECIAL PROGRAMS: AIR FORCE VISITING SCIENTIST PROGRAM



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Visiting Scientist Program

Who

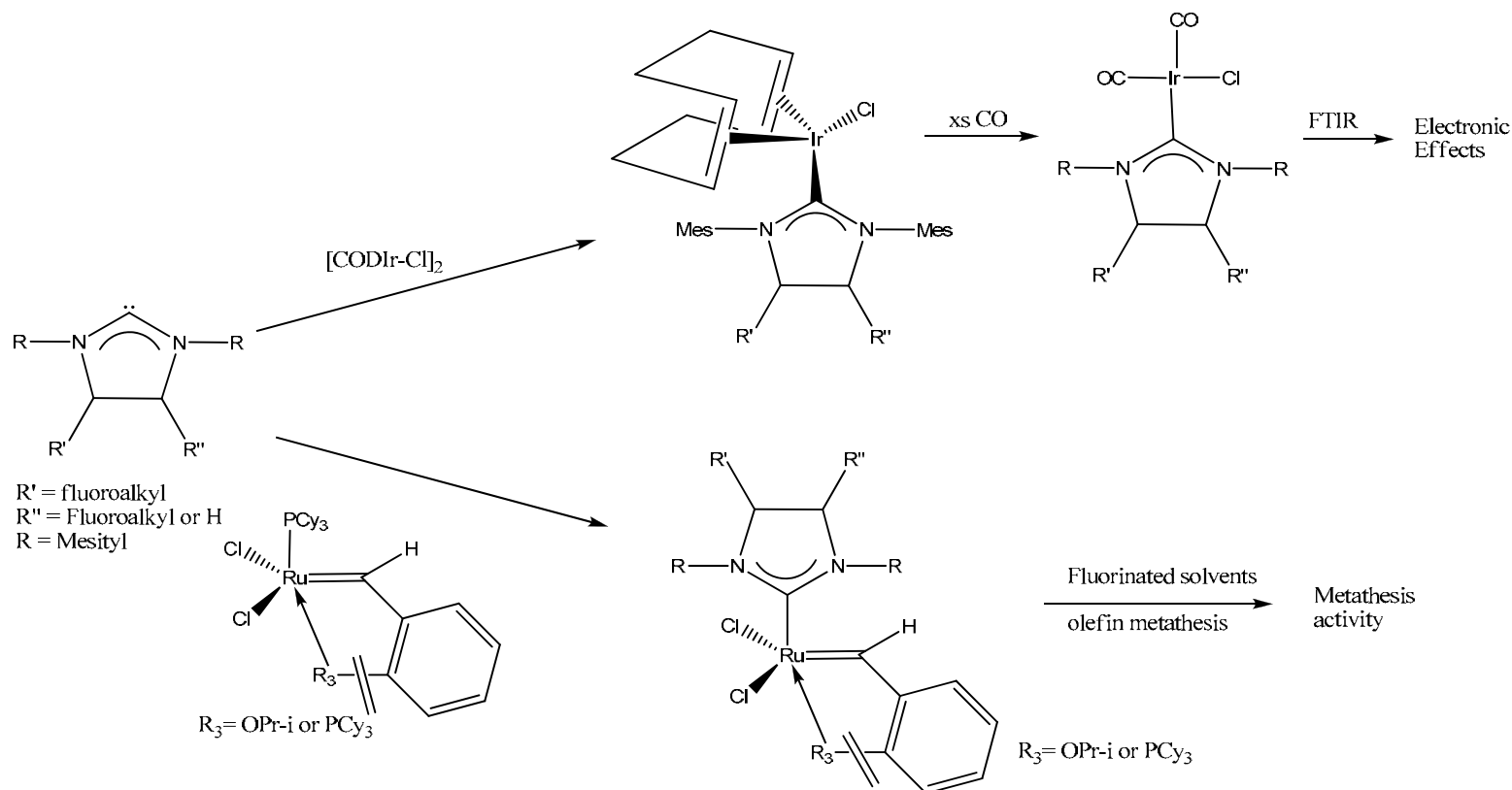
Outstanding Air Force scientists and engineers at grades GS-12 and above or the military equivalent

What

Chance to conduct full-time, hands-on research at top-notch research facilities throughout the country



