**Title and Subtitle:**
Synthesis and Reactivity of Backfluorinated NHC Carbene Complexes
(Briefing Charts)

**Authors:**
Rusty L. Blanski and Robert H. Grubbs

**Performing Organization:**
Air Force Research Laboratory (AFMC)
AFRL/RQRP
10 E. Saturn Blvd.
Edwards AFB, CA 93524-7680

**Sponsoring Agency:**
Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive
Edwards AFB CA 93524-7048

**Availability Statement:**
Distribution A: Approved for Public Release; Distribution Unlimited.

**Abstract:**
Briefing Charts presented at American Chemical Society National Meeting; Boston, MA; 17 August 2015. PA#15448.

**Security Classification:**
Unclassified

**Number of Pages:**
28
Synthesis and Reactivity of Backfluorinated NHC Carbene Complexes

Dr. Rusty Blanski
High Temp Components Group (RQRC)
Air Force Research Laboratory Edwards AFB, CA

Professor Robert H. Grubbs
California Institute of Technology,
Pasadena, California

Distribution A: Approved for public release
• 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”
• 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
• 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 imidazolinylidene ligand affect its electronic properties?
  – How does the addition of a perfluoroalkyl chain to the back of an imidazolinylidene ligand affect the catalytic properties of the ruthenium alkylidene complexes?
  – Does the addition of perfluoralkyl chains improve the solubility of Ru alkylidene complexes in fluorinated solvents?
Fluoroalkene Metathesis

- Fluoroalkene metathesis first reported by Blechert in 2001
- 1\textsuperscript{st} generation systems not effective
- 2\textsuperscript{nd} generation systems are effective
  - 2\textsuperscript{nd} Generation Grubbs-Hoveyda most effective
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.
AFOSR Visiting Scientist Program
6 Month Sabbatical to Research Institutions

AFOSR-TODAY’S BREAKTHROUGH SCIENCE FOR TOMORROW’S AIR FORCE
SPECIAL PROGRAMS: AIR FORCE VISITING SCIENTIST PROGRAM

Transition your research and enhance your career...

AIR FORCE
Visiting Scientist Program

Managed by the Air Force Office of Scientific Research

WWW.AFOSR.AF.MIL
Visiting Scientist Program

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

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

Who
What
Proposed Research

- Electronic effects will be investigated
  - Effect of perfluoroalkyl length and methylene “buffer” length
- Olefin metathesis activity will also be investigated
Synthetic Targets
Imidazolinidene Complexes

- Perfluoroalkyl chain length and "Buffer" length will be investigated
Preparation of Perfluoroalkyl Grignard Reagents

- **FCF₂CH₂CH₂Cl**: Mg, thf, reflux → FCF₂CH₂CH₂MgCl
- **F(CF₂CF₂)ₙCH₂CH₂I**: n=3,4; Mg, Et₂O, reflux → F(CF₂CF₂)ₙCH₂CH₂MgI, n=3,4
- **F(CF₂CF₂)ₙCH₂CH₂Br**: n=2,5; Mg, thf, reflux → F(CF₂CF₂)ₙCH₂CH₂MgBr, n=2,5
- **F(CF₂CF₂)ₙCH₂CH₂CH₂OH**: n=4; PPh₃Br₂, MeCN → F(CF₂CF₂)ₙCH₂CH₂CH₂Br, n=4
- **F(CF₂CF₂)ₙCH₂CH₂CH₂Br**: n=4; Mg, thf, reflux → F(CF₂CF₂)ₙCH₂CH₂CH₂MgBr, n=4

Distribution A: Approved for public release
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
$^1$H Spectrum of pfme-SIMes+Cl-
$^1$H Spectrum of pfme-SIMes-IrCOD-Cl
$^{13}$C Spectrum of pfme-SIMes-IrCOD-Cl

2 carbenes!
$^{19}$F Spectrum of pfme-SIMes-IrCOD-Cl

Suggestion: two isomers
$^1$H Spectrum of pfme-SIMes-Ir(CO)$_2$-Cl

Conclusion: two isomers
Potential Isomers in Solution

- Ligand rotation observed upon heating in toluene-\text{d}_8
Backfluorinated NHC Complexes with \((\text{CO})_2-\text{Ir-Cl}\) in CD\(_2\)Cl\(_2\) (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional Group</th>
<th>(\nu\text{CO}) 1(^{st}) CO</th>
<th>(\nu\text{CO}) 2(^{nd}) CO</th>
<th>(\nu\text{CO}) Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIMes</td>
<td>H</td>
<td>2068.0</td>
<td>1981.2</td>
<td>2024.6</td>
</tr>
<tr>
<td>pfme-SIMes</td>
<td>CF(_3)CH(_2)CH(_2)</td>
<td>2068.8</td>
<td>1981.9</td>
<td>2025.4</td>
</tr>
<tr>
<td>pfbe-SIMes</td>
<td>F(CF(_2))(_4)CH(_2)CH(_2)</td>
<td>2068.8</td>
<td>1981.9</td>
<td>2025.4</td>
</tr>
<tr>
<td>pfhe-SIMes</td>
<td>F(CF(_2))(_6)CH(_2)CH(_2)</td>
<td>2069.1</td>
<td>1982.0</td>
<td>2025.6</td>
</tr>
<tr>
<td>pfoe-SIMes</td>
<td>F(CF(_2))(_8)CH(_2)CH(_2)</td>
<td>2069.1</td>
<td>1982.0</td>
<td>2025.6</td>
</tr>
<tr>
<td>pfde-SIMes</td>
<td>F(CF(<em>2))(</em>{10})CH(_2)CH(_2)</td>
<td>2069.1</td>
<td>1982.1</td>
<td>2025.6</td>
</tr>
<tr>
<td>pfop-SIMes</td>
<td>F(CF(_2))(_8)CH(_2)CH(_2)CH(_2)</td>
<td>2068.5</td>
<td>1981.2</td>
<td>2024.8</td>
</tr>
</tbody>
</table>

When buffer length is CH\(_2\)-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**

![Diagram of Ru complex synthesis](image)
Partition study with pfheSIMes 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.
• 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

• Air Force
  • Leslie Peasant (AFOSR)
  • Dr. Ken Caster (AOARD)
  • Kristen Schario (CRADA)
  • Dr. Chastity Whitaker (CRADA)
  • Lt. Col Brian Tidball (RQRC)
  • Dr. Stephen Rodgers (RQR)
  • Dr. Taewoo Park (RQR)
  • Dr. Shawn Phillips (RQR)
  • Dr. Siva Banda (RQ)

• Cal Tech
  • Prof Grubbs
  • Linda Syme (Admin)
  • Grubbs Group
  • Farnaz Bakhshi (CRADA)
  • Dr. Dave Vandervelde (NMR)