

Cycloaddition Reactions of Ni(0) Difluorocarbene Complexes: Investigating the Formation of Various Perfluorometallacycles

Alexandra Rochon

Thesis submitted in partial fulfillment of the requirements
for the Master's degree in Chemistry

Department of Chemistry and Biomolecular Sciences
Faculty of Science
University of Ottawa

© Alexandra Rochon, Ottawa, Canada, 2019

Abstract

Formation of carbon–fluorine and carbon–fluoroalkyl bonds via transition metal complexes represents an efficient synthetic route towards a wide array of valuable fluorinated organic compounds and fluorinated metallacycles offer a potentially green and atom economical pathway towards these functionalized fluorocarbons. This thesis is focused on cycloaddition reactions of Ni=CF₂ complexes with fluoroalkenes (FAs) and acetylenes.

Cycloaddition reactions of the FAs vinylidene fluoride (CF₂=CH₂) and perfluoro(methyl vinyl ether) [CF₂=CF(OCF₃)] with the electron-rich Ni(0) fluorocarbene, Ni=CF₂[P(OMe)₃](dppe) affords stable metallacyclobutane complexes, likely through a 1,4-diradical mechanism previously investigated for analogous reactions using computational chemistry. With CF₂=CHF (TrFE), however, the observed products are the C₃ alkene *E*-CHF=CF(CF₃) and the metallacyclopentane complex, Ni(C₄H₂F₆)(dppe), derived from oxidative coupling of two additional equivalents of TrFE. It is proposed that the instability of the initially formed metallacyclobutane gives rise to a 2,1-F shift, yielding the C₃ alkene complex. Reaction of the latter with excess TrFE then liberates the C₃ alkene, forming the TrFE alkene complex followed by the observed metallacyclopentane product. In the reaction of **1a** with chlorotrifluoroethylene (CF₂=CFCl) a single regioisomer of the metallacyclobutane is observed, but reacts further in THF solvent via α-Cl migration to Ni, affording the tetrafluoroallyl complex, NiCl(CF₂CF=CFH), in which one F has been replaced by a hydrogen. Finally, reaction of **1a** with hexafluoropropene [CF₂=CF(CF₃), HFP] takes an unprecedented turn, affording the Ni trifluoromethyl perfluoroalkenyl complex from formal transfer of one F from HFP to the Ni=CF₂ moiety.

The capability of **1a** to perform cycloaddition with a broader substrate scope was investigated by reacting it with terminal aryl-acetylenes of varying electronic parameters. Reaction of **1a** with 1.5 equivalents of 4-R-phenylacetylene afforded the expected difluorometallacyclobutenes (R = H, Cl, ^tBu). Further observation revealed a second acetylene insertion to yield a nickelacyclohexadiene in the first example of a 4- to 6-membered ring expansion of perfluorometallacycles. The six-membered metallacycle then undergoes reductive elimination to furnish a difluorocyclopentadiene. The electronic parameters of the aryl-acetylene substrate play a dramatic role in the selectivity of product formation. The more electron-donating substrates 4-*tert*-butylphenylacetylene and 1-hexyne stabilize the metallacyclobutene, while the electron-withdrawing 4-chlorophenylacetylene affords a more reactive metallacyclobutene making it more prone to the second acetylene insertion. Phenylacetylene represented a middle-ground between the two systems and proved effective for further characterization studies. The electronic effect of the surrounding ancillary ligand system was also studied by substituting dppe in **1a** for P(OMe)₃ and dipe to give analogous Ni(0) difluorocarbene complexes **1b** and **1c** (dipe = 1,2-bis(diisobutylphosphino)ethane). The π -acidic phosphite ligands in **1b** gave exclusively nickelacyclohexadiene and difluorinated cyclopentadiene due to a reactive metallacyclobutene, whereas the more electron rich **1c** formed the metallacyclobutene product almost exclusively. The results presented here will allow for future investigations of fluorinated metallacycle reactivity, increasing our ability to prepare value-added fluorocarbon products for pharma, agrochemicals, and polymer applications.

Acknowledgements

Thank you to all the people who played a role in my undergraduate and Masters studies. My supervisor, Dr. Tom Baker, for your patience and guidance these past three years. The Baker group members for making the lab an enjoyable experience. Thank you especially to Karine, Chris, and Alex Daniels, for the company, the positivity, and all the help. I would also like to thank Glenn Facey for his diligence in helping me run NMRs.

Thank you to Matt, for your unconditional support during these past few stressful months, for being my constant motivator when I was discouraged, and without whom this thesis would have taken much longer to write.

Finalement, j'aimerais remercier ma mère, mon père et mes grands-parents. Merci pour votre patience avec mon horaire chargé et votre compréhension. Merci de m'avoir supporté tout au long de mon éducation. Votre support a été grandement apprécié.

Table of Contents

Abstract	ii
Acknowledgements	iv
List of Figures	vii
List of Schemes	ix
List of Tables	xii
Abbreviations	xiii
Chapter 1 – Expanding Fluorine’s Role in Organometallic Chemistry: Perfluorometallacycles as a Facile Route to Functionalized Fluorocarbons	1
1.1 General Introduction	1
1.1.1 Precedent for Studying Fluorocarbons	1
1.1.2 Nickel’s Role in Organometallic Chemistry	3
1.2 Overview of Perfluorometallacycles	4
1.2.1 Metallacyclobutanes	4
1.2.2 Perfluoro- and Partially Fluorinated Nickel Metallacycles	6
1.2.3 Reactivity of Perfluorometallacycles	9
1.3 Metal Fluoroalkyl Complexes	11
1.3.1 Stability and Properties of Metal Fluoroalkyls	11
1.3.2 Synthesis of Metal Fluoroalkyls	12
1.3.2.1 Decarbonylation of Perfluoroacyl Ligands	12
1.3.2.2 Oxidative Addition of R ^F -I	12
1.3.2.3 Using Me ₃ SiCF ₃ as the CF ₃ Source	13
1.4 Metal Fluorocarbene Complexes	14
1.4.1 Characterization of Metal Fluorocarbenes	14
1.4.2 Synthesis of Metal Fluorocarbenes	16
1.4.2.1 α -C-F Fluoride Abstraction from a Metal Fluoroalkyl	16
1.4.2.2 Activation of C _{α} -F by Reduction	17
1.4.2.3 Direct Transfer of Difluorocarbene	18
1.4.3 Reactivity of Metal Fluorocarbenes	20
1.4.3.1 Hydrolysis of M=CF ₂	21

1.4.3.2 Alkene Metathesis with Alkyl Vinyl Ethers	22
1.4.3.3 Reactivity of Nucleophilic Metal Fluorocarbenes	23
1.4.3.4 Reactivity of Cobalt Fluorocarbenes	24
1.4.3.5 Reactivity of Nickel Fluorocarbenes	28
1.5 Scope of Thesis.....	31
1.6 References	32
Chapter 2 – Investigating the Reactivity of Fluoroalkenes with an Electron-Rich Ni(0) Difluorocarbene Complex.....	
2.1 Introduction	37
2.2 Results & Discussion.....	41
2.3 Conclusion.....	55
2.4 Experimental.....	57
2.4.1 Materials and Methods	57
2.4.2 Synthesis of Nickel Complexes and Starting Materials	58
2.4.3 Reactions with Fluoroalkenes	59
2.5 References	65
Chapter 3 – Investigating the Reactivity of Terminal Alkynes with Ni(0) Difluorocarbene Complexes.....	
3.1 Introduction	67
3.2 Results & Discussion.....	71
3.2.1 Reactivity of 1a with Terminal Acetylenes.....	71
3.2.2 Influence of Ancillary Ligands on Ni=CF ₂ Reactivity with Aryl-acetylenes	79
3.3 Conclusion.....	82
3.4 Experimental.....	83
3.4.1 Materials and Methods	83
3.4.2 Synthesis of Ni Difluorocarbene Complexes	84
3.4.3 Reactivity Studies of 1a, 1b, and 1c with Phenylacetylenes	86
3.5 References	93
Chapter 4 – Conclusions & Future Work	
4.1 Conclusions & Future Work.....	94
4.2 References	100

List of Figures

- Figure 1.1.** Isolable nickel complexes in a variety of oxidation states and coordination geometries: A) Examples of the common Ni(0) and Ni(II) oxidation states; B) Examples of the less common Ni(III) and Ni(IV) oxidation states.
- Figure 1.2.** Previously reported TrFE metallacycles.
- Figure 1.3.** Head and tail of a TrFE molecule.
- Figure 1.4.** Potential metallacyclopentane isomers resulting from the oxidative coupling of TrFE at Ni(0).
- Figure 1.5.** Selected metal fluorocarbenes and their ^{19}F NMR chemical shifts.
- Figure 2.1.** ^{19}F NMR (282 MHz, THF) spectrum of **Ni-met^F-2**.
- Figure 2.2.** ^{19}F NMR (282 MHz, THF) spectrum of Ni(CF₃)[CF=CF(CF₃)](dppe), **Ni-alk^F-1**.
- Figure 2.3.** $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF) spectrum of Ni(CF₃)[CF=CF(CF₃)](dppe), **Ni-alk^F-1**.
- Figure 2.4.** ^{19}F NMR (282 MHz, THF) spectrum of **Ni-met^F-3**.
- Figure 2.5.** ^{19}F NMR (282 MHz, THF) spectrum of initial product from reaction of **1** with TrFE.
- Figure 2.6.** ^{19}F NMR (282 MHz, THF) spectrum of the crude reaction mixture of **1** and TrFE showing conversion to fluorometallacycles, **Ni-met^F-4** and **Ni-met^F-5**.
- Figure 2.7.** $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF) of reaction of **1** with TrFE.
- Figure 2.8.** ^{19}F NMR (282 MHz, THF) spectrum of **Ni-met^F-6**.
- Figure 2.9.** ^{19}F NMR (282 MHz, THF) spectrum of **Ni-met^F-6** and **Ni-alk^F-2**.
- Figure 2.10.** ORTEP depiction of **Ni-alk^F-2**. Phenyl groups and hydrogen atoms are omitted for clarity.
- Figure 3.1.** ^{19}F NMR (282 MHz, THF) spectrum of the reaction of **1a** with phenylacetylene showing the three major products, **2a**, **3a**, and **4a**.

- Figure 3.2.** ^{19}F NMR (282 MHz, THF) spectra of the reaction of **1a** with 1.5 equiv. of phenyl acetylene: A) After 24 h; B) After 48 h, with 3 total equiv. of phenylacetylene; C) After 72 h, with 2 total equiv. of $\text{P}(\text{OMe})_3$.
- Figure 3.3.** Stack ^{31}P NMR spectra plot showing growth of $\text{Ni}(\text{dppe})[\text{P}(\text{OMe})_3]_2$ in the reaction of **1a** with phenyl acetylene: A) After 48 h B) After 72 h, with excess $\text{P}(\text{OMe})_3$ (2 equiv). The region between 42 and 162 ppm are omitted for clarity.
- Figure 3.4.** ^1H , $^1\text{H}\{^{19}\text{F}\}$, ^{19}F , and $^{19}\text{F}\{^1\text{H}\}$ NMR (THF) spectra of **4a** displaying the loss of fluorine and proton couplings respectively when decoupling, and the shared 54 Hz coupling constant.
- Figure 3.5.** ^{19}F NMR spectrum (282 MHz, THF) of the reaction of **1a** with 4-chlorophenylacetylene.
- Figure 3.6.** ^{19}F NMR spectrum of the reaction of **1a** with 4-*tert*-butylphenylacetylene.

List of Schemes

- Scheme 1.1.** Chauvin mechanism for olefin metathesis.
- Scheme 1.2** Formation of $[(PPh_3)_2Ni(CF_2)_4]$ via a metallacyclopropane intermediate.
- Scheme 1.3.** Formation of nickel phosphonium ylide upon reaction of nickel metallacyclopentane with Lewis acid.
- Scheme 1.4.** Reactivity of partially fluorinated nickel metallacycles with Lewis acids.
- Scheme 1.5.** Formation of perfluorocyclobutene upon reaction of NHC-Ni metallacyclopropane with Lewis acid TMS-OTf.
- Scheme 1.6.** Synthesis of $(R^F)Mn(CO)_5$ and $(R^F)Co(CO)_4$.
- Scheme 1.7.** Synthesis of cobalt(III) perfluoroalkyl iodide complexes.
- Scheme 1.8.** Application of R_3SiR^F in metal fluoroalkyl synthesis.
- Scheme 1.9.** Fluoride abstraction by unsaturated metal centers.
- Scheme 1.10.** Reaction showing cationic cobalt intermediate, $CpCo(CF_3)(CF_2R^F)$, undergoing fluoroalkyl migration to the fluorocarbene, $R^F = F$ or CF_3 .
- Scheme 1.11.** Synthesis of cobalt and nickel fluorocarbene complexes by reduction.
- Scheme 1.12.** Synthesis of $(PNP)Rh=CF_2$.
- Scheme 1.13.** Application of the Me_3SiCF_3 reagent for the installation of a $=CF_2$ directly to the base metal cobalt.
- Scheme 1.14.** Diverse reactivity of ruthenium fluorocarbenes based on oxidation state.
- Scheme 1.15.** Metathesis with Grubbs-type $Ru=CF_2$ complex.
- Scheme 1.16.** Cross-metathesis of fluoroalkenes and electron-rich alkenes using Mo catalyst.
- Scheme 1.17.** Potential $M=CF_2$ initiated metathesis or polymerization with perfluoroalkenes.
- Scheme 1.18.** Cycloaddition reaction between cobalt(I) fluorocarbenes and TFE.

- Scheme 1.19.** Proposed cycloaddition pathways.
- Scheme 1.20.** Reactivity of cobalt perfluorocyclobutanes.
- Scheme 1.21.** Reactivity of $\text{CpCo}(=\text{CF}(\text{CF}_3))(\text{PPh}_2\text{Me})$ with phenyl acetylenes to yield cobaltacyclobutenes.
- Scheme 1.22.** Synthesis of d^{10} Ni(0) fluorocarbene complexes.
- Scheme 1.23.** Synthesis of perfluoronickelacyclobutane.
- Scheme 1.24.** Reactivity of nickel metallacyclobutane with A) Me_3SiOTf , B) HNTf_2 , showing the respective ring opened vinyl product and ring contraction product.
- Scheme 2.1.** Cycloaddition reaction between TFE and $\text{Cp}(\text{PMePh}_2)\text{Co}=\text{CFR}$ via a 1,4-diradical intermediate ($\text{R} = \text{F}, \text{CF}_3$).
- Scheme 2.2.** Synthesis of Ni(0) difluorocarbene complexes.
- Scheme 2.3.** A) Reaction of **1** with TFE to form nickel perfluorometallacyclobutane product (**Ni-met^F-1**); B) Partial isomerization of perfluorometallacyclobutane to furnish the hexafluorometallacyclopropane complex.
- Scheme 2.4.** Reaction of $\text{Ni}=\text{CFCF}_3$ with TFE to afford the metathesis products $\text{Ni}=\text{CF}_2$ and HFP.
- Scheme 2.5.** Reaction of **1** with PMVE to form **Ni-met^F-2**.
- Scheme 2.6.** Reaction of **1** with HFP.
- Scheme 2.7.** Proposed reaction pathway of **1** with HFP.
- Scheme 2.8.** Reaction of **1** with VDF to form **Ni-met^F-3**.
- Scheme 2.9.** Proposed reaction pathway from **1** and TrFE , giving the fluoroalkene, metallacyclopropane and metallacyclopentane products.
- Scheme 2.10.** Reaction of **1** with CTFE to form **Ni-met^F-6**.
- Scheme 2.11.** Reaction of **Ni-met^F-6** to form **Ni-alk^F-2**.
- Scheme 2.12.** Two expected pathways for α -Cl elimination.
- Scheme 3.1.** Enyne metathesis mechanism.

Scheme 3.2. Important examples of early isolation of metallacyclobutene complexes.

Scheme 3.3. Previous report of fluorinated cobaltacyclobutene complexes.

Scheme 3.4. Reaction of **1a** with phenylacetylene to yield **2a**.

Scheme 3.5. Further reactivity of **2a**.

Scheme 3.6. Reaction of **1a** with 4-chlorophenylacetylene or 4-*tert*-butylphenylacetylene.

Scheme 4.1. Potential application of novel Ni=CF₂/HFP reactivity.

List of Tables

- Table 1.1.** C–F bond dissociation energy (BDE; kcal/mol).
- Table 2.1.** COSY ^{19}F - ^{19}F NMR (282 MHz, THF) of **Ni-met^F-2**.
- Table 2.2.** COSY ^{19}F - ^{19}F NMR (282 MHz, THF) of **Ni-met^F-4**.
- Table 2.3.** COSY ^{19}F - ^{19}F NMR (282 MHz, THF) of **Ni-met^F-6**.

Abbreviations

Å	Angstroms, 10^{-10} m
atm	Atmosphere
BDE	Bond Dissociation Energy
CFC(s)	Chlorofluorocarbon(s)
cod	1,5-Cyclooctadiene
cdt	t,t,t-Cyclododeca-1,5,9-triene
COSY	Homonuclear Correlation Spectroscopy
Cp	η^5 -cyclopentadienyl
Cp*	η^5 -pentamethylcyclopentadienyl
CTFE	Chlorotrifluoroethylene
DCM	Dichloromethane
DEE	Diethyl ether
DFT	Density Functional Theory
dipe	1,2-bis(diisobutylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
equiv	Equivalent
FC(s)	Fluorocarbon(s)
HFA(s)	Hydrofluoroalkene(s)
HFC(s)	Hydrofluorocarbon(s)
HFP	Hexafluoropropylene
HCFC(s)	Hydrochlorofluorocarbon(s)

Hz	Hertz
L	Neutral ligand donor
M–C	Metal-carbon bond
M–R	Metal-alkyl bond
M–R ^F	Metal-perfluoroalkyl bond
NHC	N-Heterocyclic Carbene
NMR	Nuclear Magnetic Resonance
ORTEP	Oak Ridge thermal ellipsoid plot
OTf	Trifluoromethanesulfonate
PFOA	Perfluorooctanoic acid
PMVE	Perfluoro(methyl vinyl ether)
ppm	Parts Per Million
RT	Room temperature
TEP	Tolman electronic parameter
THF	Tetrahydrofuran
TFE	Tetrafluoroethylene
TMS	Trimethylsilyl
TON	Turnover number
TrFE	Trifluoroethylene
VDF	Vinylidene fluoride

Chapter 1 – Expanding Fluorine’s Role in Organometallic Chemistry: Perfluorometallacycles as a Facile Route to Functionalized Fluorocarbons

1.1 General Introduction

1.1.1 Precedent for Studying Fluorocarbons

The formation of carbon–fluorine and carbon–fluoroalkyl bonds via transition metal complexes represents an efficient synthetic route towards a wide array of valuable fluorinated organic compounds.¹⁻³ The C–F bond gives unique and sometimes extreme properties to compounds which lends to its utility in the pharmaceutical,⁴⁻⁶ agrochemical,⁷ and materials industries.⁸ Despite this great potential, molecules containing C–F bonds have contributed to ozone degradation and can be environmentally persistent.^{9,10} A greater understanding of C–F activation could have future impact on remediation of fluorinated waste.¹¹

Small functionalized fluorocarbons (FCs) are of particular interest for their effectiveness as solvents, surfactants, monomers for fluoropolymers, and refrigerants.¹²⁻¹⁴ Historically, there are three categories of fluorocarbons that have been used as refrigerants: chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Both CFCs and HCFCs have been banned from developed countries since 1995 due to significant contribution to ozone depletion and global warming.^{15,16} While HFCs also participate in global warming, they have not been shown to have any effect on ozone depletion.¹⁶ Of current interest, however, are a fourth category, hydrofluoroalkenes (HFAs), which are effective refrigerants and blowing agents with a greatly reduced global warming potential as opposed to saturated HFCs.¹⁷

The majority of current synthetic routes towards FCs often require the use of harsh conditions such as high temperatures and pressures, or the use of toxic reagents.¹⁸ For instance, perfluorooctanoic acid (PFOA), which is used in the manufacture of many stain-resistant products such as Teflon™, is harmful to the environment, animals, and humans due to its toxicity and persistence.¹⁹ This persistence arises from the stability of C–F bonds.

Fluorine is the most electronegative element (4.0 on the Pauling scale) and has three relatively non-polarizable lone pairs of electrons. The C–F bond is the strongest single bond to carbon (115 kcal/mol BDE for CH₃–F vs. 104.9 kcal/mol BDE for CH₃–H), and is highly polarized with δ^- at fluorine and δ^+ at carbon (the opposite of activated C–H bonds).²⁰ This bond strength can be attributed in part both to the excellent energy match and the overlap of the 2s and 2p orbitals of fluorine with carbon. While these properties are often highly desirable within products, they also present challenges for the introduction of C–F fragments via transition metal catalysis. Fluoro-organometallic complexes are often much more stable and therefore less reactive than analogous

hydrocarbon compounds, making further reaction thermodynamically unfavorable. There are a variety of extensively studied and novel organometallic-mediated hydrocarbon transformations, including metal-catalyzed olefin polymerization/metathesis and cross-coupling reactions; however, there remains much to learn about the analogous reactions with fluorocarbons. Further understanding of the reactivity of fluoro-organometallic complexes will offer the ability to design improved approaches for the synthesis and utilization of these compounds.^{3,12}

1.1.2 Nickel's Role in Organometallic Chemistry

Nickel is an abundant group 10 first row transition metal and is approximately 2000 and 10,000 times cheaper than its heavier counterparts, palladium and platinum.²¹ Nickel is a relatively electropositive late transition metal, aiding in facile oxidative addition; however, the microscopic reverse, reductive elimination, is more difficult.²² Nickel has 10 d-electrons in a neutral Ni(0) species and can exist in several oxidation states. Catalytic cycles generally utilize nickel in its most common oxidation states, Ni(0) and Ni(II).²¹ Though less common, Ni(I), Ni(III) and Ni(IV) are also accessible oxidation states.^{21,23} Ni(II) complexes adopt a variety of geometries, with the most common being square planar and octahedral; less common arrangements like trigonal planar are also utilized in catalysis. Reactions using nickel frequently proceed through either a 16 or 18 electron species. For instance, the oxidative addition of a substrate to a 14 electron Ni(0) complex forms a stable 16 electron square planar Ni(II) complex, which is perfectly suited for subsequent reductive elimination. Figure 1.1 displays examples of nickel complexes in a variety of geometries and oxidation states.