Proposed Research

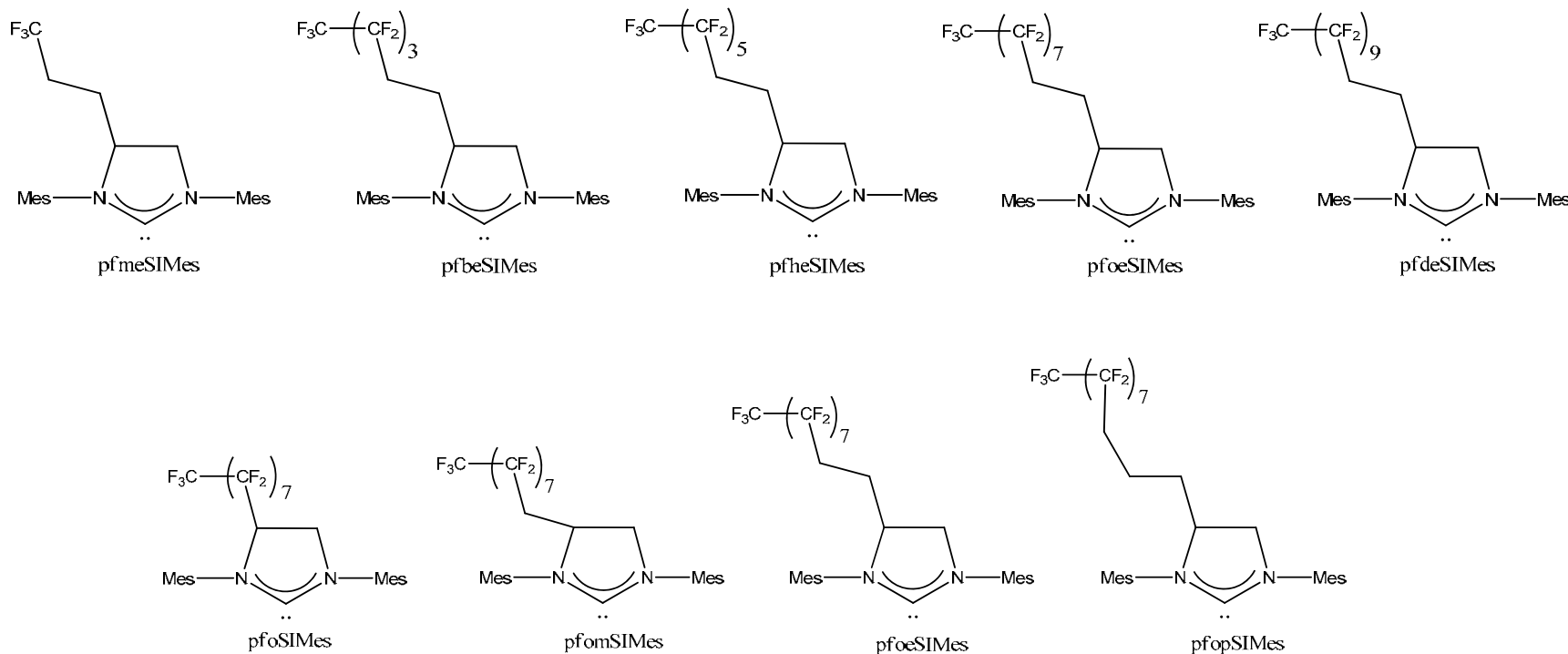


- **Electronic effects will be investigated**
 - Effect of perfluoroalkyl length and methylene “buffer” length
- **Olefin metathesis activity will also be investigated**



Synthetic Targets

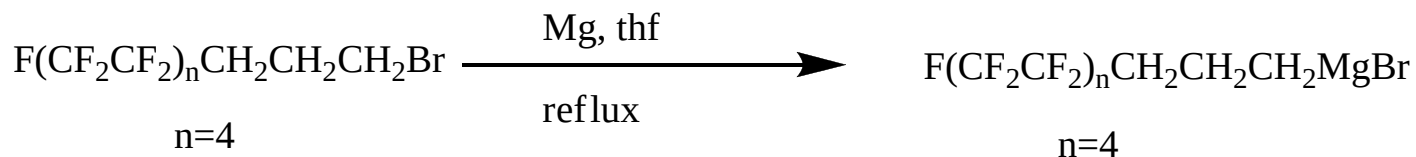
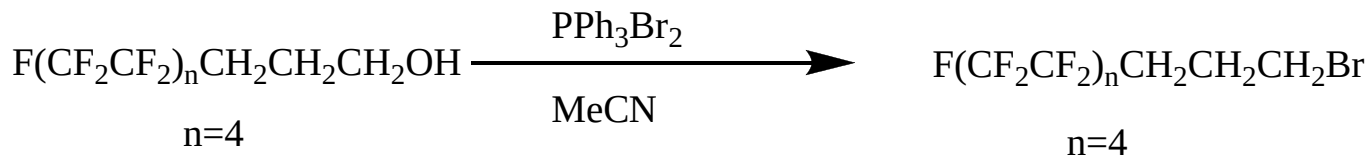
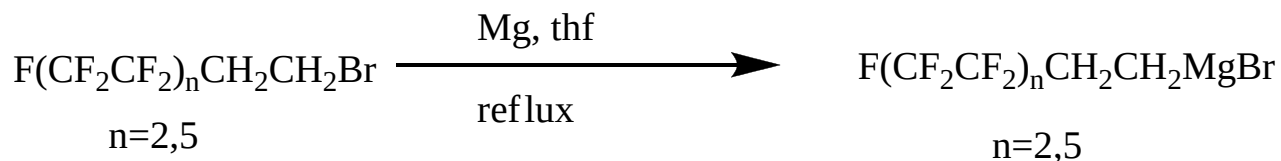
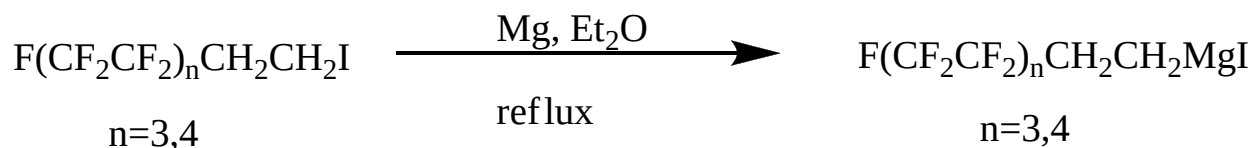
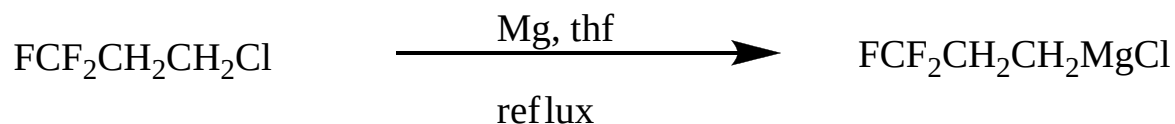
Imidazolidine Complexes



- Perfluoroalkyl chain length and “Buffer” length will be investigated



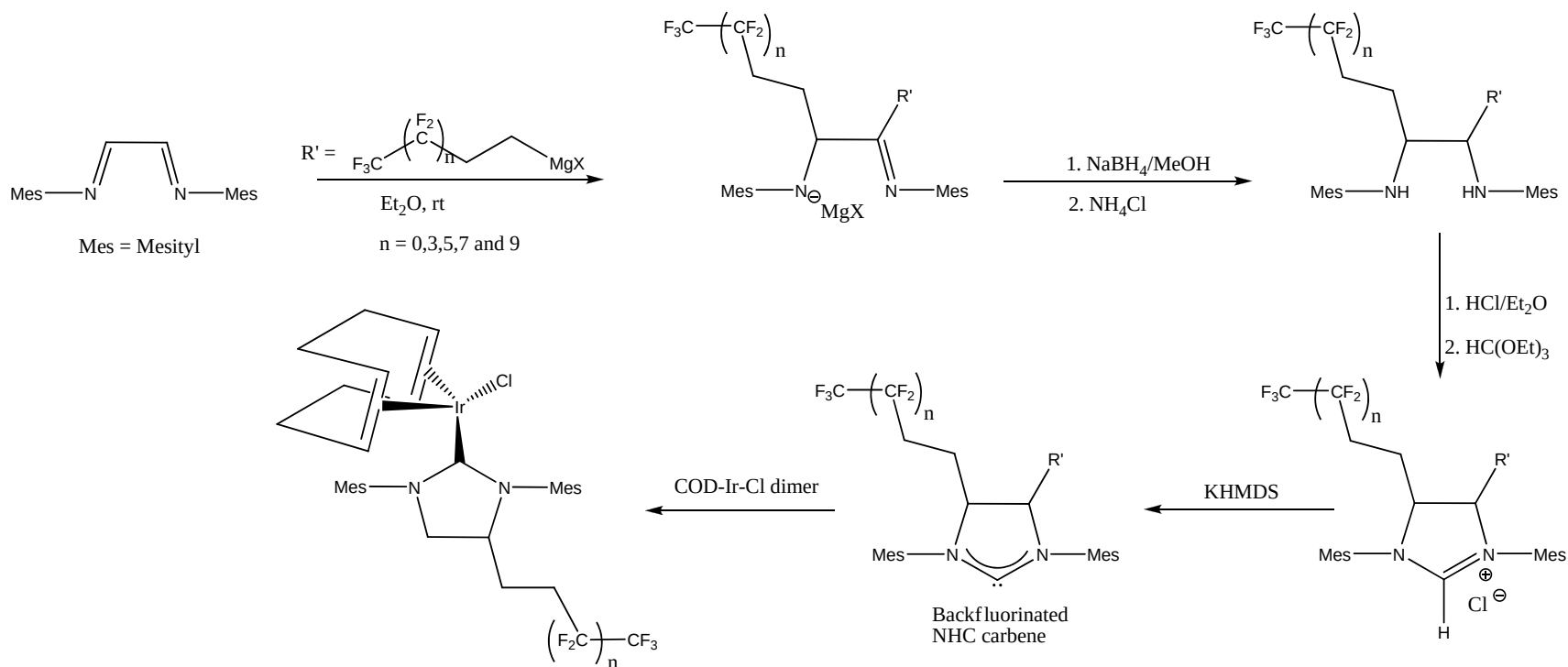
Preparation of Perfluoroalkyl Grignard Reagents