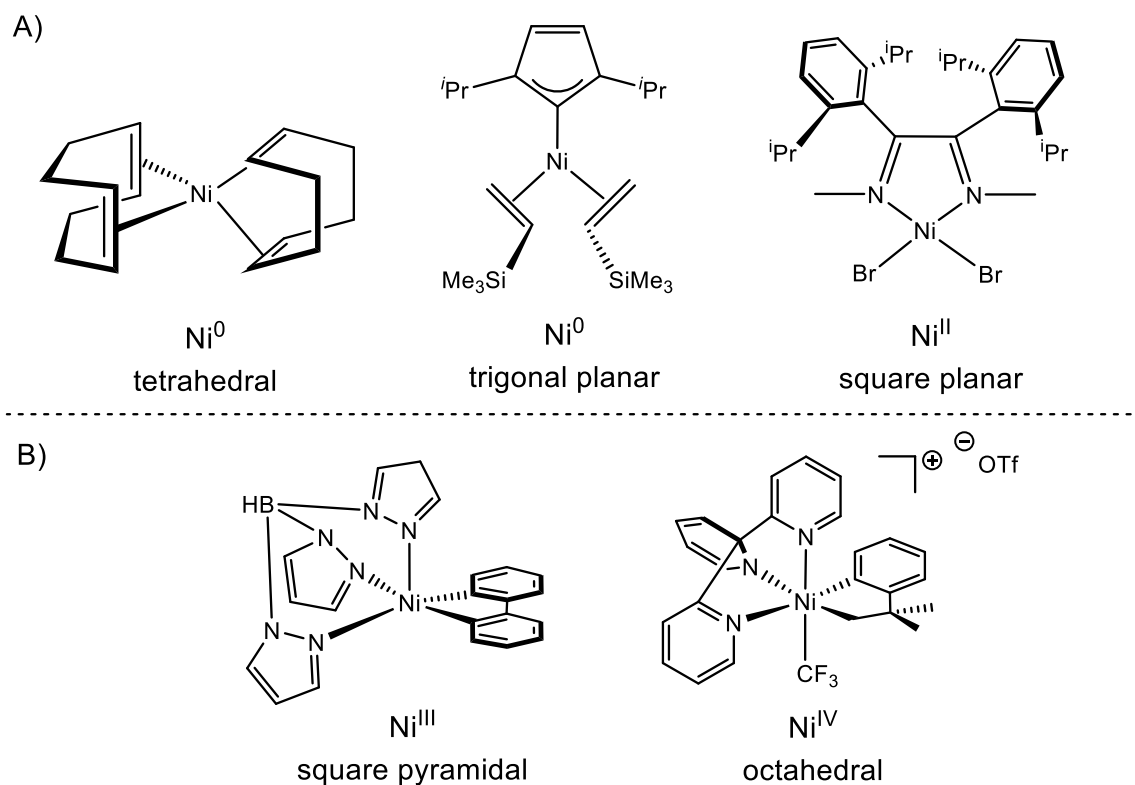


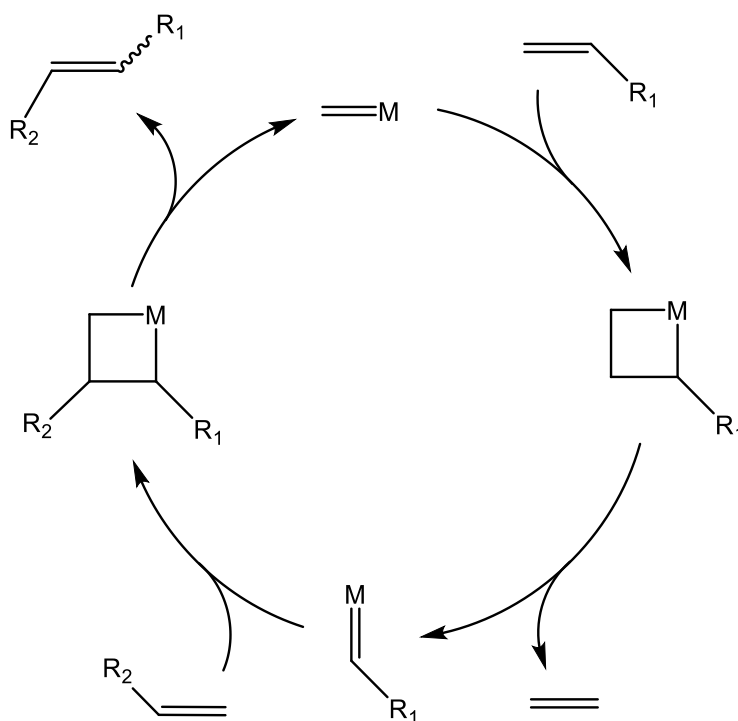
Figure 1.1. Isolable nickel complexes in a variety of oxidation states and coordination geometries: A) Examples of the common $\text{Ni}(0)^{24}$ and $\text{Ni}(\text{II})^{25}$ oxidation states; B) Examples of the less common $\text{Ni}(\text{III})^{23}$ and $\text{Ni}(\text{IV})^{26}$ oxidation states.

1.2 Overview of Perfluorometallacycles

1.2.1 Metallacyclobutanes

A metallacycle is a carbocyclic system where at least one atom is replaced by a transition metal and will typically consist of two metal–carbon bonds.²⁷ It has been shown that metallacycles often appear as reactive intermediates or precatalysts in organometallic transformations such as olefin metathesis. For instance, metallacyclobutane intermediates are directly involved in both alkene metathesis and oligomerization of ethylene. The Chauvin mechanism proceeds through a [2+2] cycloaddition of a metal alkylidene and an olefin, forming a metallacyclobutane

intermediate. This intermediate then undergoes cycloreversion to give the original or new metal alkylidene species and olefin, as shown in Scheme 1.1. This reaction generally doesn't require elevated temperatures due to the interaction with the metal's d-orbitals, which lowers the activation energy.

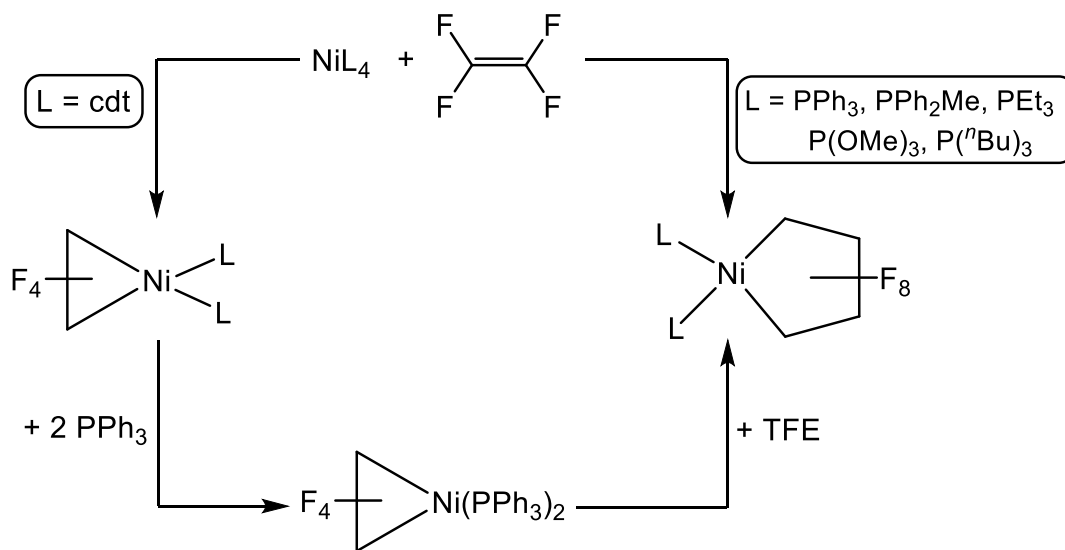


Scheme 1.1. Chauvin mechanism for olefin metathesis.

The past several decades have demonstrated the important role that metallacycles play in some of the most frequently used reactions in synthetic chemistry. While there has been great work done in understanding the nature of these metallacycles, there is much to learn about the analogous fluorinated derivatives. Perfluorinated metallacycles offer a potentially green and atom economical pathway towards functionalized fluorocarbons.^{4,28,29}

1.2.2 Perfluoro- and Partially Fluorinated Nickel Metallacycles

Seminal work by Stone in 1970 resulted in the first reported formation of perfluorometallacycle complexes.³⁰ The reaction of a Ni(0)L_4 complex with tetrafluoroethylene (TFE) resulted in the observation of either metallacyclopropane or metallacyclopentane products, as shown in Scheme 1.2. The selectivity for the formation of either the 3- or 5-membered perfluorometallacycle was heavily influenced by the choice of ancillary ligand. A series of different phosphine and phosphite ligands of varied steric and electronic properties all resulted in the formation of the 5-membered metallacycle upon oxidative cyclization of TFE. The only instance of formation of metallacyclopropane resulted from the use of the bulky cdt ligand (*t,t,t*-cyclododeca-1,5,6-triene).



Scheme 1.2 Formation of $[(\text{PPh}_3)_2\text{Ni}(\text{CF}_2)_4]$ via a metallacyclopropane intermediate.

Further investigation showed that treatment of the 3-membered perfluorometallacycle complex $[(\text{cdt})\text{Ni}(\text{CF}_2)_2]$ with two equivalents of triphenylphosphine (PPh_3) formed $[(\text{PPh}_3)_2\text{Ni}(\text{CF}_2)_2]$, from a simple ligand substitution. This complex then rapidly converts to

$[(\text{PPh}_3)_2\text{Ni}(\text{CF}_2)_4]$ in the presence of TFE, as shown in Scheme 1.2. This observation suggests that the metallacyclopropane is an intermediate to the metallacyclopentane complex in the presence of TFE.³¹

Use of small fluoro-olefins towards synthesis of metallacycles is not limited to tetrafluoroethylene. Stone *et al.* have reported the formation of nickel metallacycles when trifluoroethylene (TrFE) is used.³⁰ The reaction of TrFE with either $\text{Ni}(\text{PPh}_2\text{Me})_4$ or $(\text{PPh}_3)_2\text{Ni}(\text{C}_2\text{H}_4)$ gave five-membered metallacycles, $(\text{PR}_3)_2\text{Ni}(\text{C}_4\text{F}_6\text{H}_2)$, from the coupling of two TrFE molecules, presumably as a mixture of isomers (Figure 1.2A). This reactivity of TrFE was further supported through an independent report of three-membered metallacycle formation upon reaction of tridentate ligated Ni complexes (Figure 1.2B).³²

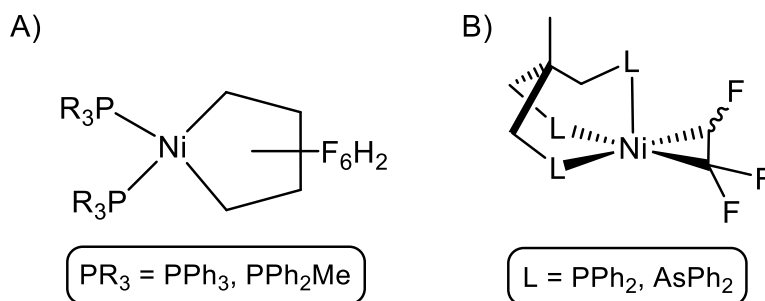


Figure 1.2. Previously reported TrFE metallacycles.

The nomenclature used for a TrFE molecule in regards to the substitution pattern of the fluorine moieties are head and tail, as shown in Figure 1.3. There are six potential regio/stereoisomers that may arise from the coupling of two TrFE molecules at a Ni(0) center: *cis/trans* head to tail, *cis/trans* head to head and *cis/trans* tail to tail, shown in Figure 1.4. The formation of a regio/stereoisomer is heavily influenced by both the steric and electronic effects of the ancillary ligands.³⁰

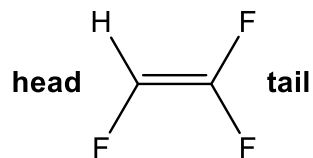


Figure 1.3. Head and tail of a TrFE molecule.

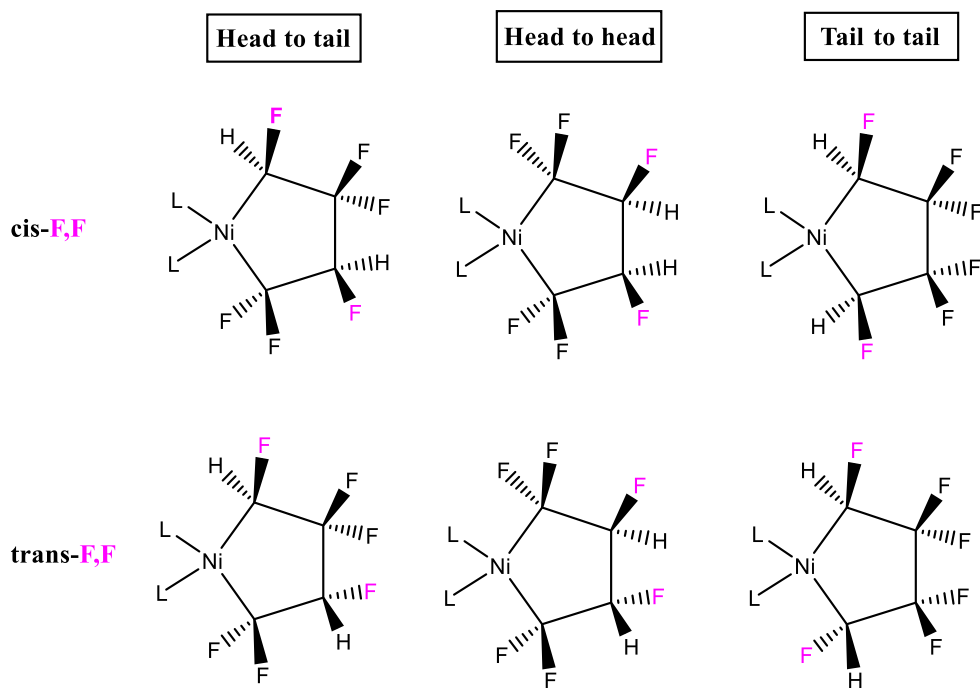


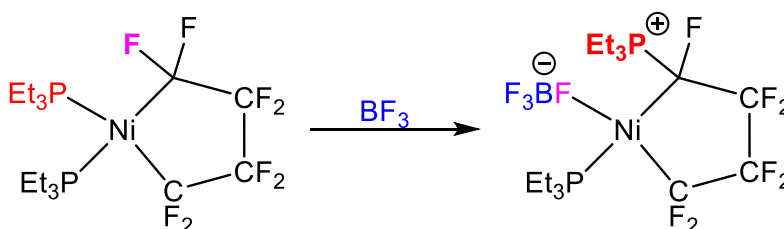
Figure 1.4. Potential metallacyclopentane isomers resulting from the oxidative coupling of TrFE at Ni(0).

The selectivity for the formation of these complexes has been extensively studied with many different phosphine/phosphite ligands of varied cone angle and Tolman electronic parameters.^{33,34} It has been found that the nature of the ligand influences either the selective formation, or, the respective ratios of formation for the different isomers, with only three of the potential six forming. Bulky ligands tend to form a minor amount of the tail to tail isomer, whereas

less bulky phosphines are more selective towards the *trans* head to head isomers, shown to be the most thermodynamically stable by DFT studies.³⁰

1.2.3 Reactivity of Perfluorometallacycles

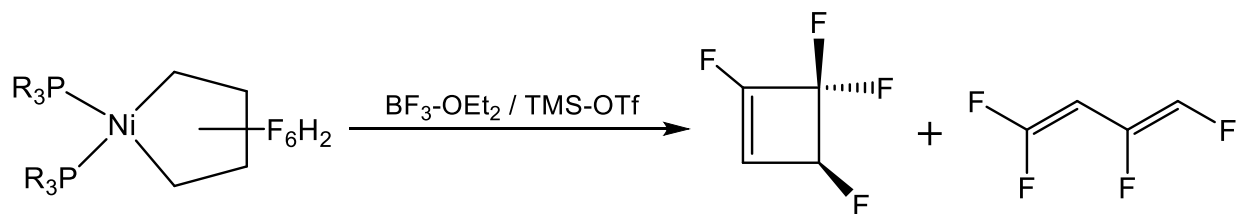
Investigating the potential of perfluorometallacycles towards further functionalization of small fluorocarbons is a necessary development for green catalysis. One example of potential reactivity of perfluorometallacycles is with Lewis acids. Burch *et al.* first investigated the reactivity of Lewis acids with perfluorometallacyclopentanes. The nickel complex, $(\text{PPh}_3)_2\text{Ni}(\text{CF}_2)_4$ undergoes an α -F abstraction upon addition of trifluoroborane. This is followed by migration of the triethylphosphine (PEt_3) moiety to give an ylide-like complex (Scheme 1.3). The empty site left by the phosphine is then occupied by the weakly coordinating tetrafluoroborate anion.³⁵



Scheme 1.3. Formation of nickel phosphonium ylide upon reaction of nickel metallacyclopentane with Lewis acid.

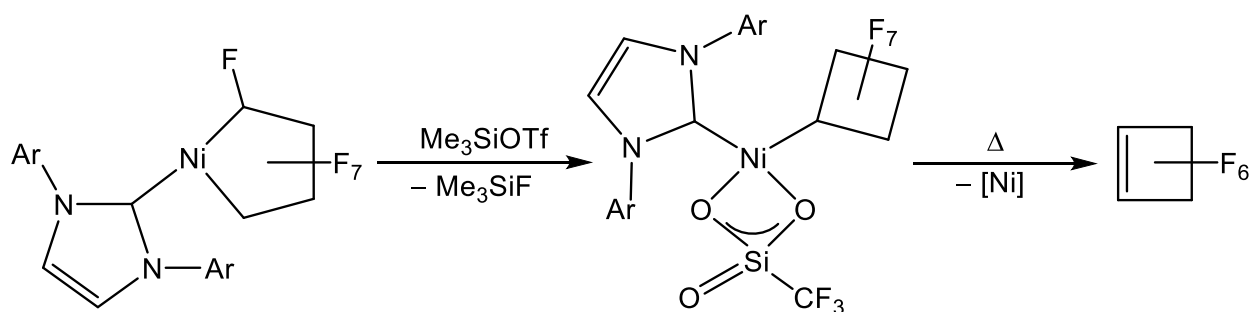
Over the last decade the reactivity of perfluorometallacycles has been well established by the Baker and Ogoshi labs; however, the reactivity of partially fluorinated nickel metallacycles is still in the beginning. It was recently shown that reaction of hydrofluoronickelacycles with the Lewis acid $\text{BF}_3 \cdot \text{OEt}_2$ results in a double fluoride activation of the head to tail regioisomers, as shown in Scheme 1.4, to give 1,1,2,3-tetrafluorocyclobutene as the major organic product, along

with a minor amount of (*Z,E*)-1,1,3,4-tetrafluorobutadiene.³⁶ When the analogous reaction was performed with the Lewis acid TMS-OTf ($\text{Me}_3\text{Si-OSO}_2\text{CF}_3$), the results showed the opposite selectivity, giving the butadiene as the major organic product ($\text{Tf} = \text{SO}_2\text{CF}_3$).



Scheme 1.4. Reactivity of partially fluorinated nickel metallacycles with Lewis acids.

In contrast, the reaction of TMS-OTf with three-coordinate NHC–Ni metallacyclopentane results in Ni-C^{F} bond cleavage and $\text{C}^{\text{F}}\text{-C}^{\text{F}}$ bond formation, resulting in a perfluorocyclobutyl complex.³⁷ This shows that the NHC remains bound to the Ni center to give the final product (Scheme 1.5). The formation of perfluorocyclobutene through $\beta\text{-F}$ elimination mechanism is observed upon heating. This example effectively demonstrates the great potential of perfluorometallacycles towards the synthesis of highly desired small functionalized fluorocarbons.



Scheme 1.5. Formation of perfluorocyclobutene upon reaction of NHC-Ni metallacyclopentane with Lewis acid TMS-OTf.

1.3 Metal Fluoroalkyl Complexes

1.3.1 Stability and Properties of Metal Fluoroalkyls

Metal complexes with σ -bonded perfluoroalkyls ($M-R^F$) are traditionally thought of as being much more stable and unreactive than their metal alkyl ($M-R$) counterparts. The strong electron-withdrawing inductive effect caused by the electronegative fluorine atom present in $M-R^F$ bonds increases the ionic nature, thus increasing the $M-C$ bond strength. A series of C-F bond dissociation energies with increasing number of M-F bonds present is shown in Table 1.1. The increase in bond strength is inversely proportional to the bond length, decreasing as the number of fluorine atoms increases.

Table 1.1. C-F bond dissociation energy (BDE; kcal/mol).³⁸

	CH ₄	CH ₃ F	CH ₂ F	CHF ₃	CF ₄
BDE (kcal/mol)	101	108	115	120	124

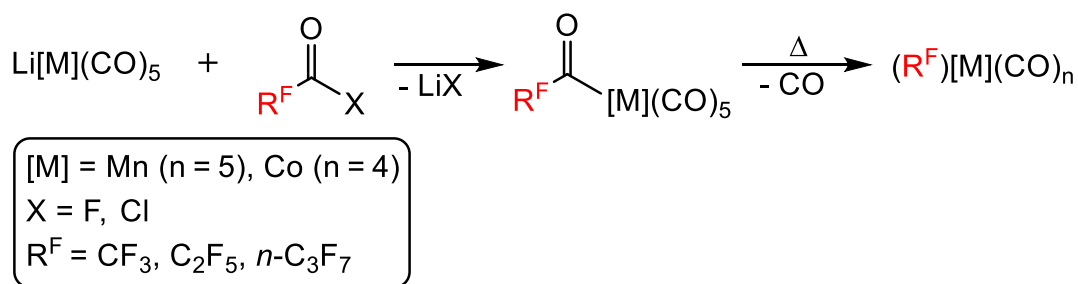
Since perfluorocarbons are considered relatively stable and inert, the functionalization or chemical modification of them is a considerable challenge. This causes differences in bond insertion reactivity and stability compared to what is observed with $M-R$ bonds. A clear demonstration of this is that while $CH_3Mn(CO)_5$ undergoes insertion with CO at elevated pressures to form $CH_3COMn(CO)_5$, the trifluoromethyl analogue $CF_3Mn(CO)_5$ does not react, even when treated with 333 atm of CO at 200 °C.³⁹ Similarly, Vicic *et al.* showed that bipyridine nickel bis(perfluoroalkyl) complexes exhibit high thermal stability relative to the dimethyl analogue,

which loses ethane upon gentle heating.⁴⁰ Computational studies revealed that there is a higher $M \leftarrow CF_3$ interaction in comparison to $M \leftarrow CH_3$, as the C–F σ^* orbitals may interact with the metal to stabilize the metal-based d-orbitals.^{41,42}

1.3.2 Synthesis of Metal Fluoroalkyls

1.3.2.1 Decarbonylation of Perfluoroacyl Ligands

The earliest examples of metal fluoroalkyl complexes were based on carbonyl complexes of Mn and Co, in the form of $(R^F)M(CO)_n$, ($M = Mn, Co$). These compounds were prepared via the decarbonylation of $(R^F)C(O)Mn(CO)_5$ or $(R^F)C(O)Co(CO)_4$, as shown in Scheme 1.6.⁴³ Notably, this reaction pathway does not require a change in metal center oxidation state. Sanford *et al.* recently reported a modern decarbonylation pathway for the synthesis of nickel and palladium fluoroalkyl complexes via oxidative addition of trifluoroacetic anhydride (TFAA) to the metal center, followed by a facile decarbonylation of the resulting fluoroacyl ligand.⁴⁴

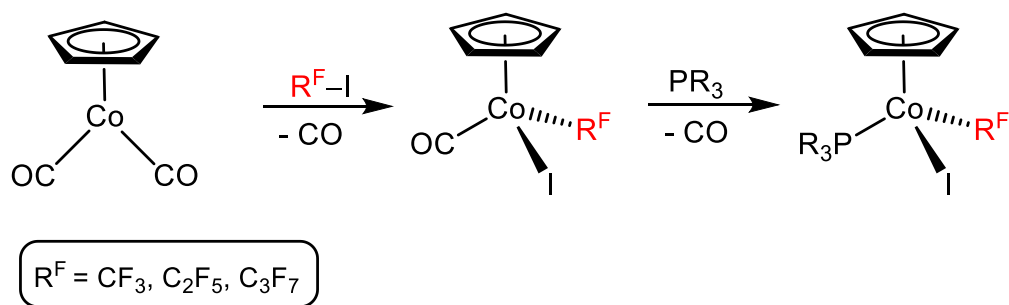


Scheme 1.6. Synthesis of $(R^F)Mn(CO)_5$ and $(R^F)Co(CO)_4$.