Synthetic Method #1

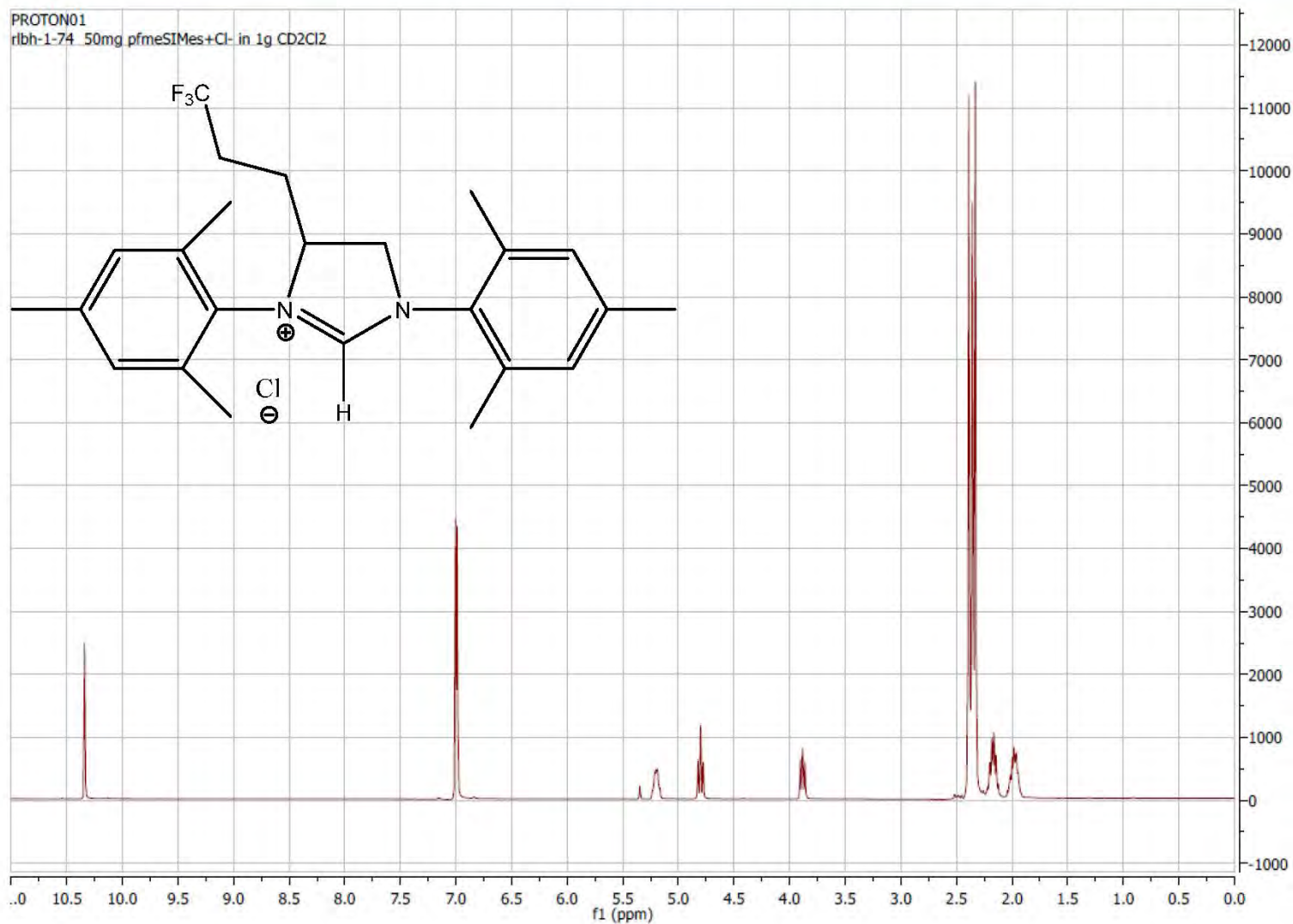
Grignard Addition/Reduction/Cyclization



- Very general reaction pathway: suitable for all Grignard reagents
- Attempts at dialkylation unsuccessful
- Slight excess of Grignard reagent ensures complete monoalkylation

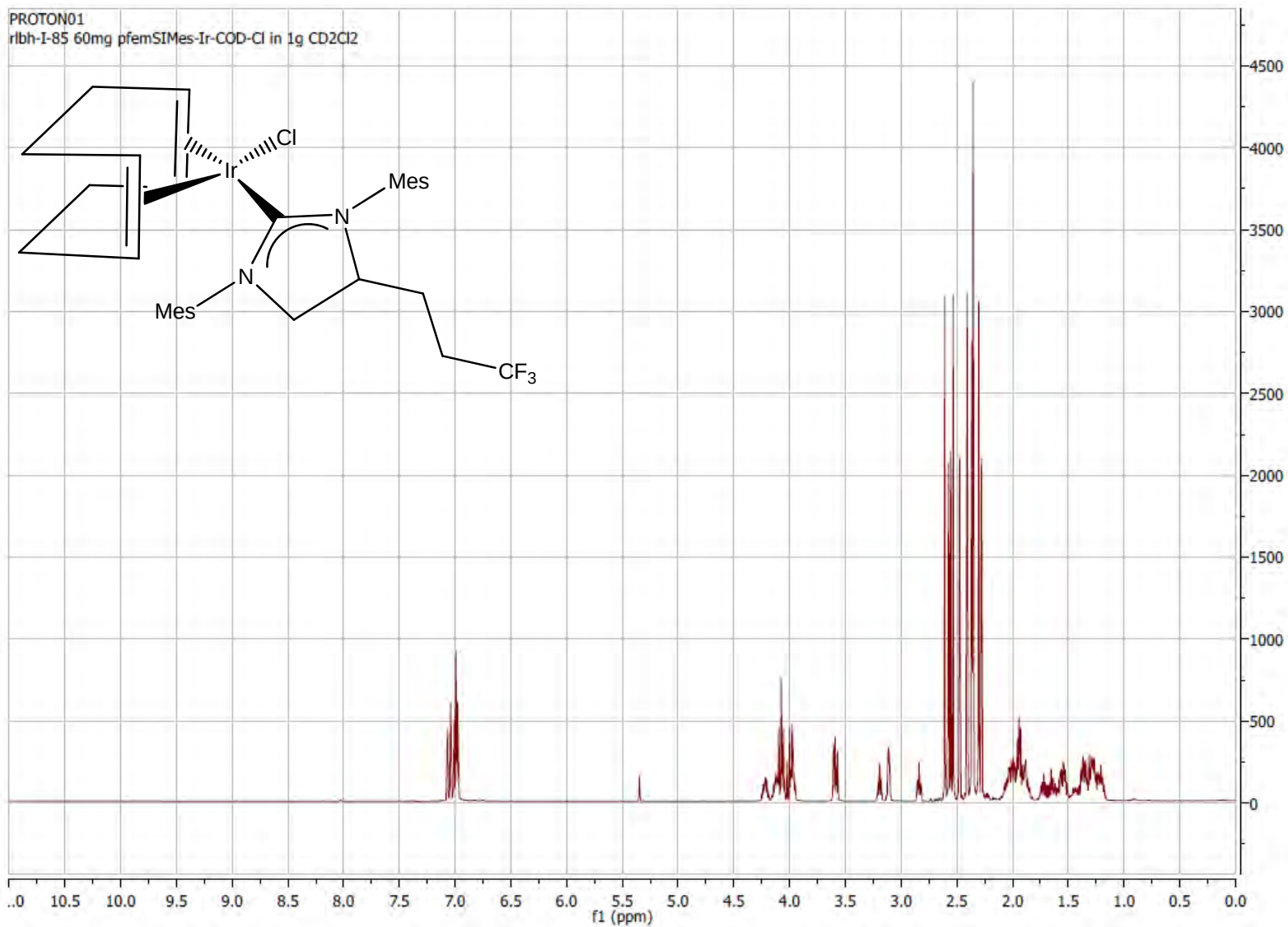


^1H Spectrum of pfme-SIMes+Cl⁻



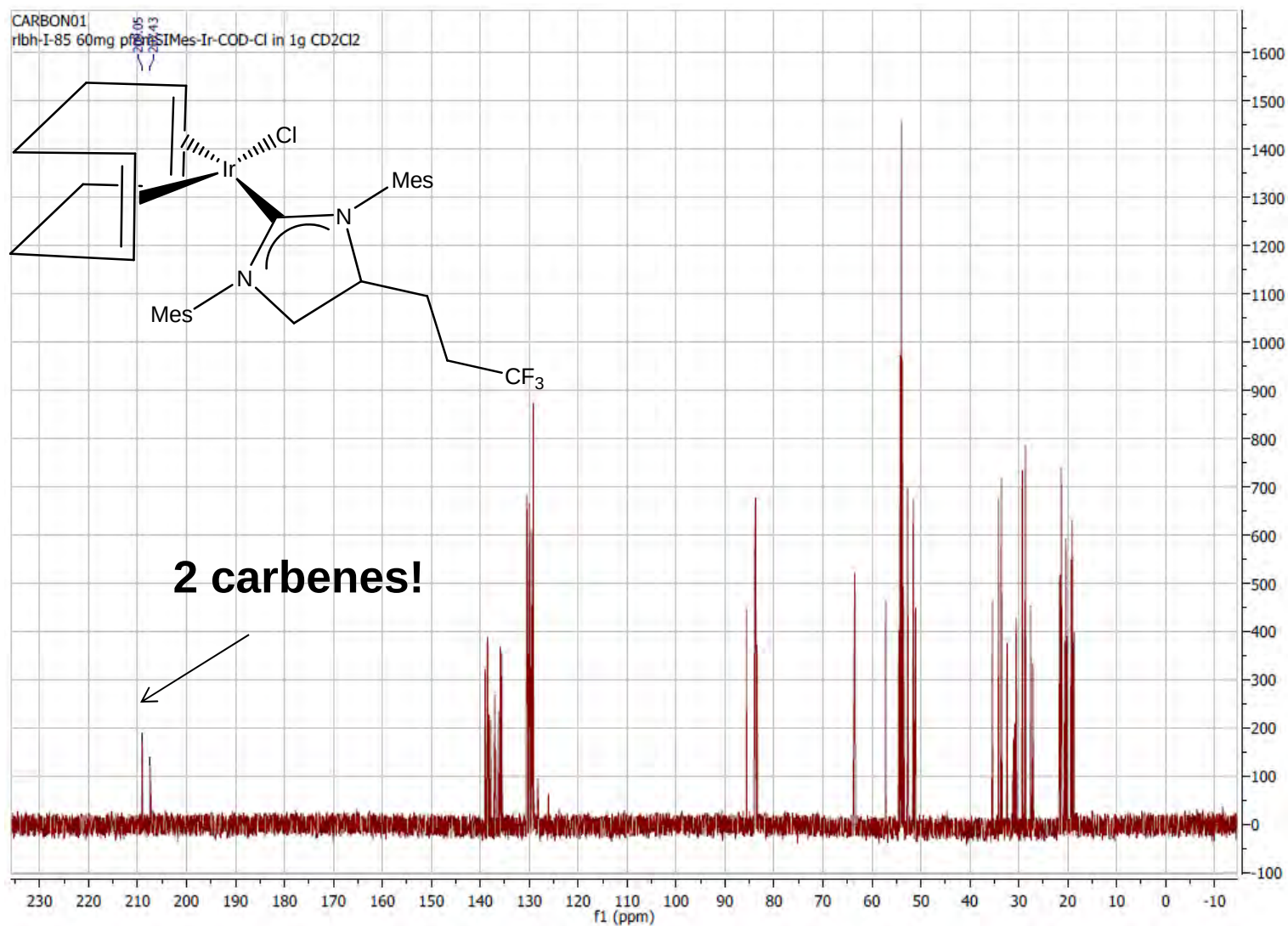


^1H Spectrum of pfme-SIMes-IrCOD-Cl



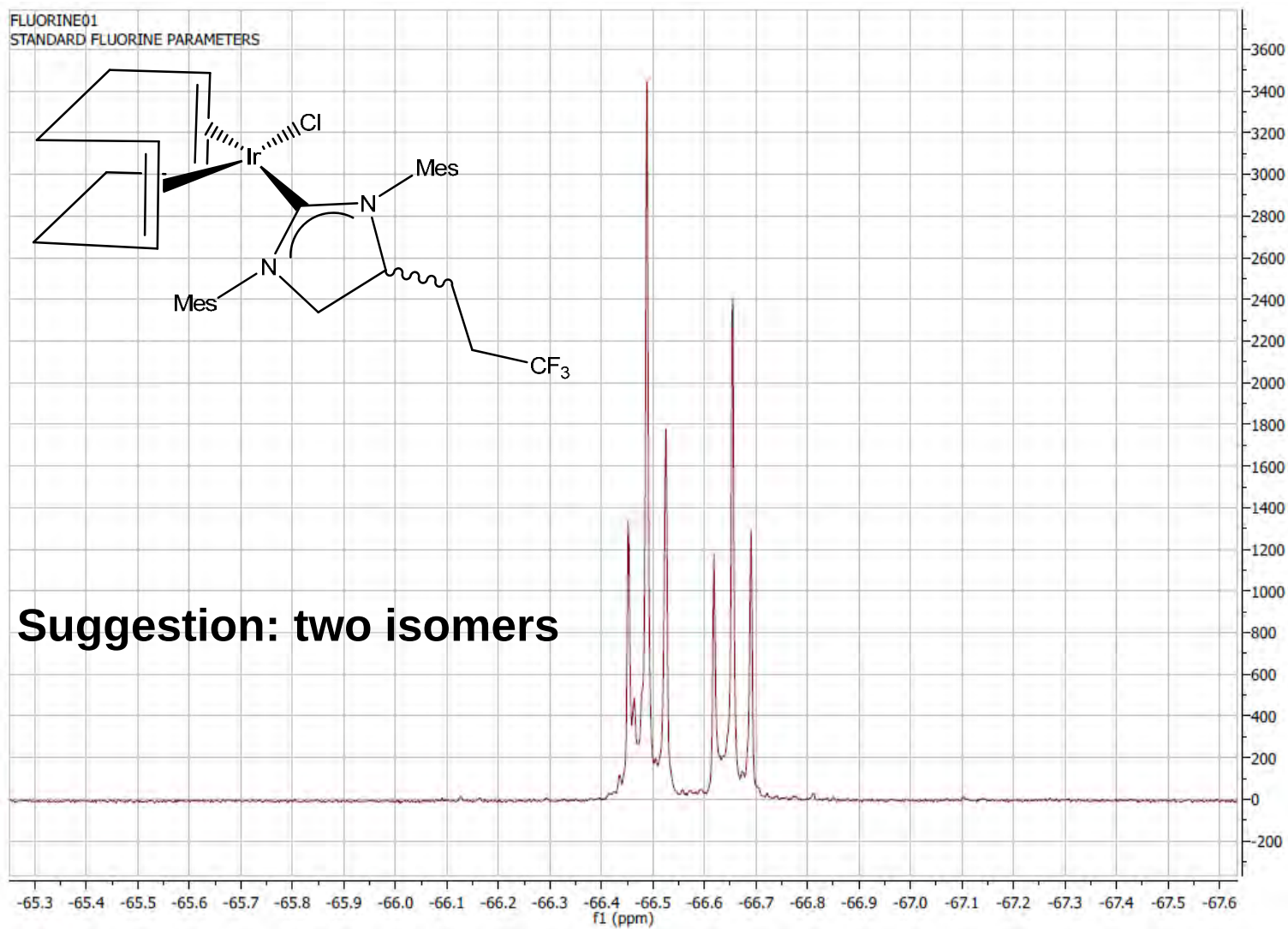


^{13}C Spectrum of pfme-SIMes-IrCOD-Cl