1.3.2.2 Oxidative Addition of R^F-I

A classical direct route to metal fluoroalkyls is through the oxidative addition of a perfluoroalkyl iodide to a low valent metal center via cleavage of the R^F-I bond. This results in an increase of the metal oxidation state by two. In 1961, during Stone's investigation of the reactivity

of $\text{Fe}(\text{CO})_5$ with perfluoroalkyl iodides, it was observed that perfluoroalkyl iron tetracarbonyl iodide complexes were formed.⁴⁵ Expansion of this work demonstrated similar reactivity between $\text{CpCo}(\text{CO})_2$ ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$) with perfluoroalkyl iodides, which resulted in the formation of $\text{CpCo}(\text{CO})(\text{I})(\text{R}^{\text{F}})$ complexes, as shown in Scheme 1.7.⁴⁶ This synthetic strategy has been effectively extended towards heavier group 9 metals. Iridium(III) perfluoroalkyl iodide complexes were prepared first by Collman,⁴⁷ while Hughes later reported $\text{Cp}^*\text{Ir}(\text{L})(\text{I})(\text{R}^{\text{F}})$ ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$) complexes.⁴⁸

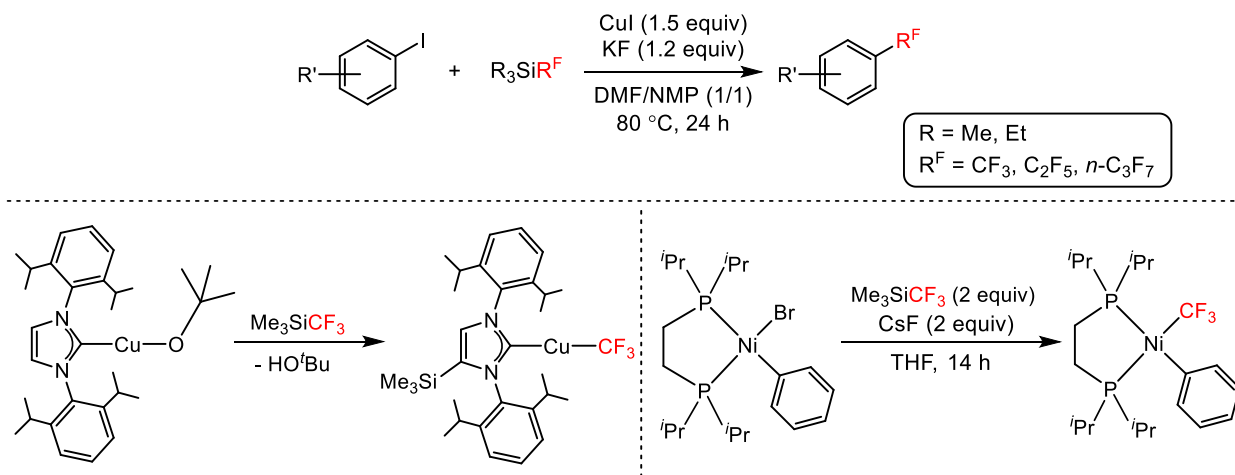


Scheme 1.7. Synthesis of cobalt(III) perfluoroalkyl iodide complexes.

1.3.2.3 Using Me_3SiCF_3 as the CF_3 Source

Trifluoromethyltrimethylsilane, Me_3SiCF_3 , has found extensive use as a CF_3 source in nucleophilic trifluoromethylation reactions.⁴⁹ Activation of Me_3SiCF_3 , typically by catalytic or stoichiometric amounts of fluoride, generates a pentacoordinated organosilicate species $[\text{Me}_3\text{Si}(\text{CF}_3)\text{F}]^-$ or $[\text{Me}_3\text{Si}(\text{CF}_3)_2]^-$, which subsequently releases the trifluoromethanide anion $[\text{CF}_3]^-$.⁵⁰ The same process applies generally to $\text{R}_3\text{SiR}^{\text{F}}$ fragments with the formation of the strong Si-F bond from R_3SiF formation as the driving force ($\text{R} = \text{Me}, \text{Et}$; $\text{R}^{\text{F}} = \text{CF}_2, \text{C}_2\text{F}_5, n\text{-C}_3\text{F}_7$). This therefore means that $\text{R}_3\text{SiR}^{\text{F}}$ compounds can be utilized for the facile conversion of M-X to M-R^{F} bonds. Several examples are shown in Scheme 1.8. In an early report, Fuchikami described the synthesis of Ar-R^{F} compounds mediated by CuI/KF and $\text{R}_3\text{SiR}^{\text{F}}$.⁵¹ Following this, an important

advance was made by Vicić *et al.* who successfully prepared trifluoromethyl copper and nickel complexes using Me_3SiCF_3 , further showing the diversity and utility of this reagent.^{52,53} The economy, commercial availability, versatility, and relative safety of Me_3SiCF_3 make it the most common choice for synthesis of metal trifluoromethyl complexes.



Scheme 1.8. Application of $\text{R}_3\text{SiR}^{\text{F}}$ in metal fluoroalkyl synthesis.

1.4 Metal Fluorocarbene Complexes

1.4.1 Characterization of Metal Fluorocarbenes

Transition-metal carbene complexes play an important role in both organometallic chemistry and organic synthesis, including annulations,⁵⁴ catalyzed alkene metathesis,⁵⁵ and cyclopropanation.⁵⁶ The distinguishing feature of transition metal carbenes is a divalent carbon ligand bonded to the metal center. While there has been much investigation on the reactivity of transition metal carbene complexes with varying electronic structures,⁵⁷ metal fluorocarbenes have not been as thoroughly studied.

The first transition-metal difluorocarbenes and fluoro(perfluoroalkyl)carbenes ($[\text{M}]=\text{CFR}$; R = F, perfluoroalkyl) were reported, but not isolated in 1978.⁵⁸ Since this seminal work, there has

been a clear absence of further study, due to the difficulty in both the synthesis and isolation of these complexes. The vast majority of metal fluorocarbenes require the use of expensive precious metals (Ru, Os, Ir).⁵⁹⁻⁶² Instances of metal fluorocarbenes supported by first row transition metals are rare.

One advantage when considering the preparation and study of metal fluorocarbenes is the useful ^{19}F NMR handle which is highly distinctive and characteristic in these complexes. In general, a lower metal oxidation state and better electron-donating ability of ancillary ligands give rise to an upfield shift of the ^{19}F NMR resonances for $\text{M}=\text{CF}_2$. This leads to positive chemical shifts for most metal fluorocarbenes. ^{19}F NMR chemical shifts (ppm) for carbene-fluorine atoms of selected metal fluorocarbene complexes are shown in Figure 1.5.^{58,59,63-66}

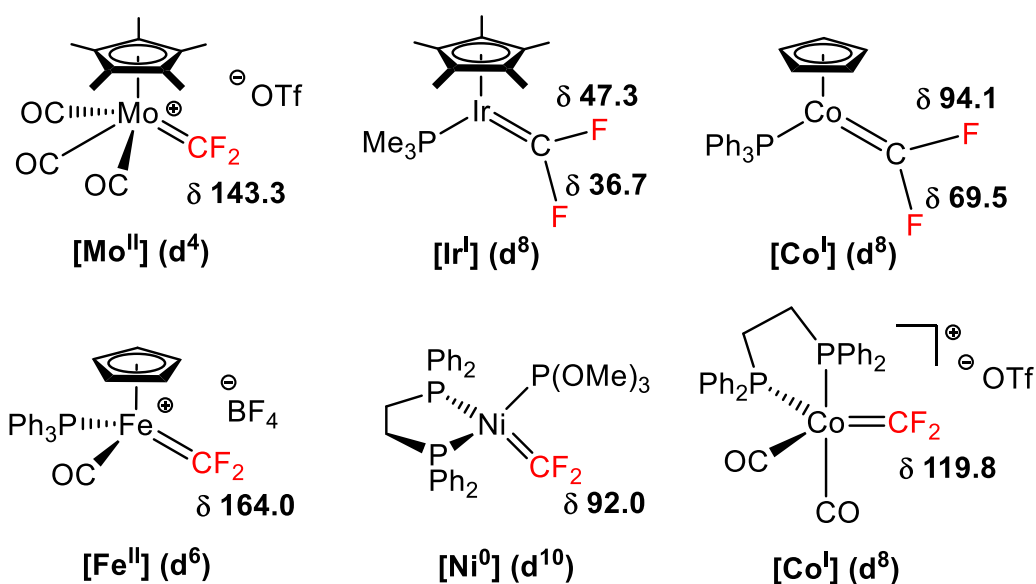
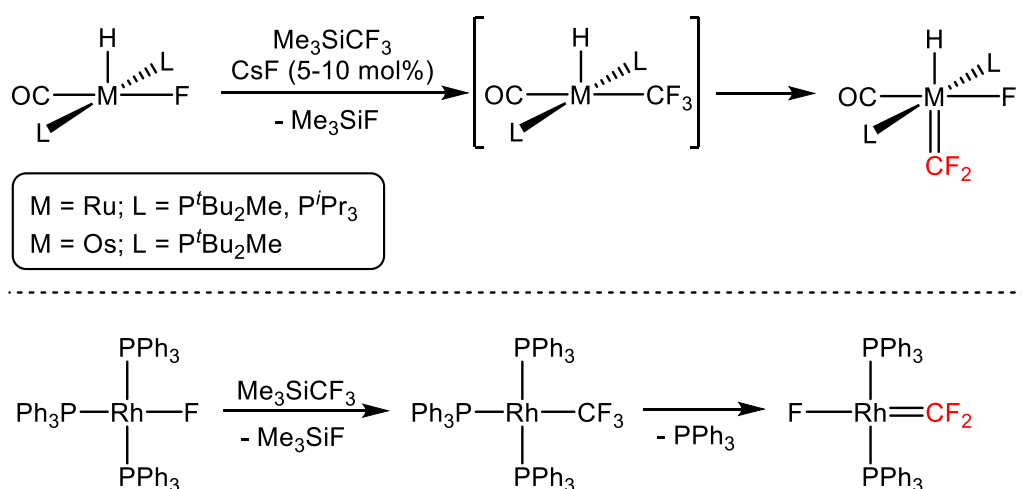


Figure 1.5. Selected metal fluorocarbenes and their ^{19}F NMR chemical shifts.

1.4.2 Synthesis of Metal Fluorocarbenes

1.4.2.1 α -C-F Fluoride Abstraction from a Metal Fluoroalkyl

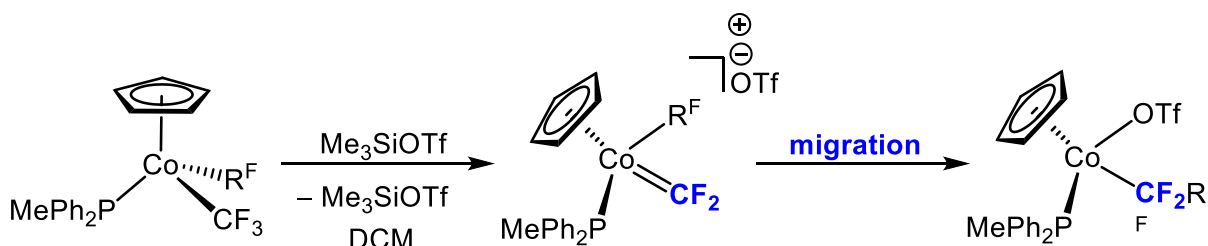
The very first metal fluorocarbenes were prepared by utilization of a Lewis acid to abstract one fluoride from a metal perfluoroalkyl, $M-CF_2R^F$ (R^F = perfluoroalkyl). There are several different options for choice of Lewis acids depending on the desired metal. For example, treatment of $M[R^F(L)_2(CO)(H)]$ (M = Ru, Os; R^F = F; L = P^tBu_2Me , P^iPr_3) with Me_3SiCF_3 and catalytic CsF afforded $M[=CF_2(R^F)(L)_2(CO)(H)]$.⁶⁷ Similarly, reaction of $Rh(PPh_3)_3(F)$ with Me_3SiCF_3 as the fluoride abstracting agent gave $Rh[=CF_2(PPh_3)_2(F)]$ as shown in Scheme 1.9.⁶⁸



Scheme 1.9. Fluoride abstraction by unsaturated metal centers.

The use of BF_3 affects fluoride abstraction from $M-CF_3$ moieties in both iron and manganese complexes to form $[Mn=CF_2(CO)_5][BF_4]$ and $[CpFe=CF_2(CO)(L)][BF_4]$ (L = CO, PPh_3).^{64,69} More recently, Baker *et al.* reported fluoride abstraction from reaction of a cobalt(I) trifluoromethyl complex with Me_3SiOTf to form $[Co=CF_2(dppe)(CO)_2][OTf]$ [$dppe$ = 1,2-bis(diphenylphosphino)ethane] and $[Co=CF_2(P_3)(CO)][OTf]$ (P_3 = $PhP(CH_2CH_2PPh_2)_2$) (*vide*

infra).⁶⁶ A similar reaction with the bis(fluoroalkyl) complex, $\text{CpCo}(\text{CF}_3)(\text{CF}_2\text{R}^{\text{F}})$, where $\text{R}^{\text{F}} = \text{F}$ or CF_3 , yielded the cationic carbene intermediate that subsequently underwent fluoroalkyl migration to the fluorocarbene (Scheme 1.10).⁷⁰



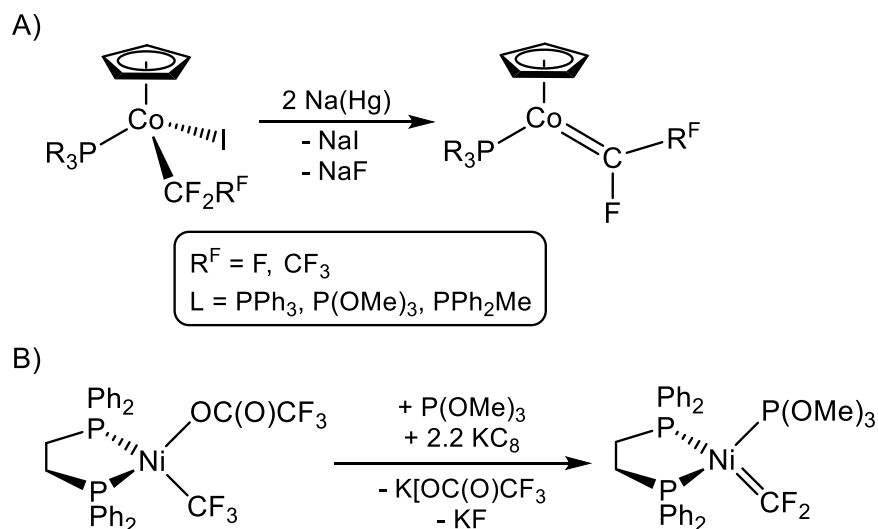
Scheme 1.10. Reaction showing cationic cobalt intermediate, $\text{CpCo}(\text{CF}_3)(\text{CF}_2\text{R}^{\text{F}})$, undergoing fluoroalkyl migration to the fluorocarbene, $\text{R}^{\text{F}} = \text{F}, \text{CF}_3$.

1.4.2.2 Activation of $\text{C}-\text{F}$ by Reduction

The use of alkali metals for the reduction of metal fluoroalkyls is another efficient route to metal fluorocarbenes via the elimination of alkali metal fluorides. This results in a two electron reduction at the metal center. Hughes *et al.* first reported the reduction of Ir(III) fluoroalkyl complexes $\text{Cp}^*\text{IrI}(\text{CF}_2\text{R}^{\text{F}})(\text{PMe}_3)$ ($\text{R}^{\text{F}} = \text{F}, \text{CF}_3, \text{C}_6\text{F}_5$) using excess potassium graphite (KC_8) to yield Ir(I) fluorocarbenes $\text{Cp}^*\text{Ir}(=\text{CFR}^{\text{F}})(\text{PMe}_3)$.⁵⁹ This method also proved extremely effective when extended for the preparation of the first example of a bis(trifluoromethyl) carbene complex, $\text{Cp}^*\text{Ir}(=\text{C}(\text{CF}_3)_2)(\text{CO})$.⁷¹

Baker *et al.* used this approach to prepare the first fluorocarbene complexes of both cobalt and nickel (*vide infra*). Cobalt(III) perfluoroalkyl iodide complexes $\text{CpCoI}(\text{CF}_2\text{R}^{\text{F}})(\text{PR}_3)$ ($\text{R}^{\text{F}} = \text{F}, \text{CF}_3$; $\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{PPh}_2\text{Me}$) underwent two-electron reduction when treated with a sodium-mercury amalgam to afford cobalt(I) fluorocarbenes $\text{CpCo}(=\text{CFR}^{\text{F}})(\text{PR}_3)$, as shown in Scheme 1.11A.^{63,72} Similarly, the nickel(II) complex $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{dppe})$ was reduced using KC_8

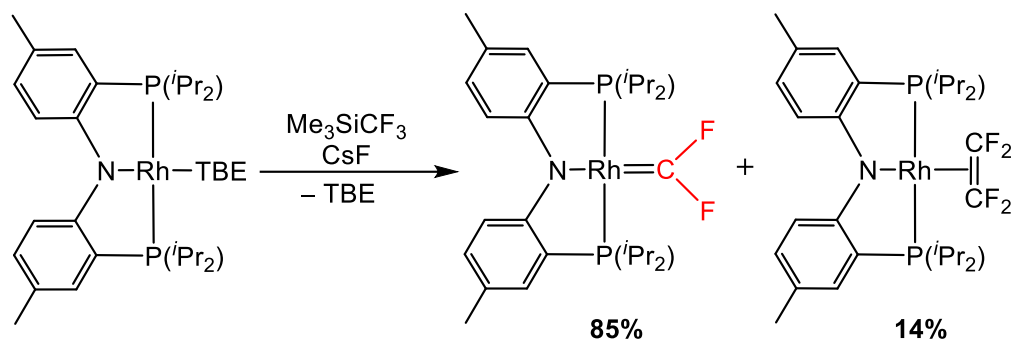
in the presence of $\text{P}(\text{OMe})_3$ to afford nickel(0) fluorocarbene $\text{Ni}(\text{=CF}_2)[\text{P}(\text{OMe})_3](\text{dppe})$ (Scheme 1.11B).⁶⁵ The unique reactivity of these cobalt and nickel fluorocarbene complexes will be featured further in this thesis.



Scheme 1.11. Synthesis of cobalt and nickel fluorocarbene complexes by reduction.

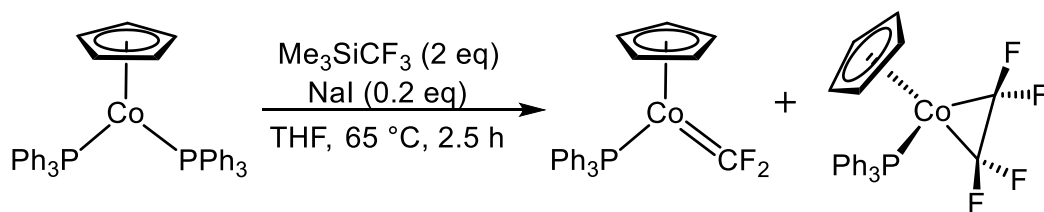
1.4.2.3 Direct Transfer of Difluorocarbene

An ideal synthetic strategy would be to directly install a CF_2 on the metal center. A previous report gave this result using $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$,⁷³ however, the toxicity of this reagent makes it highly undesirable. Instead, the Me_3SiCF_3 reagent was demonstrated to be an effective source of difluorocarbene when activated by either F^- or I^- , for the synthesis of difluorinated cyclopropanes. Furthermore, this methodology has been extended for the synthesis of a $(\text{PNP})\text{Rh}=\text{CF}_2$ complex, as shown in Scheme 1.12.⁷⁴ The reaction of $(\text{PNP})\text{Rh}(\text{TBE})$ ($\text{TBE} = \text{tert-butyl ethylene}$) with $\text{TMS}_3\text{CF}_3/\text{CsF}$ in a solution of benzene at 70°C afforded $(\text{PNP})\text{Rh}=\text{CF}_2$ and $(\text{PNP})\text{Rh}(\text{TFE})$ in 85% and 14% yields, respectively. The side product $(\text{PNP})\text{Rh}(\text{TFE})$ was proposed to result from TBE displacement by TFE , formed *in situ* by difluorocarbene dimerization.



Scheme 1.12. Synthesis of (PNP)Rh=CF₂.