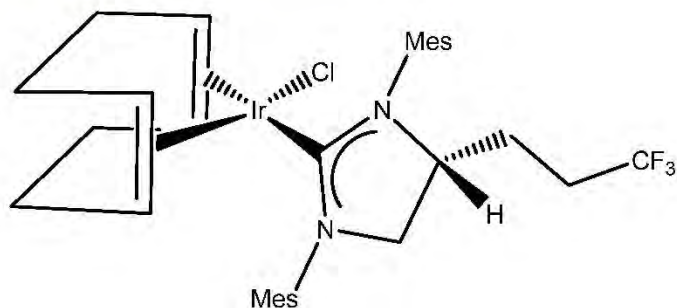


^{19}F Spectrum of pfme-SIMes-IrCOD-Cl

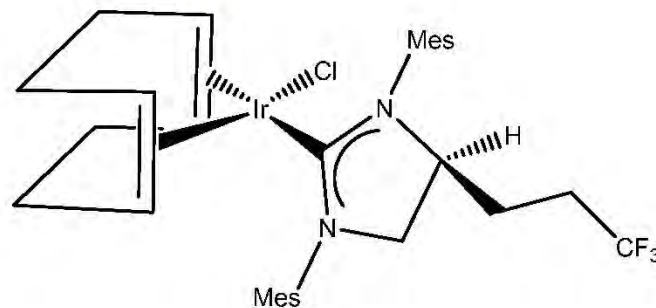




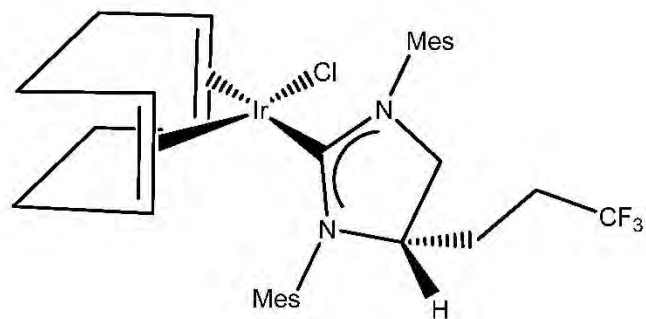
Potential Isomers in Solution



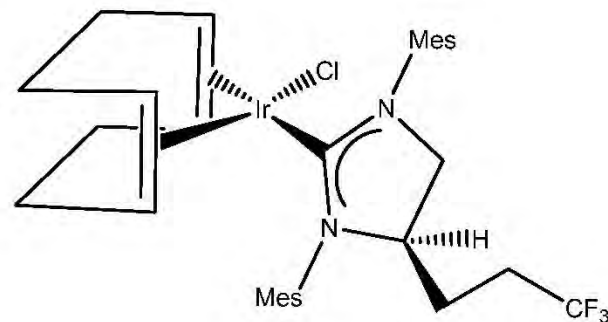
Isomer A



Isomer B



Isomer C



Isomer D

- Ligand rotation observed upon heating in toluene- d_8



Backfluorinated NHC Complexes with $(\text{CO})_2\text{-Ir-Cl}$ in $\text{CD}_2\text{Cl}_2(\text{cm}^{-1})$