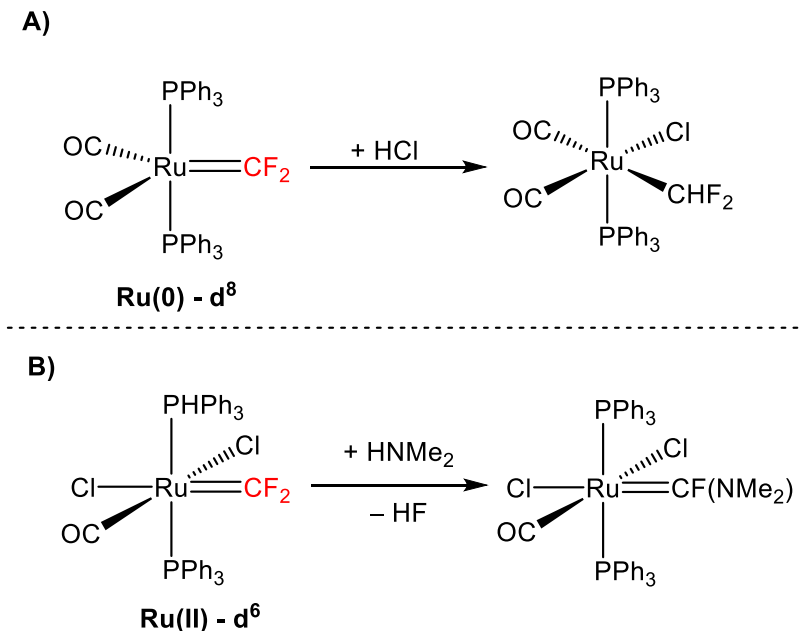
Finally, Baker *et al.* utilized this synthetic technique for the direct addition of a CF₂ carbene to a metal center. The reaction of CpCo(PPh₃)₂ with two equivalents of Me₃SiCF₃ and a catalytic amount of NaI yielded an unexpected cobalt TFE complex as well as the desired cobalt difluorocarbene.⁷⁵ It was found the nature of the ancillary ligand influenced the product formation with carbonyl ligands favoring the TFE complex, whereas ancillary PPh₃ or P(OMe)₃ favored the difluorocarbene complex. Further studies also showed that the TFE complex was formed by CF₂ addition to the cobalt fluorocarbene and not from direct reaction of TFE formed from CF₂ dimerization.



Scheme 1.13. Application of the Me₃SiCF₃ reagent for the installation of CF₂ carbene directly to the base metal cobalt.

1.4.3 Reactivity of Metal Fluorocarbenes

In comparison to its hydrocarbon analogues and metal-NHC complexes, the reactivity of isolated metal fluorocarbenes has not been well investigated. This is in large part due to the difficulty in producing a stable isolable complex (*vide supra*). Even more rare are examples of metal fluorocarbenes facilitating catalysis. Early work by Roper *et al.* found that the oxidation state of a metal has a large influence on the reactivity of the carbene carbon and whether it is nucleophilic or electrophilic.^{61,76} For instance, the ruthenium(II) fluorocarbene complex $\text{Ru}=\text{CF}_2(\text{CO})(\text{Cl})_2(\text{PPh}_3)_2$ reacts with nucleophiles like HNMe_2 and MeOH to eliminate HF and form complexes $\text{Ru}=[\text{CF}(\text{NMe}_2)](\text{CO})(\text{Cl})_2(\text{PPh}_3)_2$ and $\text{Ru}=[\text{CF}(\text{OMe})](\text{CO})(\text{Cl})_2(\text{PPh}_3)_2$, respectively (Scheme 1.14). In contrast, ruthenium(0) fluorocarbene $\text{Ru}=\text{CF}_2(\text{CO})_2(\text{PPh}_3)_2$ is resistant to nucleophiles, and can even be crystallized from wet solvents. Furthermore, $\text{Ru}=\text{CF}_2(\text{CO})_2(\text{PPh}_3)_2$ reacts with electrophiles such as H^+ , as treatment with HCl yields $\text{Ru}(\text{CF}_2\text{H})(\text{CO})_2(\text{Cl})(\text{PPh}_3)_2$. Therefore, these studies demonstrate that a metal fluorocarbene may have either nucleophilic or electrophilic type character. This provides knowledge towards the development of catalytic processes based on metal fluorocarbenes.



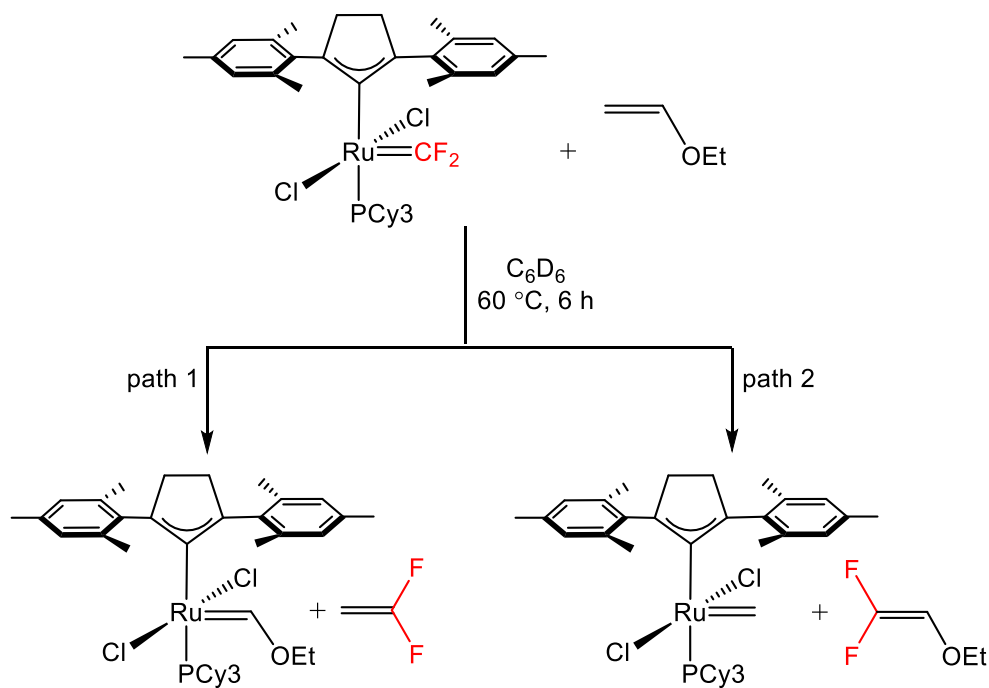
Scheme 1.14. Diverse reactivity of ruthenium fluorocarbenes based on oxidation state.

1.4.3.1 Hydrolysis of $\text{M}=\text{CF}_2$

As previously stated, metal fluorocarbenes may demonstrate either electrophilic or nucleophilic character. Those which demonstrate the former typically have a metal center in an oxidation state of +2 or greater, or are cationic. The most common reaction of electrophilic metal carbenes is the hydrolysis of $\text{M}=\text{CF}_2$ to $\text{M}-\text{CO}$. This reaction has a strong thermodynamic driving force from the formation of two $\text{H}-\text{F}$ bonds (568 kJ/mol) and a triple $\text{C}-\text{O}$ bond. Due to this very strong affinity for hydrolysis, such electrophilic metal carbenes must be handled in efficiently dried solvents to prevent decomposition. This tendency for hydrolysis is likely responsible for the absence of many reactivity studies on electrophilic-type fluorocarbene complexes. Alternatively, electron-rich nucleophilic metal fluorocarbenes, such as those based on Co [$\text{CpCo}(\text{=CFR}^{\text{F}})(\text{PR}_3)$] are resistant to hydrolysis.

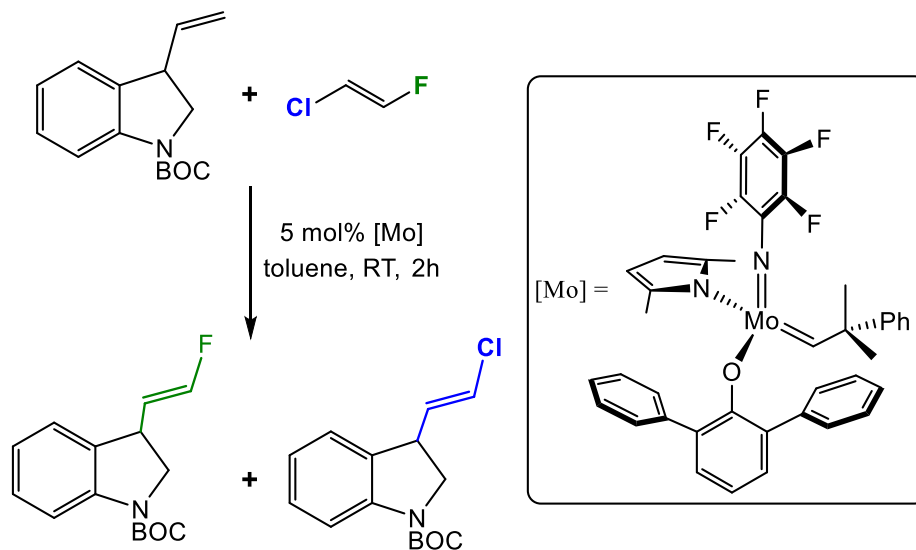
1.4.3.2 Alkene Metathesis with Alkyl Vinyl Ethers

Olefin metathesis has been thoroughly explored and established to have great tolerance toward a diverse range of functional groups.⁷⁷ Despite this wide applicability, fluorinated alkenes have been generally found to be incompatible for olefin metathesis. Ruthenium fluorocarbene complexes have been shown to have slow phosphine dissociation (a proposed initial catalytic step) and furthermore have great thermodynamic stability which prevent them from reacting at an appreciable rate. A recent report from Takahira, however, demonstrated the catalytic cross metathesis of fluoroalkenes and electron-rich enol ethers with up to 13 TON (turnover number), although it was found that the key catalytic species is not the $[\text{Ru}]=\text{CF}_2$ fragment.⁷⁸ Further studies showed the Ru difluorocarbene complex undergoes metathesis with the enol ethers to give the ether-containing carbene complex, as shown in Scheme 1.15, which subsequently undergoes cross-metathesis with the fluorinated alkene.



Scheme 1.15. Metathesis with Grubbs-type $\text{Ru}=\text{CF}_2$ complex.

Recent work by Hoveyda, Schrock *et al.* has demonstrated that d^0 Mo complexes are also able to affect cross-metathesis with selected fluoroalkenes (Scheme 1.16).⁷⁹

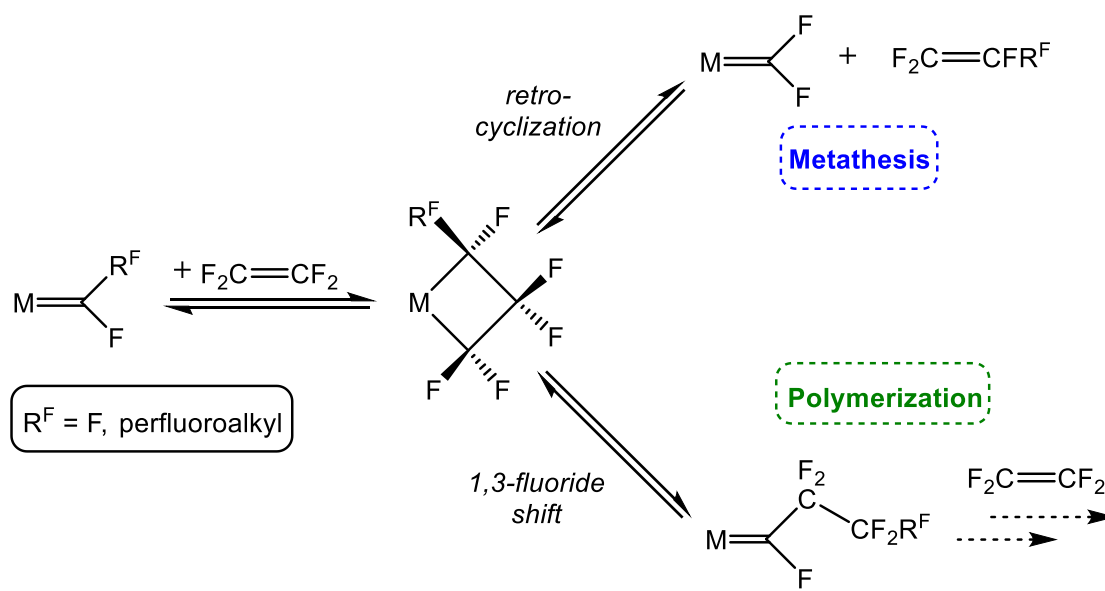


Scheme 1.16. Cross-metathesis of fluoroalkenes and electron-rich alkenes using a Mo catalyst.

1.4.3.3 Reactivity of Nucleophilic Metal Fluorocarbenes

Metal alkylidene complexes have been applied in many different areas of catalysis, most prominently of which is olefin metathesis.⁸⁰ This catalytic transformation has been thoroughly investigated, expanded, and optimized over the past several decades. Metal fluorocarbenes and metal fluoroalkyls are more challenging when trying to design catalysis. If catalysis for the metathesis or polymerization of polyfluoroalkenes, as shown in Scheme 1.17, could be designed to overcome these limitations, it would be a powerful step forward towards further green catalysis. The proposed metathesis mechanism for fluoroalkenes follows that of Chauvin, and the proposed polymerization mechanistic pathway is based on a fluorine version of the Green-Rooney mechanism.^{72,81} This route intentionally avoids migratory insertion into unreactive $M-R^F$ bond.

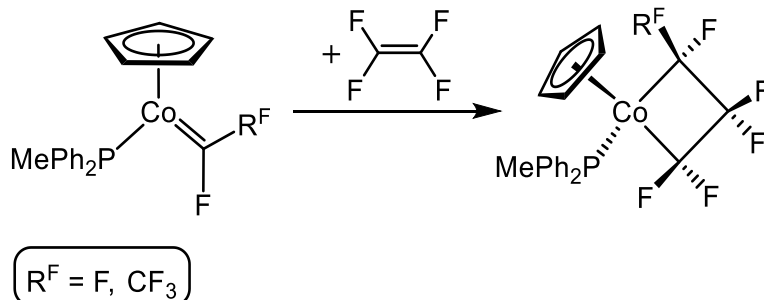
One of the goals of the Baker group has been to synthesize metal fluorocarbene complexes with nucleophilic character in order to promote reactivity with electron-deficient fluoroalkenes.



Scheme 1.17. Potential $\text{M}=\text{CF}_2$ initiated metathesis or polymerization with perfluoroalkenes.

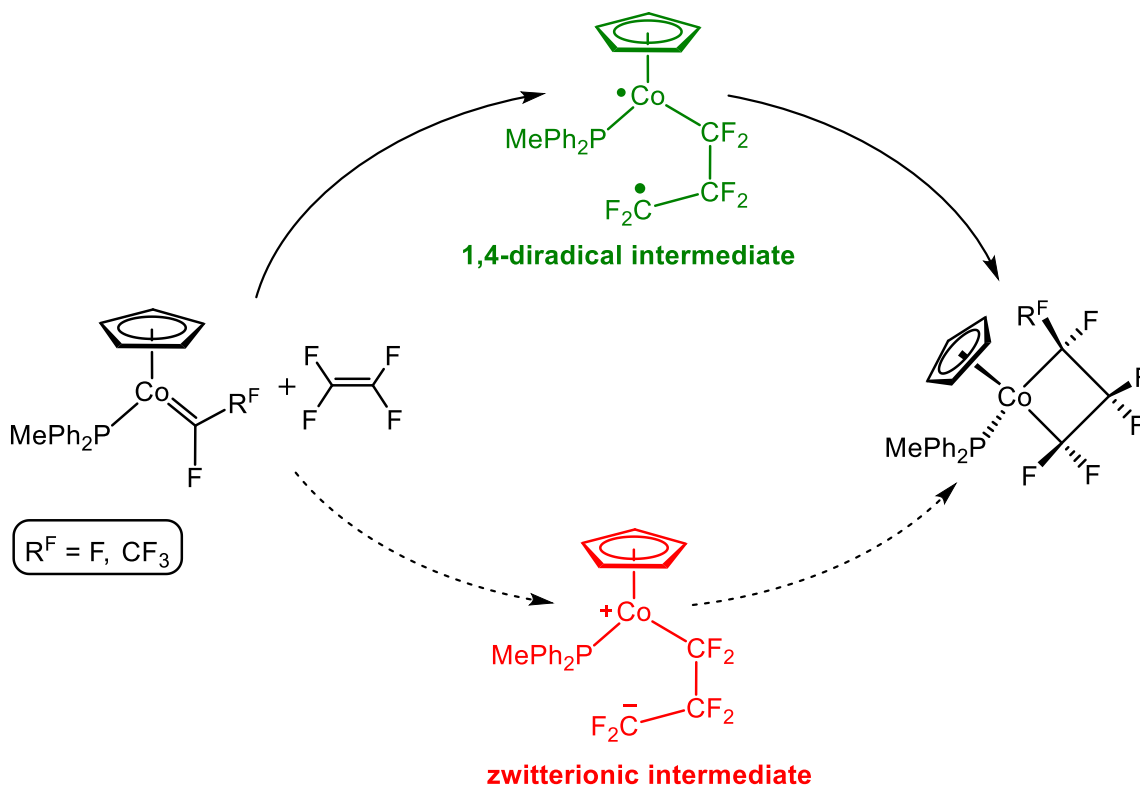
1.4.3.4 Reactivity of Cobalt Fluorocarbenes

A series of cobalt(I) fluorocarbene complexes with varying ancillary phosphine ligands of the form $\text{CpCo}(\text{=CFR}^{\text{F}})(\text{PR}_3)$ were synthesized ($\text{R}^{\text{F}} = \text{F, C}_3$; $\text{PR}_3 = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{PPh}_2\text{Me}$).⁷² The nucleophilic character of these complexes was investigated through test reactions with simple electrophiles (H^+ and Me^+). It was found that reaction of the fluorocarbene with lutidinium bromide and MeOTf resulted in respective protonation and methylation at the carbene carbon. Further reactivity with fluoroalkenes was investigated by reacting $\text{CpCo}(\text{=CFR}^{\text{F}})(\text{PPh}_2\text{Me})$ with an excess of TFE. After 4 days at room temperature, the perfluorometallacyclobutane complex shown in Scheme 1.18 was observed as a product of [2+2] cycloaddition. The electron-rich phosphine PPh_2Me was necessary for a reasonable reaction rate, as $\text{P}(\text{OMe})_3$ and PPh_3 resulted in noticeably lower rates.



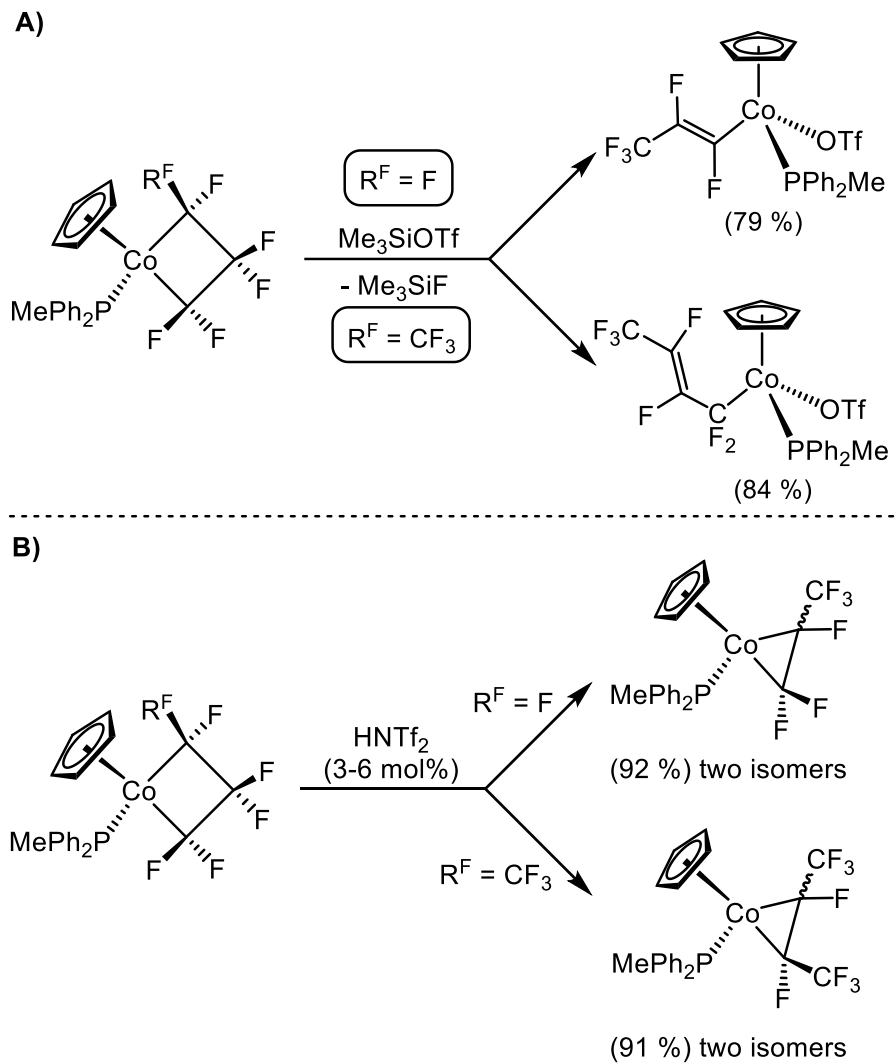
Scheme 1.18. Cycloaddition reaction between cobalt(I) fluorocarbenes and TFE.

Preliminary kinetic studies into the mechanism were investigated by performing the analogous reaction in the presence of 20 equivalents of PPh_2Me . It was found that the reaction rate did not significantly decrease in the presence of excess phosphine, suggesting that phosphine dissociation is not a key step in the addition of TFE. Interestingly, this result stands in direct contrast to a report by Hughes, which found an iridium(I) fluoroalkylidene-ethylene complex, $\text{Cp}^*\text{Ir}(=\text{CF}(\text{CF}_3))(\text{C}_2\text{H}_4)$, remained conformationally locked with a large calculated barrier to metallacyclobutane formation.⁸² DFT calculations on the mechanistic pathway of the [2+2] cycloaddition reaction between $\text{CpCo}(=\text{CF}_2)(\text{PPh}_2\text{Me})$ and TFE confirmed that the reaction proceeds without coordination of TFE to the Co center (Scheme 1.19). Instead the reaction most likely proceeds via a Co(II) 1,4-singlet diradical intermediate formed by attack of the fluorocarbene carbon on the TFE carbon.⁸³ Alternate formation of the zwitterionic Co(III) intermediate was shown to be a significantly higher energy process. The stability of the singlet-diradical intermediate comes from formation of a strong $\text{CF}_2\text{--CF}_2$ bond coupled with the radical stabilizing effect of a difluoromethylene group.⁸³ The perfluorometallacyclobutane products were found to be thermally stable with no evidence of cycloreversion.



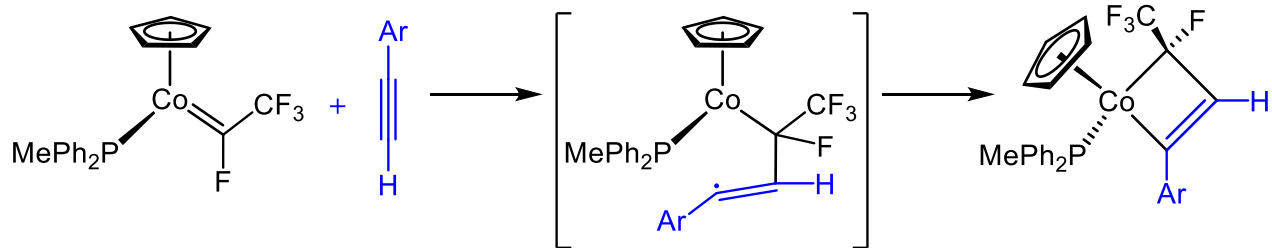
Scheme 1.19. Proposed cycloaddition pathways.

The reactivity of these perfluorometallacyclobutanes was investigated with Lewis and Brønsted acids (Scheme 1.20). When cobalt perfluorocyclobutane complexes were treated with Me_3SiOTf , fluoride abstraction was observed to yield the perfluoro-*trans*-vinyl or perfluoro-*trans*-allyl products, as shown in Scheme 1.20A. Alternatively, catalytic amounts of HNTf_2 resulted in clean isomerization/ring-contraction reactions, producing cobalt hexafluoropropene or perfluoro-2-butene complexes (Scheme 1.20B). Further studies performed with stoichiometric $[\text{HPPPh}_2\text{Me}][\text{NTf}_2]$ suggest that both ring-opening and catalytic ring-contraction reactions likely proceed via $\beta\text{-C-F}$ activation through a π -perfluoroallyl intermediate, as opposed to an $\alpha\text{-C-F}$ activation which had been previously observed for perfluorometallacyclopentanes.³⁵



Scheme 1.20. Reactivity of cobalt perfluorocyclobutanes.

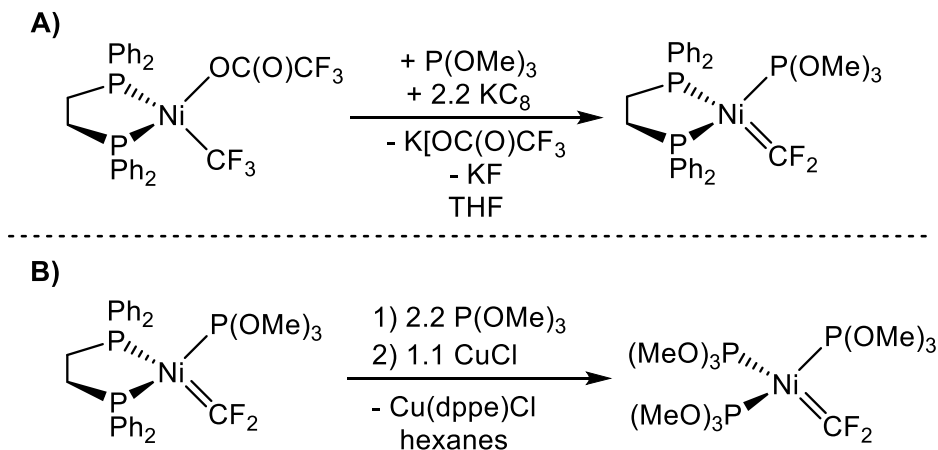
In another study from the Baker group, reactions of the $\text{Co}=\text{CF}(\text{CF}_3)$ fluorocarbene with aryl-acetylenes were shown to afford fluorinated cobaltacyclobutenes (Scheme 1.21). A series of DFT and kinetic studies were conducted into the [2+2] cycloaddition reaction mechanism, and a 1, 4-diradical species was again identified as the key intermediate.⁸⁴ While the expanded scope of reactivity proved promising, the instability of these products prevented further investigations into their reactivity.



Scheme 1.21. Reactivity of $\text{CpCo}(=\text{CF}(\text{CF}_3))(\text{PPh}_2\text{Me})$ with phenyl acetylenes to yield cobaltacyclobutenes.

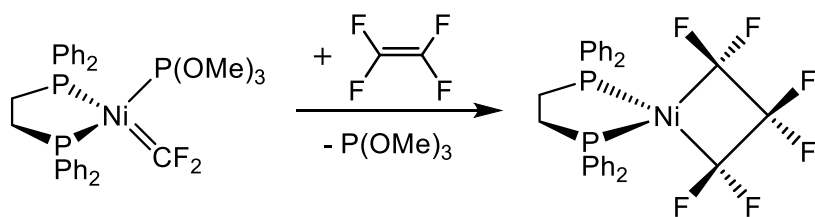
1.4.3.5 Reactivity of Nickel Fluorocarbenes

While the successful synthesis of the cobalt (I) fluorocarbene complexes was a significant advancement, the extremely slow reactivity with TFE (47 h) was a significant limitation. To further explore the reactivity of these systems, other first row transition metals were considered. Following the procedure developed by Hughes for the synthesis of iridium fluorocarbenes (*vide supra*), a two-electron reduction of $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{dppe})$ in the presence of $\text{P}(\text{OMe})_3$ using potassium graphite was performed.⁶⁵ This reaction gave the desired d^{10} Ni(0) difluorocarbene complex (Scheme 1.22A). To explore the effects of having the metal in a different electronic ligand environment, the complex was treated with $\text{P}(\text{OMe})_3$ in the presence of CuI , resulting in the analogous $\text{Ni}=\text{CF}_2[\text{P}(\text{OMe})_3]_3$ complex (Scheme 1.22B).



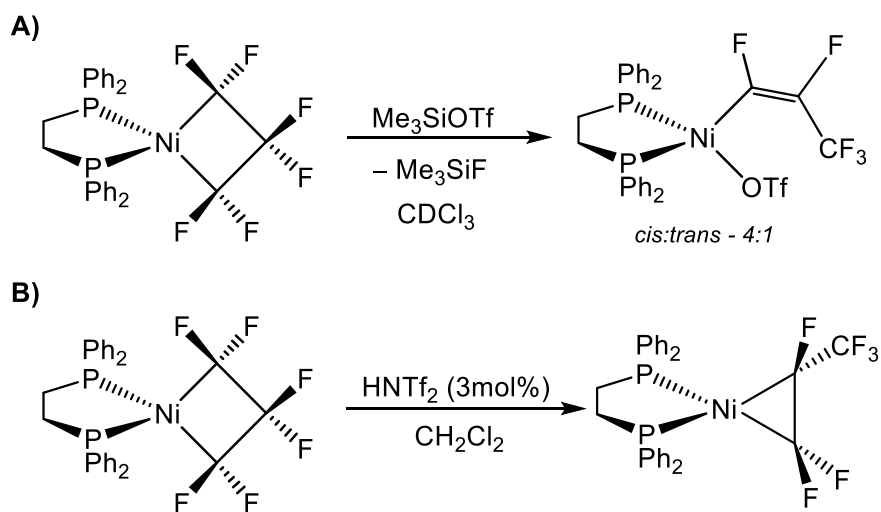
Scheme 1.22. Synthesis of d^{10} Ni(0) fluorocarbene complexes.

Initial reactivity studies of these complexes were performed by treating each of the nickel difluorocarbene complexes with TFE. In contrast to the previous Co work, both Ni compounds reacted appreciably at room temperature to form the perfluoronickelacycle products (Scheme 1.23). The reactions go to near completion after 2 and 4 h respectively, offering a significant improvement to previously reported reactivity with the Co system. Moreover, the reaction with 20 equivalents of $P(OMe)_3$ significantly decreased the rate of reaction, suggesting a dissociative mechanism in which loss of $P(OMe)_3$ is an initial step. This also stands in contrast to the previously studied Co system. Initial investigations of the formation of such d^{10} nickel difluorocarbene, and their reactivity with a small fluoro-olefin were extremely promising and deemed worthy of further study in this thesis.



Scheme 1.23. Synthesis of perfluoronickelacyclobutane.

Finally, reactivity of the nickelacycle products was investigated since it is the first intermediate in the conventional Chauvin mechanism. Fluoride abstraction using Me_3SiOTf yields the ring-opened vinyl product $\text{Ni}(\text{dppe})(\text{cis- and trans-CF}=\text{CFCF}_3)(\text{OTf})$, as shown in Scheme 1.24A. Further reactivity studies demonstrated that reaction with catalytic HNTf_2 causes isomerization/ring-contraction to hexafluoropropylene complex (Scheme 1.24B). These reactions also likely proceed by β -fluoride activation and a cationic perfluoroallyl complex ($[\text{Ni}](\eta^1\text{-}, \eta^2\text{-}, \text{ or } \eta^3\text{-C}_3\text{F}_5)^+$). While no cycloreversion reactions were observed for potential extension into metathesis, this nickel fluorocarbene offers a promising possibility for further optimization to improve reactivity.



Scheme 1.24. Reactivity of nickel metallacyclobutane with A) Me_3SiOTf , B) HNTf_2 , showing the respective ring opened vinyl product and ring contraction product.

1.5 Scope of Thesis

This thesis outlines the synthesis and characterization of a variety of nickel metallacycle complexes from simple fluorinated olefin and acetylene starting materials. Two additional chapters will discuss the synthesis and use of a Ni(0) difluorocarbene complex and its utility in the generation of nickel metallacycles. Chapter 2 initially details an optimized synthesis of the nickel fluorocarbene complex. It goes on to discuss a series of reactivity studies with fluoro-olefins to determine the scope of reactivity of the nickel difluorocarbene complex. These reactions form a variety of perfluoronickelacycles, some of which demonstrate further reactivity. Chapter 3 details reactivity studies of the nickel fluorocarbene complex towards a diverse range of terminal acetylenes with varied steric and electronic parameters. These reactions all result in the conversion to a nickel metallacyclobutene, followed by insertion of a second equivalent of aryl-acetylene with formation of the first fluorinated metallacyclohexadiene. Finally reductive elimination of the latter gives Ni(0) and the difluorocyclopentadiene derivatives. The results presented herein will allow for future investigations of fluorinated metallacycle reactivity, increasing our ability to prepare value-added fluorocarbon products for pharma, agrochemicals, and polymer applications.

1.6 References

- (1) Campbell, M. G.; Hoover, A. J.; Ritter, T. In *Organometallic Fluorine Chemistry*; Springer: **2014**, p 1-53.
- (2) LaBerge, N. A.; Love, J. A. In *Organometallic Fluorine Chemistry*; Springer: **2015**, p 55-111.
- (3) Ohashi, M.; Ogoshi, S. In *Organometallic Fluorine Chemistry*; Springer: **2014**, p 197-215.
- (4) Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. *Chem. Rev.* **2013**, *114*, 2432-2506.
- (5) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881-1886.
- (6) Isanbor, C.; O'Hagan, D. *J. Fluor. Chem.* **2006**, *127*, 303-319.
- (7) Jeschke, P. *ChemBioChem.* **2004**, *5*, 570-589.
- (8) Berger, R.; Resnati, G.; Metrangolo, P.; Weber, E.; Hulliger, J. *Chem. Soc. Rev.* **2011**, *40*, 3496-3508.
- (9) Tressaud, A. *Fluorine and the environment: atmospheric chemistry, emissions & lithosphere*; Elsevier, **2006**; Vol. 1.
- (10) Tressaud, A. *Fluorine and the environment: agrochemicals, archaeology, green chemistry and water*; Elsevier, **2006**; Vol. 2.
- (11) Hu, J.-Y.; Zhang, J.-L. In *Organometallic Fluorine Chemistry*; Springer: **2015**, p 143-196.
- (12) Dolbier Jr, W. R. *J. Fluor. Chem.* **2005**, *126*, 157-163.
- (13) Siqing, W. *Chem. Prod. Tech.* **2010**, *5*, 005.
- (14) Singh, R. R.; Pham, H. T.; Wilson, D. P.; Thomas, R. H.; Shankland, I.; (**2009**). U.S. Patent No. 7,534,366. Washington, DC: U.S. Patent and Trademark Office.
- (15) Montzka, S.; McFarland, M.; Andersen, S.; Miller, B.; Fahey, D.; Hall, B.; Hu, L.; Siso, C.; Elkins, J. *J. Phys. Chem A.* **2014**, *119*, 4439-4449.
- (16) Pinnock, S.; Hurley, M. D.; Shine, K. P.; Wallington, T. J.; Smyth, T. J. *J. Geophys. Res. Atmos.* **1995**, *100*, 23227-23238.

- (17) Yang, L.; da Rocha, S. R. *J. Phys. Chem. B.* **2014**, *118*, 10675-10687.
- (18) Ritter, S. K. *Chem. Eng. News.* **2010**, *88*, 12-17.
- (19) Steenland, K.; Fletcher, T.; Savitz, D. A. *Environ. Health Perspect.* **2010**, *118*, 1100-1108.
- (20) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255-263.
- (21) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299.
- (22) Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573-16579.
- (23) Schultz, J. W.; Fuchigami, K.; Zheng, B.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2016**, *138*, 12928-12934.
- (24) Elsby, M. R.; Johnson, S. A. *J. Am. Chem. Soc.* **2017**, *139*, 9401-9407.
- (25) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169-1204.
- (26) Camasso, N. M.; Sanford, M. S. *Science* **2015**, *347*, 1218-1220.
- (27) Cámpora, J.; Palma, P.; Carmona, E. *Coord. Chem. Rev.* **1999**, *193*, 207-281.
- (28) Ojima, I. *Fluorine in medicinal chemistry and chemical biology*; John Wiley & Sons, **2009**.
- (29) Im, J.; Walshe-Langford, G. E.; Moon, J.-W.; Löffler, F. E. *Environ. Sci. Technol.* **2014**, *48*, 13181-13187.
- (30) Cundy, C.; Green, M.; Stone, F. J. *Chem. Soc. A.* **1970**, 1647-1653.
- (31) Greco, A.; Green, M.; Shakshooki, S.; Stone, F. J. *Chem. Soc., Dalton Trans.* **1970**, 1374-1375.
- (32) Maples, P.; Green, M.; Stone, F. J. *Chem. Soc., Dalton Trans.* **1973**, 388-392.
- (33) Bernhardt, P. V.; Gallego, C.; Martinez, M.; Parella, T. *Inorg. Chem.* **2002**, *41*, 1747-1754.
- (34) Van Leeuwen, P.; Roobeek, C. *Tetrahedron.* **1981**, *37*, 1973-1983.
- (35) Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7*, 1642-1648.

- (36) Giffin, K. A.; Pua, L. A.; Piotrkowski, S.; Gabidullin, B. M.; Korobkov, I.; Hughes, R. P.; Baker, R. T. *J. Am. Chem. Soc.* **2017**, *139*, 4075-4086.
- (37) Andrella, N. O.; Sicard, A. J.; Gorelsky, S. I.; Korobkov, I.; Baker, R. T. *Chem. Sci.* **2015**, *6*, 6392-6397.
- (38) Richmond, T. G. *Angew. Chem. Int. Ed.* **2000**, *39*, 3241-3244.
- (39) King, R.; King Jr, A.; Iqbal, M.; Frazier, C. *J. Am. Chem. Soc.* **1978**, *100*, 1687-1694.
- (40) Yamaguchi, Y.; Ichioka, H.; Klein, A.; Brennessel, W. W.; Vicic, D. A. *Organometallics* **2012**, *31*, 1477-1483.
- (41) Algarra, A. s. G.; Grushin, V. V.; Macgregor, S. A. *Organometallics* **2012**, *31*, 1467-1476.
- (42) Taw, F. L.; Clark, A. E.; Mueller, A. H.; Janicke, M. T.; Cantat, T.; Scott, B. L.; Hay, P. J.; Hughes, R. P.; Kiplinger, J. L. *Organometallics* **2012**, *31*, 1484-1499.
- (43) McClellan, W. *J. Am. Chem. Soc.* **1961**, *83*, 1598-1600.
- (44) Maleckis, A.; Sanford, M. S. *Organometallics* **2014**, *33*, 3831-3839.
- (45) King, R.; Stafford, S.; Treichel, P.; Stone, F. *J. Am. Chem. Soc.* **1961**, *83*, 3604-3608.
- (46) Brzezinska, Z.; Cullen, W. *Inorg. Chem.* **1979**, *18*, 3132-3138.
- (47) Collman, J. P.; Sears Jr, C. T. *Inorg. Chem.* **1968**, *7*, 27-32.
- (48) Hughes, R. P.; Smith, J. M.; Liable-Sands, L. M.; Concolino, T. E.; Lam, K.-C.; Incarvito, C.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **2000**, 873-880.
- (49) Liu, X.; Xu, C.; Wang, M.; Liu, Q. *Chem. Rev.* **2014**, *115*, 683-730.
- (50) Kolomeitsev, A.; Movchun, V.; Rusanov, E.; Bissky, G.; Lork, E.; Röschenthaler, G.-V.; Kirsch, P. *Chem. Commun.* **1999**, 1017-1018.
- (51) Urata, H.; Fuchikami, T. *Tetrahedron Lett.* **1991**, *32*, 91-94.
- (52) Dubinina, G. G.; Furutachi, H.; Vicic, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 8600-8601.
- (53) Kieltsch, I.; Dubinina, G. G.; Hamacher, C.; Kaiser, A.; Torres-Nieto, J.; Hutchison, J. M.; Klein, A.; Budnikova, Y.; Vicic, D. A. *Organometallics* **2010**, *29*, 1451-1456.

- (54) Sohn, S. S.; Rosen, E. L.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14370-14371.
- (55) Fürstner, A. *Alkene metathesis in organic synthesis*; Springer, **2003**; Vol. 1.
- (56) Straub, B. F.; Hofmann, P. *Angew. Chem. Int. Ed.* **2001**, *40*, 1288-1290.
- (57) Dyson, G.; Frison, J.-C.; Simonovic, S.; Whitwood, A. C.; Douthwaite, R. E. *Organometallics* **2008**, *27*, 281-288.
- (58) Reger, D.; Dukes, M. *J. Organomet. Chem.* **1978**, *153*, 67-72.
- (59) Hughes, R. P.; Laritchev, R. B.; Yuan, J.; Golen, J. A.; Rucker, A. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 15020-15021.
- (60) Huang, D.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. *J. Am. Chem. Soc.* **2000**, *122*, 8916-8931.
- (61) Clark, G. R.; Hoskins, S. V.; Jones, T. C.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1983**, 719-721.
- (62) Brothers, P. J.; Burrell, A. K.; Clark, G. R.; Rickard, C. E.; Roper, W. R. *J. Organomet. Chem.* **1990**, *394*, 615-642.
- (63) Harrison, D. J.; Gorelsky, S. I.; Lee, G. M.; Korobkov, I.; Baker, R. T. *Organometallics* **2012**, *32*, 12-15.
- (64) Crespi, A. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1830-1835.
- (65) Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics* **2015**, *34*, 5683-5686.
- (66) Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics* **2015**, *34*, 4598-4604.
- (67) Richmond, T. G.; Shriver, D. F. *Organometallics* **1983**, *2*, 1061-1062.
- (68) Koola, J. D.; Roddick, D. M. *Organometallics* **1991**, *10*, 591-597.
- (69) Richmond, T. G.; Crespi, A. M.; Shriver, D. F. *Organometallics* **1984**, *3*, 314-319.
- (70) Leclerc, M. C.; Bayne, J. M.; Lee, G. M.; Gorelsky, S. I.; Vasiliu, M.; Korobkov, I.; Harrison, D. J.; Dixon, D. A.; Baker, R. T. *J. Am. Chem. Soc.* **2015**, *137*, 16064-16073.
- (71) Yuan, J.; Hughes, R. P.; Rheingold, A. L. *Eur. J. Inorg. Chem.* **2007**, *2007*, 4723-4725.

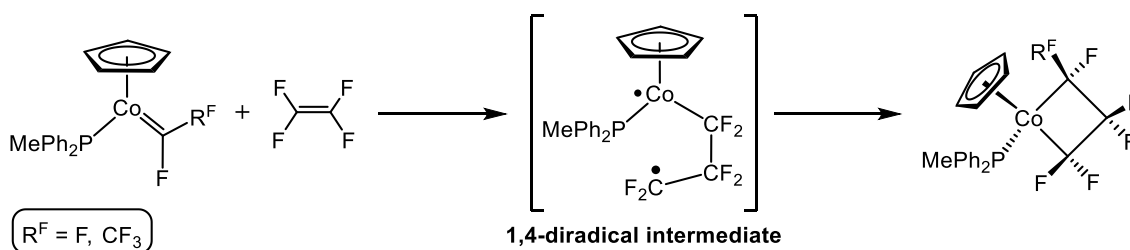
- (72) Harrison, D. J.; Lee, G. M.; Leclerc, M. C.; Korobkov, I.; Baker, R. T. *J. Am. Chem. Soc.* **2013**, *135*, 18296-18299.
- (73) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmecky, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722-733.
- (74) Wang, F.; Luo, T.; Hu, J.; Wang, Y.; Krishnan, H. S.; Jog, P. V.; Ganesh, S. K.; Prakash, G. S.; Olah, G. A. *Angew. Chem.* **2011**, *123*, 7291-7295.
- (75) Lee, G. M.; Harrison, D. J.; Korobkov, I.; Baker, R. T. *Chem. Commun.* **2014**, *50*, 1128-1130.
- (76) Michelin, R. A.; Ros, R.; Guadalupi, G.; Bombieri, G.; Benetollo, F.; Chapuis, G. *Inorg. Chem.* **1989**, *28*, 840-846.
- (77) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18-29.
- (78) Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2001**, *40*, 3441-3444.
- (79) Nguyen, T. T.; Koh, M. J.; Shen, X.; Romiti, F.; Schrock, R. R.; Hoveyda, A. H. *Science* **2016**, *352*, 569-575.
- (80) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243.
- (81) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85-93.
- (82) Yuan, J.; Hughes, R. P.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2010**, *29*, 1942-1947.
- (83) Fuller, J. T.; Harrison, D. J.; Leclerc, M. C.; Baker, R. T.; Ess, D. H.; Hughes, R. P. *Organometallics* **2015**, *34*, 5210-5213.
- (84) Lee, G. M.; Leung, A. S.; Harrison, D. J.; Korobkov, I.; Hughes, R. P.; Baker, R. T. *Organometallics* **2017**, *36*, 2853-2860.