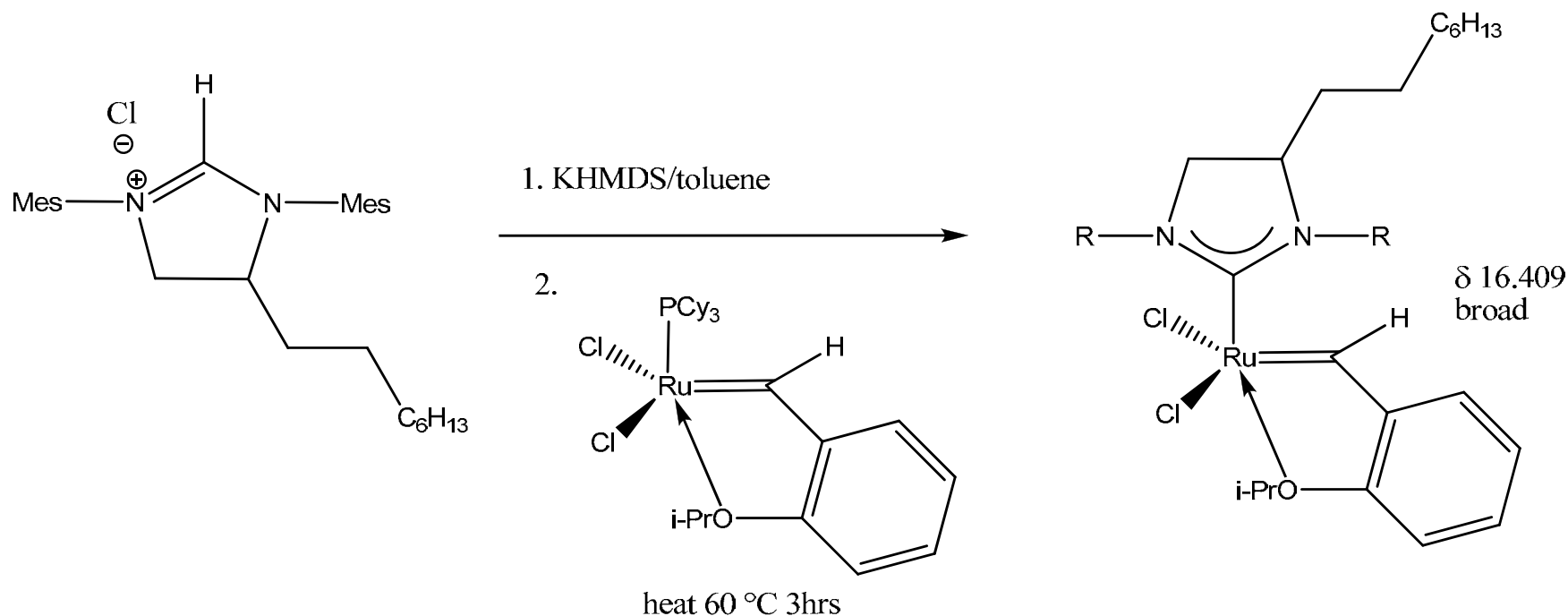


Compound	Functional Group	νCO 1 st CO	νCO 2 nd CO	νCO Avg.
SIMes	H	2068.0	1981.2	2024.6
pfme-SIMes	$\text{CF}_3\text{CH}_2\text{CH}_2$	2068.8	1981.9	2025.4
pfbe-SIMes	$\text{F}(\text{CF}_2)_4\text{CH}_2\text{CH}_2$	2068.8	1981.9	2025.4
pfhe-SIMes	$\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2$	2069.1	1982.0	2025.6
pfoe-SIMes	$\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2$	2069.1	1982.0	2025.6
pfde-SIMes	$\text{F}(\text{CF}_2)_{10}\text{CH}_2\text{CH}_2$	2069.1	1982.1	2025.6
pfop-SIMes	$\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{CH}_2$	2068.5	1981.2	2024.8

When buffer length is $\text{CH}_2\text{-CH}_2$, the perfluoroalkyl group appears to have a small electronic effect



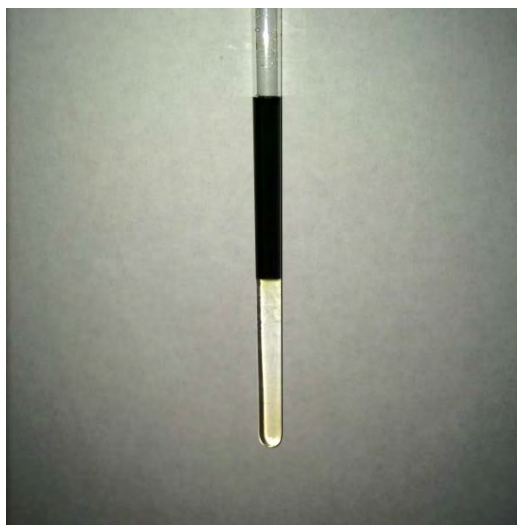
Synthesis of Ru Complexes



- Green solid (same color as 2nd generation catalyst)
- Complex demonstrates metathesis activity
- Perfluorodecylethyl, perfluorooctylethyl and perfluorooctylpropyl complexes also synthesized



Partition Study



- **Partition study with pfheSfMes 2nd Generation Grubbs-Hoveyda catalyst with toluene (upper phase) and perfluoromethyl cyclohexane (lower phase)**
 - Insufficient backfluorination to improve solubility in perfluoromethylcyclohexane



Backfluorinated NHC Carbene complexes



- **Conclusions**

- A series of backfluorinated imidazolinium NHC carbene complexes were synthesized
- Each backfluorinated NHC carbene-COD-iridium chloride complex is a mixture of two observable isomers due to the lack of rotation of the NHC carbene ligand
- The backfluorinated NHC carbene-dicarbonyl-iridium chloride complex is single compound due to rotation of the NHC carbene ligand
- An IR study of the backfluorinated NHC carbene-dicarbonyl-iridium chloride complexes determined that the addition of a perfluoroalkyl chain slightly changes the electronics of the molecule.



Backfluorinated NHC Carbene complexes



- **Conclusions – Cont'd**
 - The IR study of the backfluorinated NHC carbene-dicarbonyl-iridium chloride complexes also suggest that the electronic effects of the perfluoroalkyl group is independent of perfluoroalkyl chain length
 - A series of the longer chain backfluorinated NHC Ruthenium alkylidene complexes were synthesized
 - These complexes demonstrated metathesis activity similar to the nonfluorinated alkylidene complex



Backfluorinated NHC Carbene Complexes



- **Future Work**
 - Look for methods to increase the amount of backfluorination of imidazolinium complexes
 - Investigate the electronic effects of side fluorination of aromatic rings of imidazolinium complexes
 - Investigate the use of the technology for other applications in order to improve sustainability



Acknowledgements



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