Chapter 2 – Investigating the Reactivity of Fluoroalkenes with an Electron-Rich Ni(0) Difluorocarbene Complex

2.1 Introduction

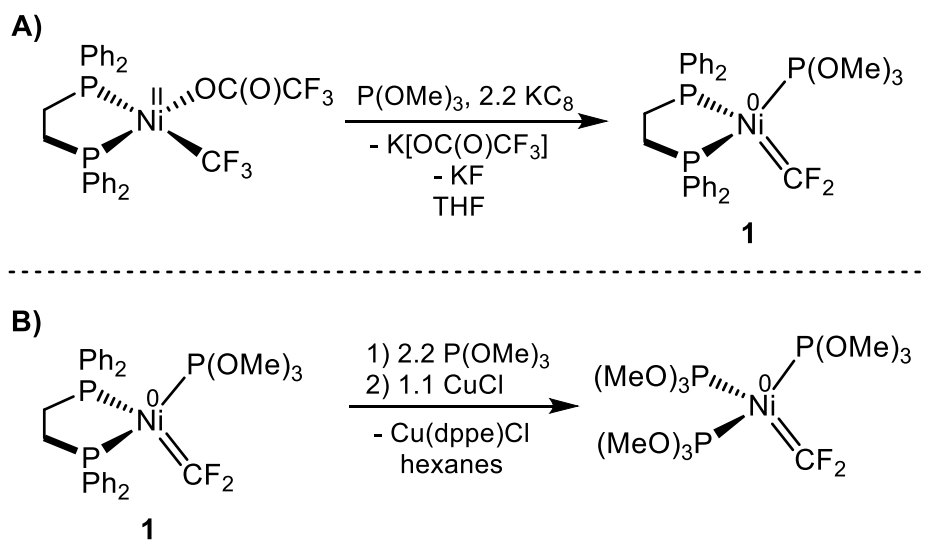
Reactions involving metal alkylidenes are some of the most valuable and desired catalytic transformations.^{1,2} While the reactivity of metal-carbenes has been thoroughly studied and established,³ the use of metal-fluorocarbenes in transition metal catalysis has only recently been investigated.⁴ Fluorinated alkenes are relatively inert, and even when activated by metals, remain relatively stable in comparison to their hydrocarbon counterparts. The ability to activate and functionalize small fluoroalkenes could lead to development of catalytic pathways that would be invaluable towards the synthesis of a wide variety of products used in multiple industries.^{5,6}

The Baker group is interested in the development of economical first-row transition metal fluorocarbene complexes for catalytic applications.^{7,8} In one example relevant to this thesis, nucleophilic d^8 $\text{Cp}(\text{PPh}_2\text{Me})\text{Co}=\text{CFR}$ complexes were prepared ($\text{R} = \text{F}, \text{CF}_3$) and shown to undergo cycloaddition with tetrafluoroethylene (TFE) via a novel closed-shell diradical mechanism that does not involve formation of an intermediate η^2 -alkene complex (Scheme 2.1).^{9,10} In contrast to their hydrocarbon analogues, the resulting metallacyclopentanes were very stable (ca. -25 kcal/mol vs. $\text{Co}=\text{CF}_2 + \text{TFE}$).



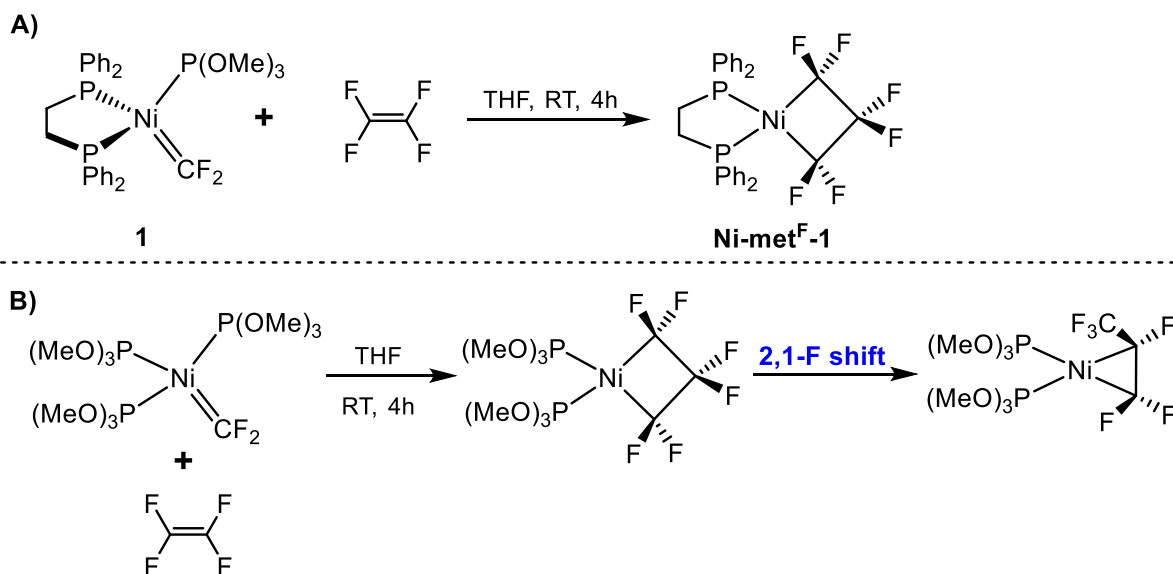
Scheme 2.1. Cycloaddition reaction between TFE and $\text{Cp}(\text{PMePh}_2)\text{Co}=\text{CFR}$ via a 1,4-diradical intermediate ($\text{R} = \text{F}, \text{CF}_3$).

In a subsequent study, Baker *et al.* reported the first examples of isolable nickel difluorocarbene complexes that are formally d^{10} $\text{Ni}(0)$.¹¹ Reducing the nickel complex $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{dppe})$ with potassium graphite in the presence of stoichiometric $\text{P}(\text{OMe})_3$ resulted in clean conversion to the desired product $\text{Ni}=\text{CF}_2[\text{P}(\text{OMe})_3](\text{dppe})$ (**1**), as shown in Scheme 2.2A. In order to compare the reactivity of the $\text{Ni}=\text{CF}_2$ fragment in a varied ligand environment, an alternate analogue of the nickel difluorocarbene was synthesized by reacting **1** with 2.2 equivalents of $\text{P}(\text{OMe})_3$ in the presence of CuCl to yield the product $\text{Ni}=\text{CF}_2[\text{P}(\text{OMe})_3]_3$, as shown in Scheme 2.2B.¹¹ With these two fluorocarbene compounds that contain both electron-rich and π -acidic ligand systems around the nickel center, reactivity studies with small fluoroalkenes were pursued.



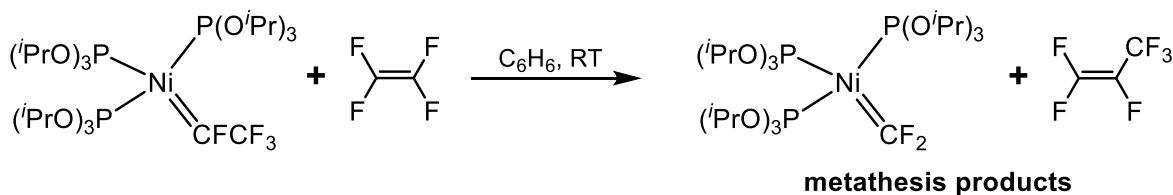
Scheme 2.2. Synthesis of Ni(0) difluorocarbene complexes.

To investigate the potential of these Ni fluorocarbenes towards fluoroalkene metathesis, reactions with tetrafluoroethylene (TFE) were investigated.¹¹ While both complexes reacted rapidly at room temperature to afford perfluorometallacyclobutanes, the latter was only stable with dppe as the ancillary ligand; the analogous tris- P(OMe)_3 complex underwent isomerization to the hexafluoropropylene (HFP) complex via a 2,1-F shift, as shown in Scheme 2.3B.¹¹ Reactivity of the perfluorometallacyclobutane product **Ni-met^F-1** was investigated, and it was shown that reaction with catalytic HNTf_2 causes isomerization/ring contraction to yield an analogous HFP complex. Furthermore, fluoride abstraction using Me_3SiOTf yielded the perfluoropropenyl complex via Ni–C bond cleavage and 2,1-F shift (for further details, see Introduction: Section 1.4.3.5).



Scheme 2.3. A) Reaction of **1** with TFE to form nickel perfluorometallacyclobutane product (**Ni-met^F-1**); B) Partial isomerization of perfluorometallacyclobutane to furnish the hexafluorometallacyclopropane complex.

In a recent study, $\text{Ni}=\text{CF}(\text{CF}_3)[\text{P}(\text{O}^i\text{Pr})_3]_3$ was shown to afford metathesis products when treated with TFE, as shown in Scheme 2.4.¹² An accompanying computational study identified a tetrahedral transition state that allowed the metathesis pathway to compete with formation of stable metallacyclobutanes that were again formed via a diradical intermediate. Furthermore, DFT calculations showed that the metathesis products ($\text{Ni}=\text{CF}_2 + \text{HFP}$) were significantly more thermodynamically stable than $\text{Ni}=\text{CF}(\text{CF}_3) + \text{TFE}$.



Scheme 2.4. Reaction of $\text{Ni}=\text{CF}(\text{CF}_3)$ with TFE to afford the metathesis products $\text{Ni}=\text{CF}_2$ and HFP.

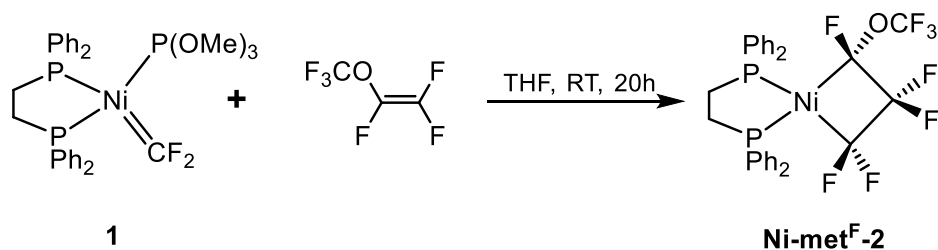
Observation of the metathesis products shown in Scheme 2.4 represents great progress towards fluorinated olefin metathesis. However, the difficulty in preparing more electron-rich Ni=CF(CF₃) complexes ultimately hinders further progress for this system. In this chapter, the electron-rich dppe Ni=CF₂ complex **1** is further explored as a potential metathesis precursor by expanding the currently known fluoroalkene scope to include varying degrees of fluorination and functional groups.

2.2 Results & Discussion

In order to expand the fluoroalkene scope, we first optimized the synthesis of the dppe Ni fluorocarbene (**1**). Various issues through the synthetic process such as duration of stirring at a specific temperature, amount of KC₈, and solvent have a strong influence on both final yield and solubility of the isolated product. As the published procedure often gave **1** as a viscous impure oil, we found that additional KC₈ (2.8 vs 2.2 equiv.) and longer stirring time at -78 °C resulted in a more consistent synthesis (See Experimental Section 2.4.2 for details).

As the previously reported Ni=CF(CF₃)[P(OⁱPr)₃]₃ complex was shown to afford metathesis products from reaction with both hexafluoropropene (HFP) and perfluoro(methyl vinyl ether) (PMVE),¹³ we began our investigations with these perfluorinated alkenes to see if **1** would demonstrate similar reactivity. As discussed below, while reaction of **1** with PMVE affords a single regioisomer of the expected metallacyclobutane, reaction with HFP affords the unexpected Ni(CF₃)[CF=CF(CF₃)](dppe) product.

A solution of **1** in THF was charged with an excess of PMVE resulting in a dark red solution. After 20 h at room temperature the reaction mixture changed to a light yellow. Analysis of the ^{19}F NMR spectrum showed complete consumption of **1** with selective formation of the metallacyclobutane **Ni-met^F-2**, shown in Scheme 2.5.



Scheme 2.5. Reaction of **1** with PMVE to form **Ni-met^F-2**.

The ^{19}F NMR spectrum, shown in Figure 2.1, displays a singlet at -55.8 ppm assigned to the OCF_3 , and a set of doublet of multiplets at -112.4 and -119.5 ppm due to the geminal $\beta\text{-CF}_2$ pair ($^2J_{\text{FF}} = 241$ Hz). The geminal $\alpha\text{-CF}_2$ pair are found at -117.4 and -121.5 ppm ($^2J_{\text{FF}} = 206$ Hz), and the multiplet resonance at -133.0 ppm is assigned to the $\alpha\text{-F}$ on the same carbon as the OCF_3 group. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a single broad multiplet at 44.8 ppm ($\Delta\nu_{1/2} = 79$ Hz). No evidence of TFE or $\text{Ni}=\text{CF}(\text{OCF}_3)$ metathesis products was observed.

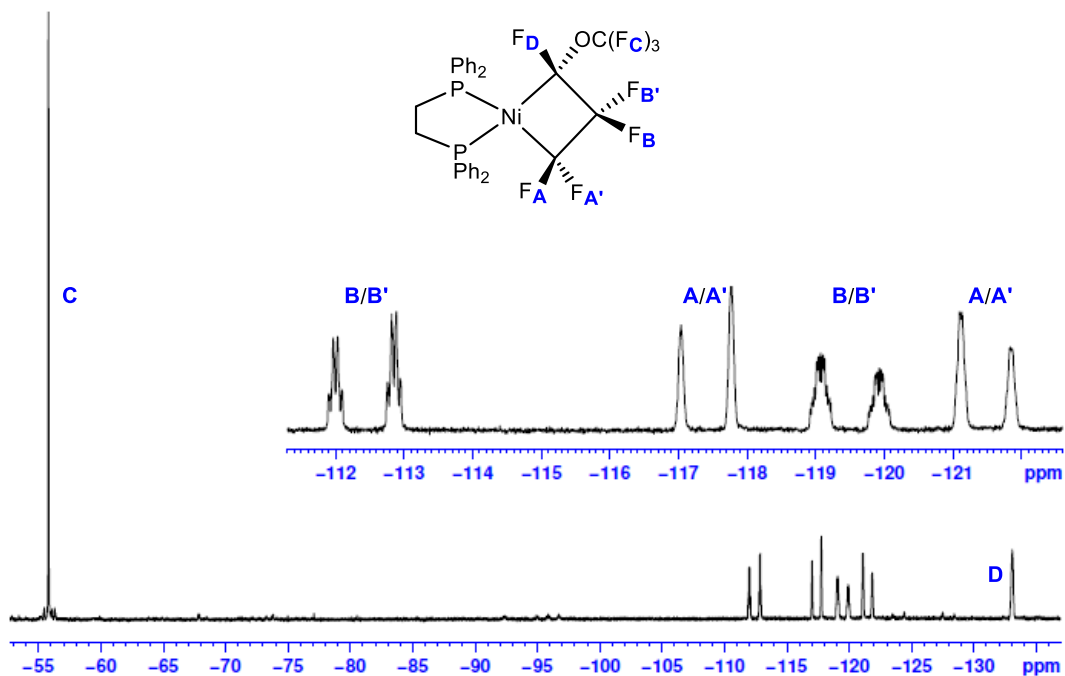
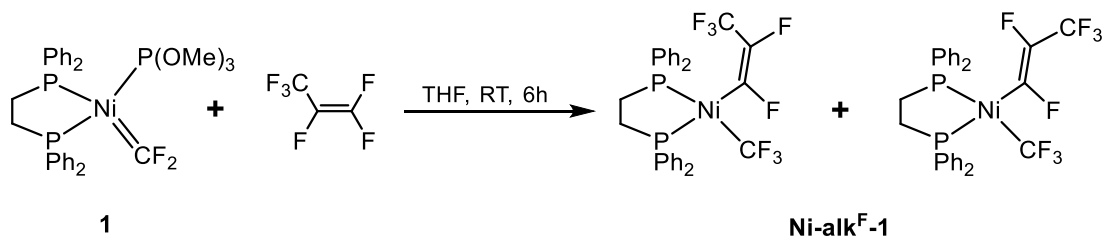


Figure 2.1. ^{19}F NMR (282 MHz, THF) spectrum of **Ni-met^F-2**.

The analogous reaction of **1** with HFP was complete after just 6 h, affording a yellow solution. The unexpected ^{19}F NMR spectrum of the reaction mixture consisted of four major resonances in a 3:3:1:1 ratio indicative of the product **Ni-alk^F-1** (Scheme 2.6). The large doublet splitting observed for the multiplets at -146.2 and -176.4 ppm ($^3J_{\text{FF}} = 132$ Hz) is typical of *trans* vinylic fluorines that are both also coupled to the CF_3 resonance at -67.7 ppm (dd, $^3J_{\text{FF}} = 23$ Hz). Finally, the resonance at -92.2 ppm assigned to the Ni- CF_3 is also coupled to the two ligand Ps ($^3J_{\text{FP}} = 12$ Hz).



Scheme 2.6. Reaction of **1** with HFP.

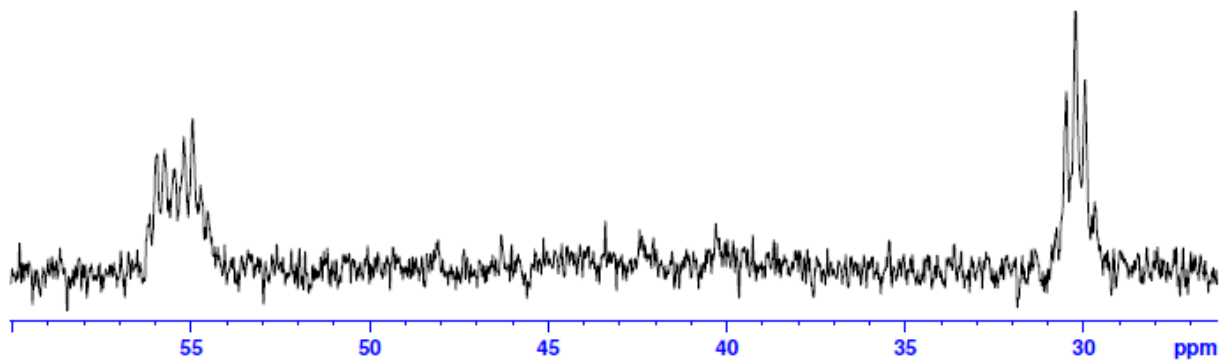
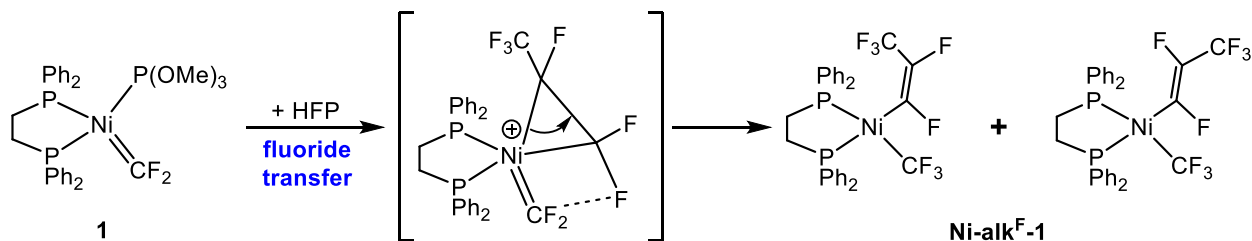


Figure 2.3. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF) spectrum of $\text{Ni}(\text{CF}_3)[\text{CF}=\text{CF}(\text{CF}_3)](\text{dppe})$, **Ni-alk^F-1**

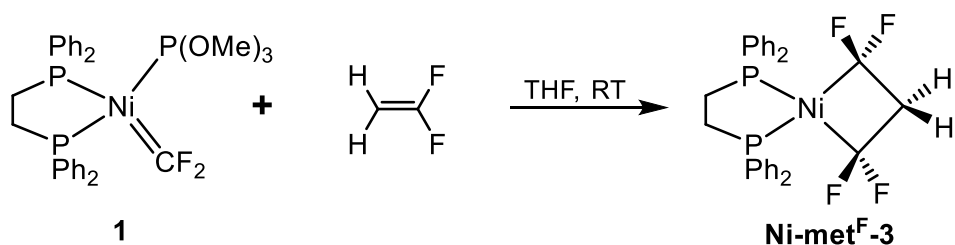
The reaction of **1** with HFP to yield the unexpected **Ni-alk^F-1** product involves a formal fluoride transfer from HFP to the Ni fluorocarbene carbon and coordination of the resulting perfluoropropenyl cation to Ni, affording the Ni(II) product. As HFP is known to react with nucleophilic carbonylmetallate anions to give fluoride and metal σ -alkenyl complexes via a single electron-transfer pathway,¹⁴ a similar pathway here could be followed by fluoride capture by the electrophilic Ni(II) fluorocarbene carbon (Scheme 2.7).



Scheme 2.7. Proposed reaction pathway of **1** with HFP.

To observe the effects of reducing the degree of alkene fluorination, we next investigated reactions of **1** with trifluoroethylene (TrFE) and 1,1-difluoroethylene (vinylidene fluoride, VDF). While the latter afforded a single regioisomer of the expected metallacyclobutane, the analogous product from TrFE was further converted to a new fluoroalkene and a metallacyclopentane product.

A solution of **1** in THF was charged with an excess of VDF resulting in a dark red solution. After allowing the reaction mixture to sit for 25 h, a dark orange solution resulted, and the crude ^{19}F NMR spectrum displayed a new broad resonance at -88.2 ppm along with excess VDF. The broad resonance continued to grow in over the following days. Continual daily monitoring showed the broad resonance beginning to sharpen to show multiplicity, and after 5 days of total reaction, it had completely transformed into a triplet of doublets at 88.6 ppm ($^3J_{FH} = 50$, $^3J_{FP} = 39$ Hz), which was assigned to the expected metallacycle product **Ni-met^F-3**, (Scheme 2.8). The reaction progress as monitored by ^{19}F NMR is shown in Figure 2.4. The $^{31}\text{P}\{^1\text{H}\}$ NMR shows a broad triplet at 44.1 ppm ($^3J_{PF} = 39$ Hz).



Scheme 2.8. Reaction of **1** with VDF to form **Ni-met^F-3**.

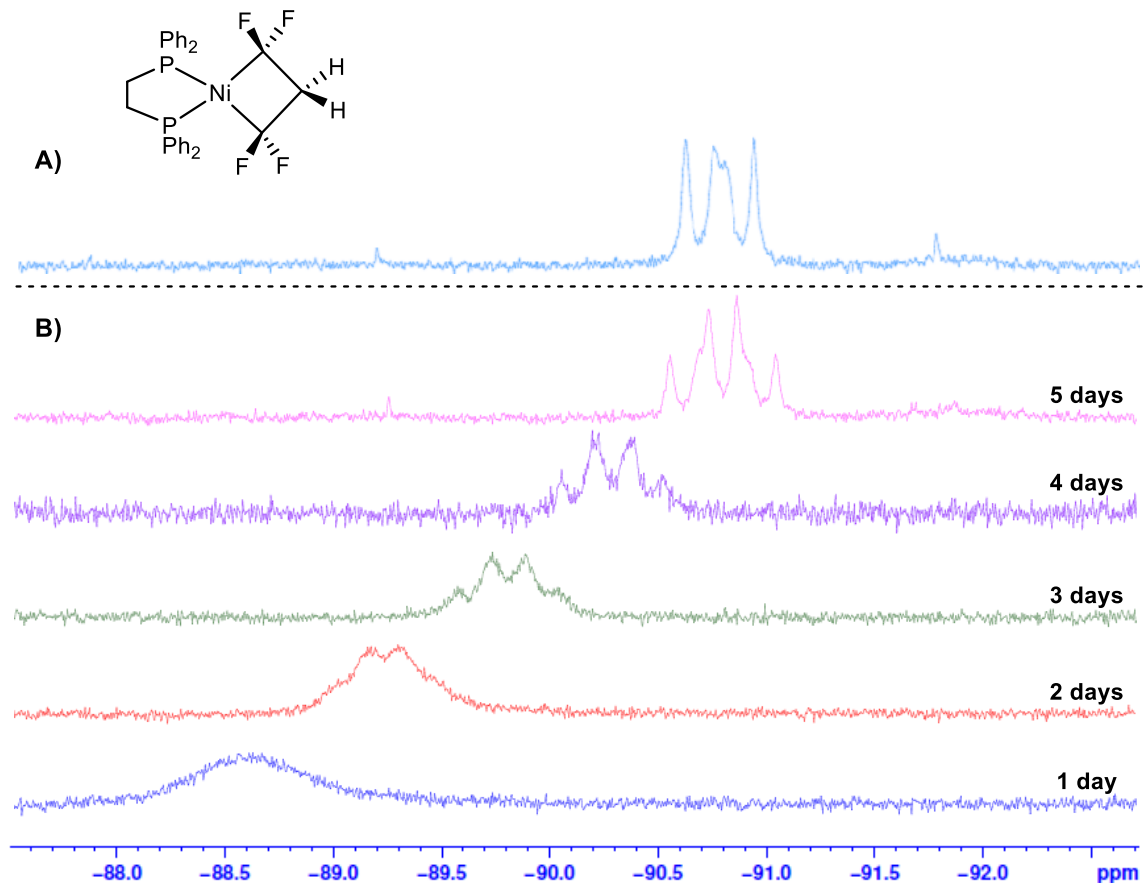


Figure 2.4. ^{19}F NMR (282 MHz, THF) spectrum of **Ni-met^F-3**.

A solution of **1** in THF was charged with an excess of TrFE resulting in a dark red solution. The ^{19}F NMR spectrum of the crude reaction mixture after 2 h showed both the characteristic carbene resonance of **1** at 91.2 ppm and several small signals. After 19 h at room temperature the color of the solution changed to orange, giving rise to a new set of multiplet resonances at -58.8, -73.5 and -78.0 ppm in a 3:1:1 ratio (Figure 2.5). Analysis of the ^{19}F NMR spectrum was consistent with assignment of these resonances to the fluoroalkene, *E*-CHF=CF(CF₃).¹⁵

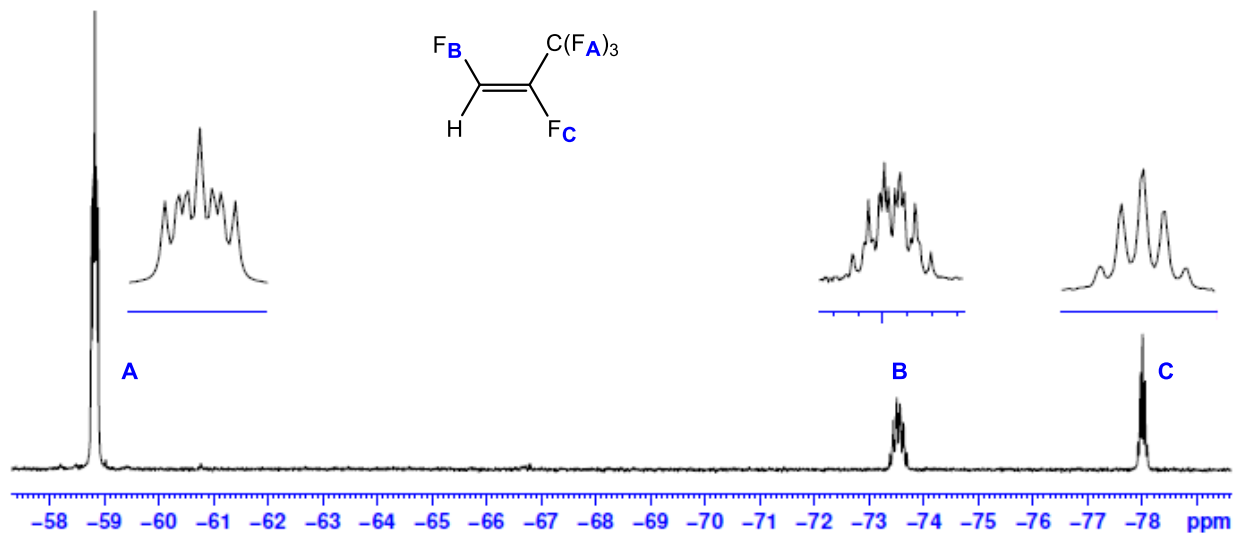


Figure 2.5. ^{19}F NMR (282 MHz, THF) spectrum of initial product from reaction of **1** with TrFE.

After leaving the reaction mixture for a further 2 days, multiple peaks began to grow in, accompanied by the original *E*-CHFCF(CF₃) signals. After monitoring for 3 more days, other resonances began to grow in and sharpen significantly. The peaks at -87.5, -98.9, and -213.0 ppm, which integrate to 3:1:1, are proposed to be due a perfluorometallacyclopropane product, **Ni-met^F-4**. A ^{19}F - ^{19}F COSY NMR spectrum showed clear correlation between these 3 signals. In contrast, the resonances at -226.0, -221.2, -129.6, -110.0, -107.0, and -85.6 ppm are proposed to be the *cis*-head-to-tail perfluorometallacyclopentane **Ni-met^F-5**, on the basis of the similarity of its ^{19}F NMR spectrum to analogous $\text{P}_2\text{Ni}(\text{C}_4\text{F}_6\text{H}_2)$ complexes prepared previously in the Baker group.⁸ Evaporating the reaction mixture *in vacuo* was accompanied by disappearance of the fluoroalkene. Figure 2.6 shows the structure of both products, along with the crude ^{19}F NMR spectrum and assignments. Minor doublets may be due to alkene complex from the other regioisomer of the metallacyclopropane, $\text{P}_2\text{Ni}[\text{CH}(\text{CF}_3)=\text{CF}_2]$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows multiplets at 48.0 and 45.8 ppm which integrate 1:1 and are representative of the major metallacyclopentane product

Ni-met^F-5. The resonance at 45.8 ppm is overlapped with another multiplet that is paired with the multiplet at 38.2 ppm, with each integrating to 0.25, indicative of **Ni-met^F-4** (Figure 2.7).

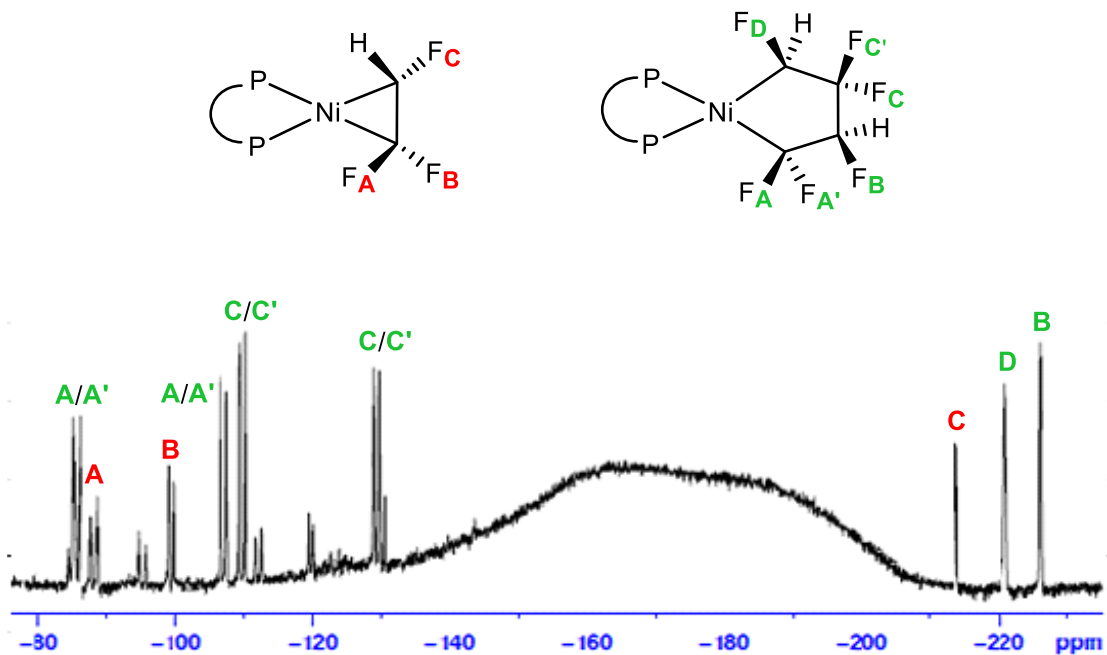


Figure 2.6. ¹⁹F NMR (282 MHz, THF) spectrum of the crude reaction mixture of **1** and TrFE showing conversion to fluorometallacycles, **Ni-met^F-4** and **Ni-met^F-5**.

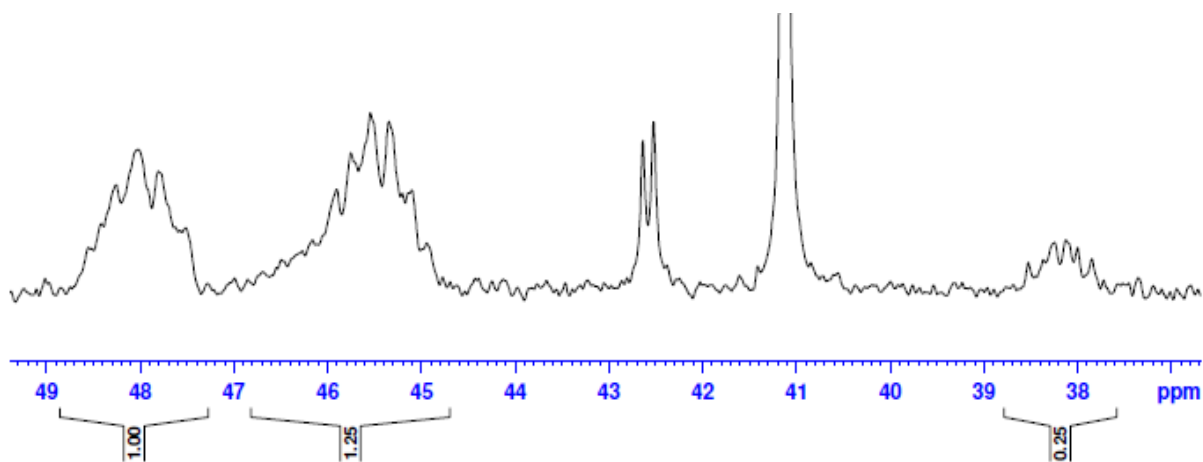
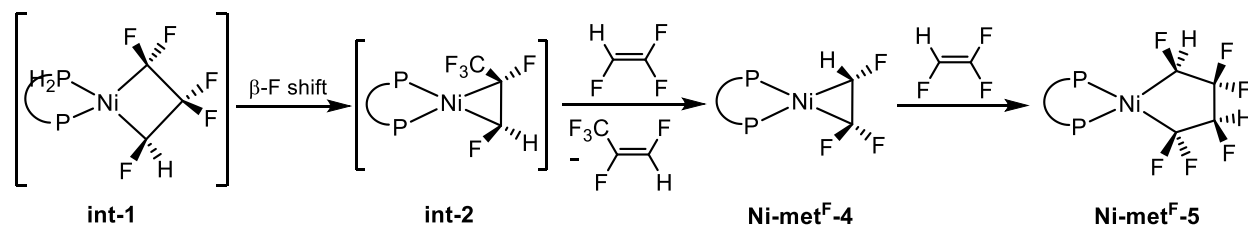


Figure 2.7. ³¹P{¹H} NMR (121 MHz, THF) of reaction of **1** with TrFE.

The reaction of **1** and TrFE is proposed to proceed through regioselective formation of an unobserved short-lived metallacyclobutane (**int-1**) that rapidly undergoes a 2,1-F shift to convert to the alkene complex (**int-2**) (Scheme 2.9). Further reaction with TrFE affords the observed free alkene and **Ni-met^F-4**, which then reacts with a third equivalent of TrFE to give the final metallacyclopentane product **Ni-met^F-5**. The final step of this reaction profile was previously reported by Baker *et al.* in a study of the formation of 3- and 5-membered hydrofluoronickelacycles from Ni(0) precursors and TrFE.⁸ Furthermore, the β -F shift from a 4-membered perfluorometallacycle to a 3-membered perfluorometallacycle is also a known reaction in these systems,⁹ driven by formation of the stable CF₃ group. However, the observation of a perfluorometallacyclobutane, propane, and pentane in one reaction system through interconversion has not been previously observed. This reaction offers additional insight into the behaviour of such partially fluorinated metallacycles.



Scheme 2.9. Proposed reaction pathway from **1** and TrFE, giving the fluoroalkene, metallacyclopropane and metallacyclopentane products.

Finally, it seemed beneficial to investigate what effect a different halogen substituent on the alkene would have on metallacycle formation and stability. Chlorotrifluoroethylene (CTFE) is a common reagent and proved to be a good candidate. The addition of **1** in a solution of THF with an excess of CTFE gave a dark red solution. Allowing the reaction mixture to sit for 14 h yielded

a light orange solution. The ^{19}F NMR spectrum showed geminal pairs at -102.9/-121.4 ppm ($\alpha\text{-CF}_2$) and -107.2/-119.0 ppm ($\beta\text{-CF}_2$), along with a multiplet at -140.4 due to the $\alpha\text{-CFCl}$ group (Figure 2.7).

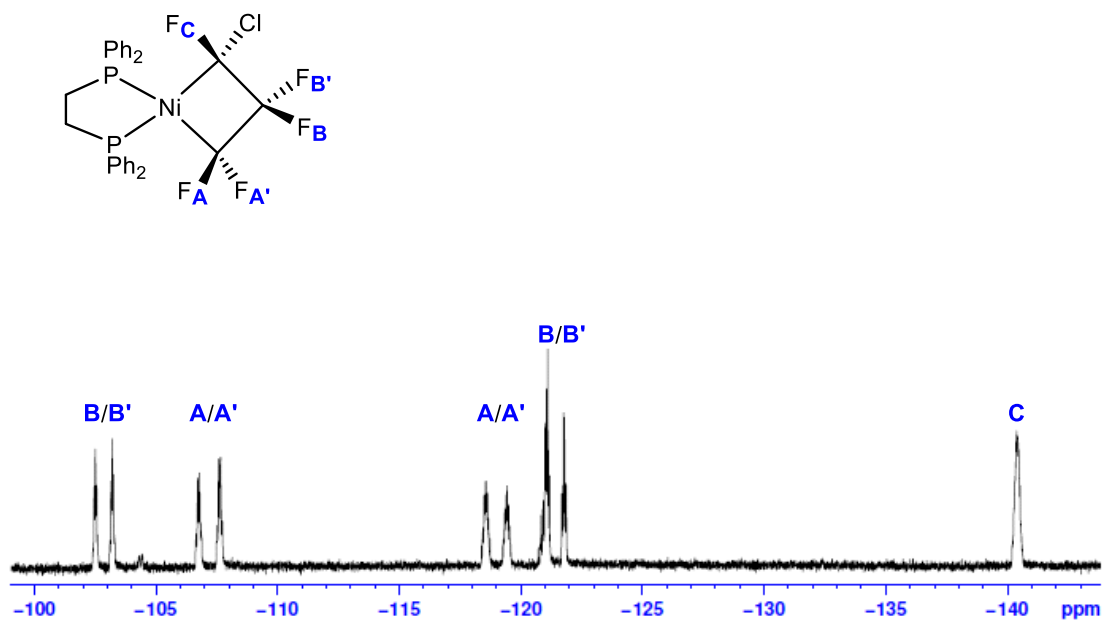
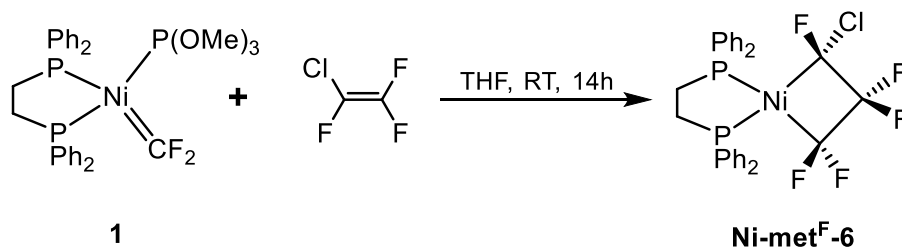


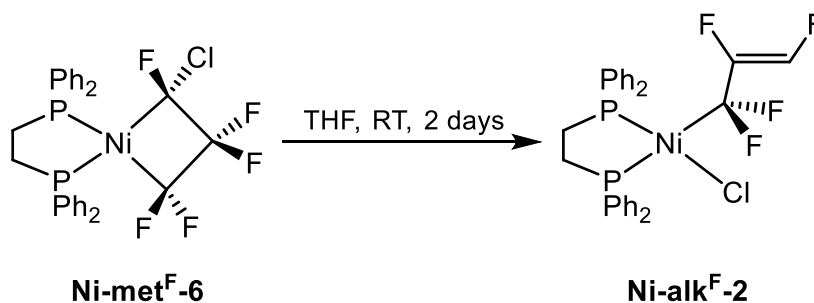
Figure 2.8. ^{19}F NMR (282 MHz, THF) spectrum of **Ni-met^F-6**.

A ^{19}F - ^{19}F COSY NMR spectrum was consistent with regioselective formation of metallacyclobutane **Ni-met^F-6** (Scheme 2.10). Notably, this is the first example of a perfluorometallacyclobutane with a Cl substituent in the alpha position of the metallacycle.



Scheme 2.10. Reaction of **1** with CTFE to form **Ni-met^F-6**.

Further observation of the reaction mixture 2 days later showed the conversion of **Ni-met^F-6** to a new product, with resonances at -82.4, -145.5, and -174.1 ppm in a 2:1:1 ratio. This was assigned to a Ni tetrafluoroallyl complex, **Ni-alk^F-2**, as shown in Scheme 2.11. Interestingly, this complex features the formation of a Ni–Cl bond.



Scheme 2.11. Reaction of **Ni-met^F-6** to form **Ni-alk^F-2**.

The CF_2 resonance at -82.4 ppm is a triplet of doublets ($^3J_{\text{FP}} = 36$ and $^3J_{\text{FF}} = 21$ Hz) from coupling to the ancillary dppe ligand and β -fluorine (Figure 2.9). The signal at -145.5 ppm is also a triplet of doublets ($^3J_{\text{FF}} = 21$ and $^3J_{\text{FF}} = 14$ Hz), resulting from the coupling to the two α -fluorines and the *cis* γ -fluorine. Finally, the γ -fluorine peak at -174.1 ppm is a doublet of doublets ($^3J_{\text{FH}} = 75$ and $^3J_{\text{FF}} = 14$ Hz), from coupling to the adjacent proton and the *cis* β -fluorine. The replacement of a γ -fluorine by hydrogen was noted and constitutes an unusual mechanistic step in the formation of **Ni-alk^F-2**.

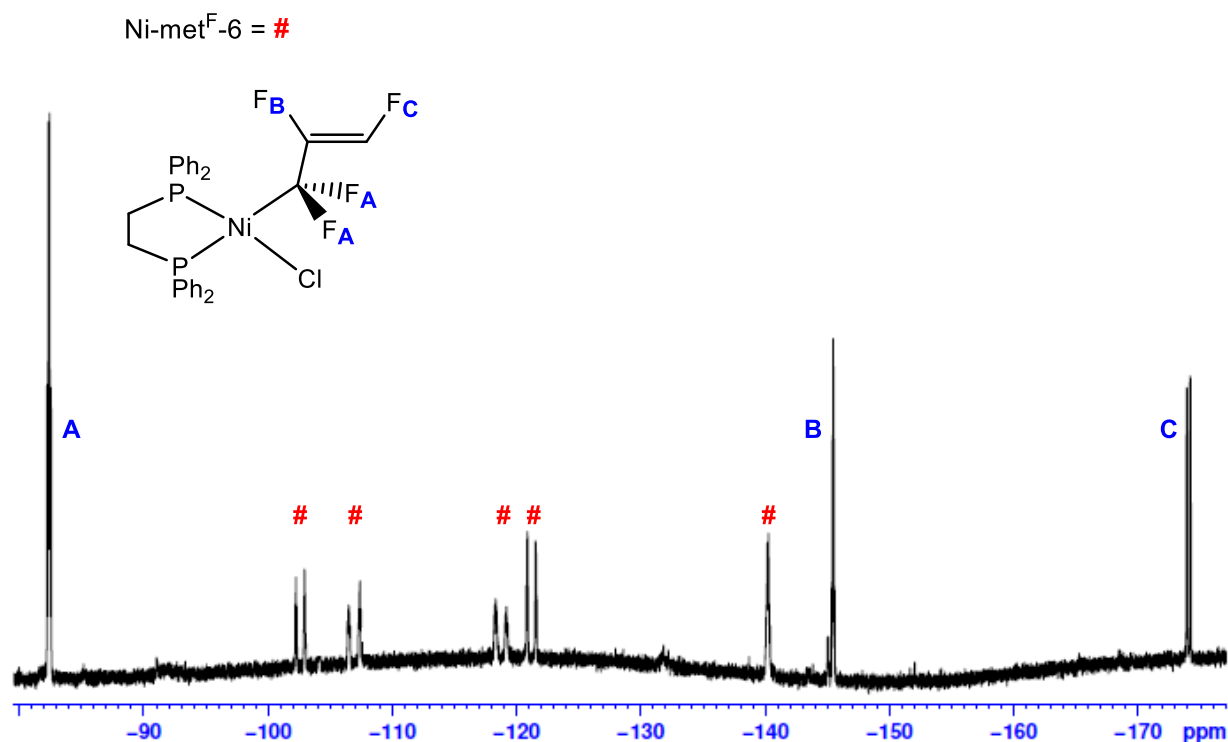


Figure 2.9. ¹⁹F NMR (282 MHz, THF) spectrum of Ni-met^F-6 and Ni-alk^F-2.

The relative stability of Ni-alk^F-2 made it a promising candidate for isolation. A THF solution of **1** was charged to a vial with a Teflon lined cap featuring a septum. Approximately 10 mL of CTFE was charged to the vial and the reaction mixture was stirred for 14 h, resulting in a color change from dark red to light orange. The reaction mixture was evaporated *in vacuo* and a ¹⁹F NMR spectrum of the crude solid showed Ni-met^F-6, and also the beginning of conversion to Ni-alk^F-2. The solid was dissolved in THF in an attempt to investigate if the presence of CTFE was necessary for the conversion of Ni-met^F-6 to Ni-alk^F-2. The solution was left at room temperature for 2 days and the resulting ¹⁹F NMR spectrum indeed showed increased formation of Ni-alk^F-2 with noticeable decrease of Ni-met^F-6, indicating that this transformation does not require excess CTFE. The solution was then evaporated *in vacuo*, re-dissolved in toluene, and

filtered through a plug of Celite. The solution was placed in the freezer at $-35\text{ }^{\circ}\text{C}$ overnight, resulting in the formation of single crystals suitable for X-ray diffraction.

The molecular structure of **Ni-alk^F-2**, as shown in Figure 2.10, is consistent with the NMR data. The structure of **Ni-alk^F-2** is square planar as expected for a 16 electron Ni(II) complex and features a nickel chloride bond and a tetrafluoroallyl chain with *cis* vinylic-Fs. The Ni–Cl bond distance (2.193 \AA) matches well with other previously reported nickel chloride complexes.¹⁶ The Ni(1)–C(1) bond distance is 1.951 \AA , while the subsequent carbon bonds feature lengths of 1.551 and 1.398 between C(1)–C(2) and C(2)–C(3) respectively, supporting the assignment of a double bond between C(2) and C(3).

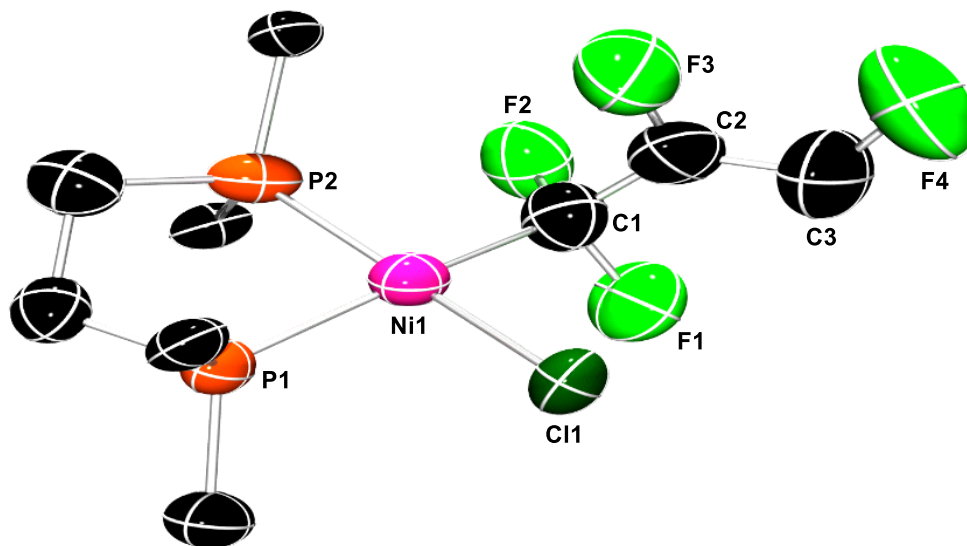
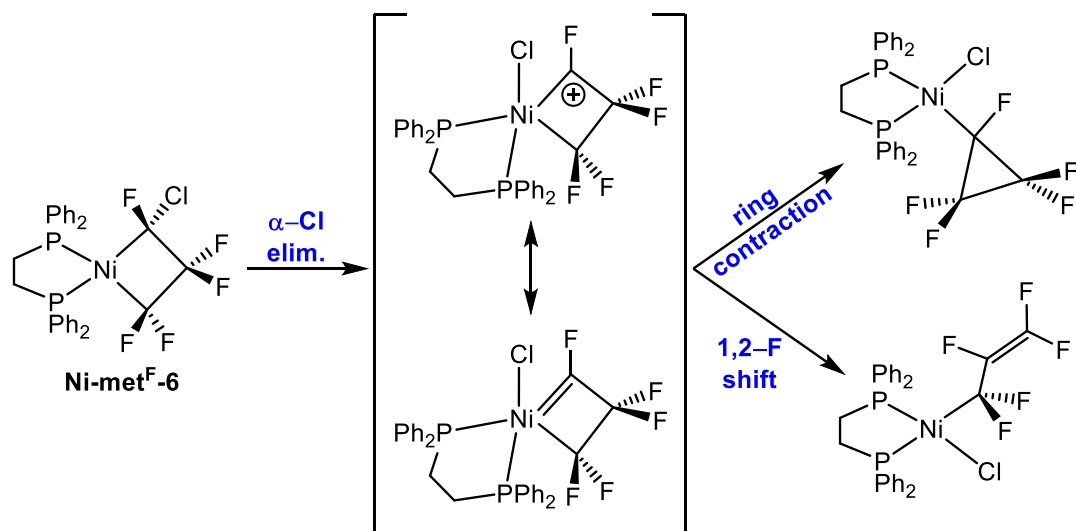


Figure 2.10. ORTEP depiction of **Ni-alk^F-2**. Phenyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths (\AA): Ni(1)-Cl(1) $2.193(6)$, Ni(1)-P(1) $2.224(5)$, Ni(1)-P(2) $2.146(5)$, Ni(1)-C(1) $1.951(7)$, C(1)-C(2) $1.441(6)$, C(1)-F(1) $1.451(11)$, C(1)-F(2) $1.369(12)$, C(2)-C(3) $1.398(7)$, C(2)-F(3) $1.307(9)$, C(3)-F(4) $1.350(8)$.

Formation of a Ni–Cl bond is presumably the result of α -Cl elimination, subsequently forming an α -carbonium ion or Ni perfluorocarbene (Scheme 2.12). This is in stark contrast to previously observed reactivity where β -elimination is often the preferred reaction pathway. Subsequent steps could involve ring contraction to a Ni-cyclopropyl or β -F elimination, but it is difficult to account for incorporation of the hydrogen, presumably as $\text{H}\cdot$ from THF or H^+ from adventitious moisture. When the experiment was repeated in either acetonitrile or benzene, we did not observe formation of $\text{Ni-alk}^{\text{F-2}}$, further supporting the role of THF in this unusual reaction.



Scheme 2.12. Two expected pathways for α -Cl elimination.

2.3 Conclusion

While the ultimate objective of fluorinated alkene metathesis remains a future goal, much progress in the understanding and optimization of such systems is constantly being made. It was recently found that reaction of the $\text{Ni}=\text{CF}(\text{CF}_3)[\text{P}(\text{O}^i\text{Pr})_3]_3$ complex with TFE notably afforded metathesis products $\text{Ni}=\text{CF}_2$ and $\text{F}_2\text{C}=\text{CFCF}_3$ but this and related examples were always

accompanied by stable metallacycle formation via a competing pathway.^{12,13} Moreover, attempts to expand the ancillary ligand set with this reactive fluorocarbene have been unsuccessful. In this chapter we assessed the potential of the electron-rich dppe Ni=CF₂ complex **1** to react with a broader scope of fluoro-olefins to both stabilize the metallacycle products for future study and observe metathesis products. It was shown that **1** demonstrates great affinity for the expected cycloaddition reactions where the =CF₂ fragment selectively attacks the less electron-rich carbon to furnish a variety of perfluorometallacycles. Furthermore, several of the resulting complexes are also capable of undergoing further reactivity.

Although reactions of **1** with PMVE and HFP failed to generate metathesis products, the former gave a single stable metallacyclobutane **Ni-met^F-2**, and the latter cleanly generated the first example of a first-row perfluoroalkylmetal perfluoroalkenyl complex **Ni-alk^F-1**. In previous work, the reaction of Ni=CF(CF₃)[P(O^{*i*}Pr)₃]₃ with PMVE resulted in the formation of 3 different metallacyclobutane isomers, two of which occur with the OCF₃ moiety on the β-C. The reaction of PMVE with **1** results in the synthesis of only **Ni-met^F-2**, where the OCF₃ moiety is on the α-C, demonstrating a greater regioselectivity than the previous Ni=CF(CF₃)[P(O^{*i*}Pr)₃]₃ complex. These reactions shed light on the electronic properties of these fluoroalkenes and both complexes will likely be pursued for further reactivity investigations. While vinylidene difluoride and **1** also gave a single metallacyclobutane, **Ni-met^F-3**, monitoring the reaction by ¹⁹F NMR spectroscopy showed an unusual broad resonance that persisted for days, suggesting perhaps some stability of the proposed open-shell diradical intermediate. The reaction of TrFE with **1** confirmed the instability of the CHF unit in nickel fluorocyclobutanes discovered previously in the Baker group using the Ni=CF(CF₃) fluorocarbene.¹² The 2,1-F shift from this proposed nickelacyclobutane then forms the alkene complex (or metallacyclopropane) of *E*-CF(CF₃)=CHF that is subsequently

liberated by an additional equivalent of TrFE to give **Ni-met^F-4**. Interestingly, regioselective conversion of **Ni-met^F-4** to metallacyclopentane **Ni-met^F-5** is unprecedented; in previous studies even the bulky Ni(C₂HF₃)(PPh₃)₂ metallacyclopropane reacted with TrFE to give 4 different regioisomers of the nickelacyclopentane.⁸ Finally, the use of CTFE resulted in the expected metallacyclobutane **Ni-met^F-6** with the Cl in the α position of the metallacycle. However, unexpected reactivity resulted in α -Cl elimination to furnish **Ni-alk^F-2** featuring a Ni–Cl bond and a tetrafluoroallyl complex that has undergone F substitution by H at the end of the chain.

Although the electron-rich Ni=CF₂ complex investigated here has not demonstrated metathesis activity, this first example has shown several examples of new reactivity and preliminary results suggest that even more electron-rich analogs can be successfully prepared for further studies.

2.4 Experimental

2.4.1 Materials and Methods

Unless otherwise stated, all reactions were carried out under an atmosphere of oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, Et₂O and THF were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contours) solvent purification system. Benzene-d₆, toluene-d₈, and THF-d₈ were degassed by three freeze-pump-thaw cycles, and subsequently dried by running through a column of activated alumina. All solvents were stored over activated (heated at ~ 250 °C for >8 h under vacuum) 4 Å molecular sieves. Glassware was oven-dried at 150 °C for >2 h. All reagents were purchased from commercial suppliers unless otherwise stated.

Tetrafluoroethylene (TFE) was made by depolymerizing polytetrafluoroethylene (Scientific Polymer Products, powdered) under vacuum, using a slightly modified literature procedure [10-20 mTorr, 650 °C, 15-20 g scale, product stabilized with ~ 0.3 wt. % R(+)-limonene (Aldrich, 97%)], giving TFE of $\geq 97\%$ purity. ^1H , ^{19}F and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on either Bruker Avance or AvanceII spectrometers; 300 MHz with respect to proton nuclei. ^1H NMR spectra were referenced to residual protons (C_6D_6 , δ 7.15) or (toluene- d_8 , δ 2.17) with respect to tetramethylsilane at δ 0.00. ^{19}F NMR spectra were referenced to an external sample of 80% CCl_3F in CDCl_3 at 0.00 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. The reagents $\text{P}(\text{OMe})_3$, HTFE, VDF, HFP, PMVE and CTFE were all purchased from commercial suppliers. The compounds $\text{Ni}(\text{COD})_2$,¹⁷ KC_8 ,¹¹ $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{PPh}_3)_2$ and $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{dppe})$ were prepared according to literature procedures.

2.4.2 Synthesis of Nickel Complexes and Starting Materials

Optimized synthesis of $\text{Ni}=\text{CF}_2[\text{P}(\text{OMe})_3](\text{dppe})$ (1). In a 100 mL round-bottom Schlenk flask equipped with a magnetic stir bar, $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{dppe})$ (1.0 g, 1.57 mmol) was dissolved in 30 mL of super-dry THF (run through a column of activated alumina) resulting in a dark orange solution. While stirring, $\text{P}(\text{OMe})_3$ (185 μL , 1.57 mmol) was added, causing a color change to a dark reddish-orange solution. A solid addition funnel was charged with KC_8 (592 mg, 4.38 mmol, 2.8 equiv.) and attached to the Schlenk flask. The reaction vessel was removed from the glovebox, placed in a pre-prepared dry ice-acetone bath, and attached to the Schlenk line. The solution was allowed to cool at -78 °C for 30 min. While stirring, the KC_8 was added slowly over the course of 10 min, resulting in a color change to a brownish-yellow solution. After addition, the solution was

left to stir at -78 °C for a further 30 min. The dry ice-acetone bath was removed to allow the temperature of the solution to rise. After approximately 10 min of warming, the solution was evaporated *in vacuo*, affording a brown solid. The reaction vessel was shipped back into the glovebox and the brown solid was extracted with diethyl ether (5x5 mL) and filtered through Celite to yield a red solution. The solution was transferred to a 100 mL round bottom Schlenk flask, concentrated to approximately 5 mL, charged with 40 mL of hexane, and placed in the freezer at -35 °C overnight. While cold, the solution was filtered through a frit and the resultant precipitate was washed with hexane. The solid was dried to give 701 mg of a red solid (71% yield).

2.4.3 Reactions with Fluoroalkenes

Reaction of 1 with CF₂=CF(OCF₃). A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with perfluoro(methyl vinyl ether) (PMVE) (3 mL, 0.12 mmol, excess). The reaction was left at room temperature to react for 20 h resulting in the formation of **Ni-met^F-2**.

¹⁹F NMR (282 MHz, 23 °C, THF) -55.8 (singlet, 3H, OCF₃); -112.4 (doublet of multiplets, 1F, β-CF, ²J_{FF} = 241 Hz); -117.4 (doublet of multiplets, 1F, α-CF, ²J_{FF} = 206.5 Hz); -119.5 (doublet of multiplets, 1F, β-CF, ²J_{FF} = 241 Hz); -121.5 (doublet of multiplets, 1F, α-F, ²J_{FF} = 206.5 Hz); -133.0 ppm (multiplet, 1F, α-CFOCF₃).

³¹P{¹H} NMR (121 MHz, 23 °C, THF) 44.8 ppm (broad multiplet, 2P, Ph₂PCH₂CH₂PPh₂, Δν_{1/2} = 79 Hz).

Table 2.1. COSY ^{19}F - ^{19}F NMR (282 MHz, THF) of **Ni-met^F-2**.

Shifts (ppm), multiplicity, coupling (Hz)	COSY correlates to F at δ (ppm)	Assignment
-133.4, dm	-119.5, -112.4	α -CFOCF ₃
-121.5, dm, 206.5	-119.5, -117.4 (strong), -112.4	α -CF ₂
-119.5, dm, 241	-133.4, -121.5, -117.4, -112.4 (strong)	β -CF ₂
-117.4, dm, 206.5	-121.5 (strong), -119.5, -112.4	α -CF ₂
-112.4, dm, 241	-133.4, -121.5, -119.5 (strong), -117.4	β -CF ₂

Reaction of 1 with CF₂=CF(CF₃). A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with hexafluoropropene (HFP) (3 mL, 0.12 mmol, excess). The reaction was left at room temperature to react for 6 h resulting in the formation of **Ni-alk^F-1** (two isomers).

^{19}F NMR (282 MHz, 23 °C, THF) *Isomer 1*: -67.7 (doublet of doublets, 3F, CF₃, $^3J_{\text{FF}} = 23.5$, $^4J_{\text{FF}} = 12$ Hz); -92.2 (multiplet, 3F, CF₃); -146.2 (doublet of multiplets, 1F, CF, $^2J_{\text{FF}} = 133$ Hz); -176.4 ppm (doublet of multiplets, 1F, CF, $^2J_{\text{FF}} = 133$ Hz). *Isomer 2*: -63.7 (multiplet, 3F, CF₃); -90.0 (m, 3F, CF₃); -127.2 (multiplet, 1F, CF); -163.0 ppm (multiplet, 1F, CF).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 23 °C, THF) *Isomer 1*: 55.3 (overlapped multiplet, 1P, Ph₂PCH₂CH₂PPh₂); 30.2 ppm (overlapped multiplet, 1P, Ph₂PCH₂CH₂PPh₂). *Isomer 2*: 55.3

(overlapped multiplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$); 30.2 ppm (overlapped multiplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$).

Reaction of 1 with $\text{CF}_2=\text{CH}_2$. A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with vinylidene fluoride (VDF) (3 mL, 0.12 mmol, excess). The reaction was left at room temperature to react for 24 h resulting in the observation of **Ni-met^F-3** as a broad resonance on the ^{19}F NMR spectrum. Continual monitoring for a further 4 days resulted in the sharpening of the resonance.

^{19}F NMR (282 MHz, 23 °C, THF) -88.7 ppm (doublet of triplets, 4F, $\alpha\text{-CF}$, $^3J_{\text{FH}} = 50.5$, $^3J_{\text{FP}} = 39$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 23 °C, THF) 44.0 ppm (broad triplet, 2P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $^3J_{\text{PF}} = 39$ Hz).

Reaction of 1 with $\text{CF}_2=\text{CHF}$. A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with trifluoroethylene (TrFE) (3 mL, 0.12 mmol, excess). The reaction was left at room temperature to react for 4 h resulting in the observation of the free alkene. After 24 h, resonances grew in, which were assigned to the metallacyclopropane product **Ni-met^F-4**, and the *cis*-head-to-tail isomer of the metallacyclopropane product **Ni-met^F-5**.

$\text{Ni}[\text{CFHCF}_2][\text{dppe}]$ (**Ni-met^F-4**):

^{19}F NMR (282 MHz, 23 °C, THF) -87.5 (doublet of multiplets, 1F, CF_2 , $^2J_{\text{FF}} = 270$, $^3J_{\text{FP}} = 43$ Hz); -98.8 (doublet of multiplets, 1F, CF_2 , $^2J_{\text{FF}} = 270$ Hz); -213.0 ppm (doublet of multiplets, 1F, CHF, $^2J_{\text{FH}} = 57$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 23 °C, THF) 45.8 (multiplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 38.2 ppm (multiplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$).

Table 2.2. COSY ^{19}F - ^{19}F NMR (282 MHz, THF) of **Ni-met^F-4**.

Shifts (ppm), multiplicity, coupling (Hz)	COSY correlates to F at δ (ppm)	Assignment
-213.0, dm, 57	-98.8, -87.5	CHF
-98.8, dm, 270	-213.0, -87.5 (strong)	CF_2
-87.5, dm, 270, 43	-213, -98.8 (strong)	CF_2

Ni[\text{CF}_2\text{CFHCF}_2\text{CFH}][\text{dppe}] (**Ni-met^F-5**):

^{19}F NMR (282 MHz, 23 °C, THF) -85.6 (doublet of multiplets, 1F, $\alpha\text{-CF}$, $^2J_{\text{FF}} = 270$, $^3J_{\text{FP}} = 41$ Hz); -107.0 (doublet of multiplets, 1F, $\alpha\text{-CF}$, $^2J_{\text{FF}} = 270$, $^3J_{\text{FP}} = 41$ Hz); -110.0 (doublet of multiplets, 1F, $\beta\text{-CF}$, $^2J_{\text{FF}} = 220$ Hz); -129.6 (doublet of multiplets, 1F, $\beta\text{-CF}$, $^2J_{\text{FF}} = 220$ Hz); -221.2 (multiplet, 1F, $\alpha\text{-CFH}$); -226.0 ppm (doublet of multiplets, 1F, $\beta\text{-CFH}$, $^2J_{\text{FH}} = 48.5$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 23 °C, THF) 48.0 (multiplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), 45.4 (multiplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$).

NMR Scale Reaction of 1 with $\text{CF}_2=\text{CFCl}$: Observation of Ni-met^F-6. A solution of **1** (15 mg, 0.02 mmol) in 0.3 mL of THF was prepared in the glovebox and put in a screw-cap NMR tube fit

with a septum, resulting in a dark red solution. The NMR tube was removed from the glovebox and subsequently charged with chlorotrifluoroethylene (CTFE) (3 mL, 0.12 mmol, excess). The reaction was left at room temperature to react for 8 h resulting in the formation of **Ni-met^F-6**. Crude ¹⁹F NMR showed conversion to another product, **Ni-alk^F-2**, in small amounts.

¹⁹F NMR (282 MHz, 23 °C, THF) -102.9 (doublet of multiplets, 1F, α -CF, $^2J_{FF} = 196.5$ Hz); -107.2 (doublet of multiplets, 1F, β -CF, $^2J_{FF} = 243$ Hz); -119.0 (doublet of multiplets, 1F, β -CF, $^2J_{FF} = 243$ Hz); -121.4 (doublet of multiplets, 1F, α -CF, $^2J_{FF} = 196.5$ Hz); -140.4 ppm (multiplet, 1F, α -CFCl).

³¹P{¹H} NMR (121 MHz, 23 °C, THF) 45.2 (multiplet, 1P, Ph₂PCH₂CH₂PPh₂); 47.2 ppm (multiplet, 1P, Ph₂PCH₂CH₂PPh₂).

Table 2.3. COSY ¹⁹F-¹⁹F NMR (282 MHz, THF) of **Ni-met^F-6**.

Shifts (ppm), multiplicity, coupling (Hz)	COSY correlates to F at δ (ppm)	Assignment
-140.4, m	-119.0, -107.2	α -CFCl
-121.4, dm, 196.5	-119.0, -107.7, -102.9 (strong)	α -CF ₂
-119.0, dm, 243	-140.4, -121.4, 107.2 (strong), -102.9	β -CF ₂
-107.2, dm, 243	-140.4, -121.4, 119.0 (strong), -102.9	β -CF ₂
-102.9, dm, 196.5	-121.4 (strong), -119.0, -107.7	α -CF ₂

Scale Up Reaction of 1 with CF₂=CFCl for Isolation of Ni-alk^F-2. A solution of **1** (80 mg, 0.13 mmol) in 2.0 mL of THF was prepared in the glovebox and put in vial fit with a septum cap, resulting in a dark red solution. The vial was removed from the glovebox and subsequently charged

with chlorotrifluoroethylene (CTFE) (10 mL, 0.41 mmol, excess). The reaction was left at room temperature to stir for 16 h resulting in an orange solution and the formation of **Ni-met^F-6**. The crude ¹⁹F NMR spectrum showed **Ni-alk^F-2** was also present in small amounts. The solution was evaporated *in vacuo* resulting in 33 mg of a dark orange solid. Approximately 8 mg of solid was dissolved in THF and charged to an NMR tube. The solution was left for 48 h, and the crude ¹⁹F NMR spectrum revealed near full conversion to **Ni-alk^F-2**. The solution was transferred to a vial and evaporated *in vacuo* resulting in a yellow solid. The solid was dissolved in minimal toluene and filtered through a plug of celite. The solution was placed in the freezer at -35 °C overnight, resulting in the formation of yellow crystals suitable for X-ray diffraction.

¹⁹F NMR (282 MHz, 23 °C, THF) -82.4 (triplet of doublets, 2F, Ni-CF₂, ³J_{FP} = 35.5, ³J_{FF} = 20.5 Hz); -145.5 (doublet of triplets, 1F, Ni-CF₂CF, ³J_{FF} = 20.5, ³J_{FF} = 14.5 Hz); -174.1 ppm (doublet of doublets, 1F, Ni-CF₂CF=CF, ²J_{FH} = 75, ³J_{FF} = 14.5 Hz).

³¹P{¹H} NMR (121 MHz, 23 °C, THF) 39.7 (broad multiplet, 1P, Ph₂PCH₂CH₂PPh₂); 58.9 ppm (broad multiplet, 1P, Ph₂PCH₂CH₂PPh₂).

2.5 References

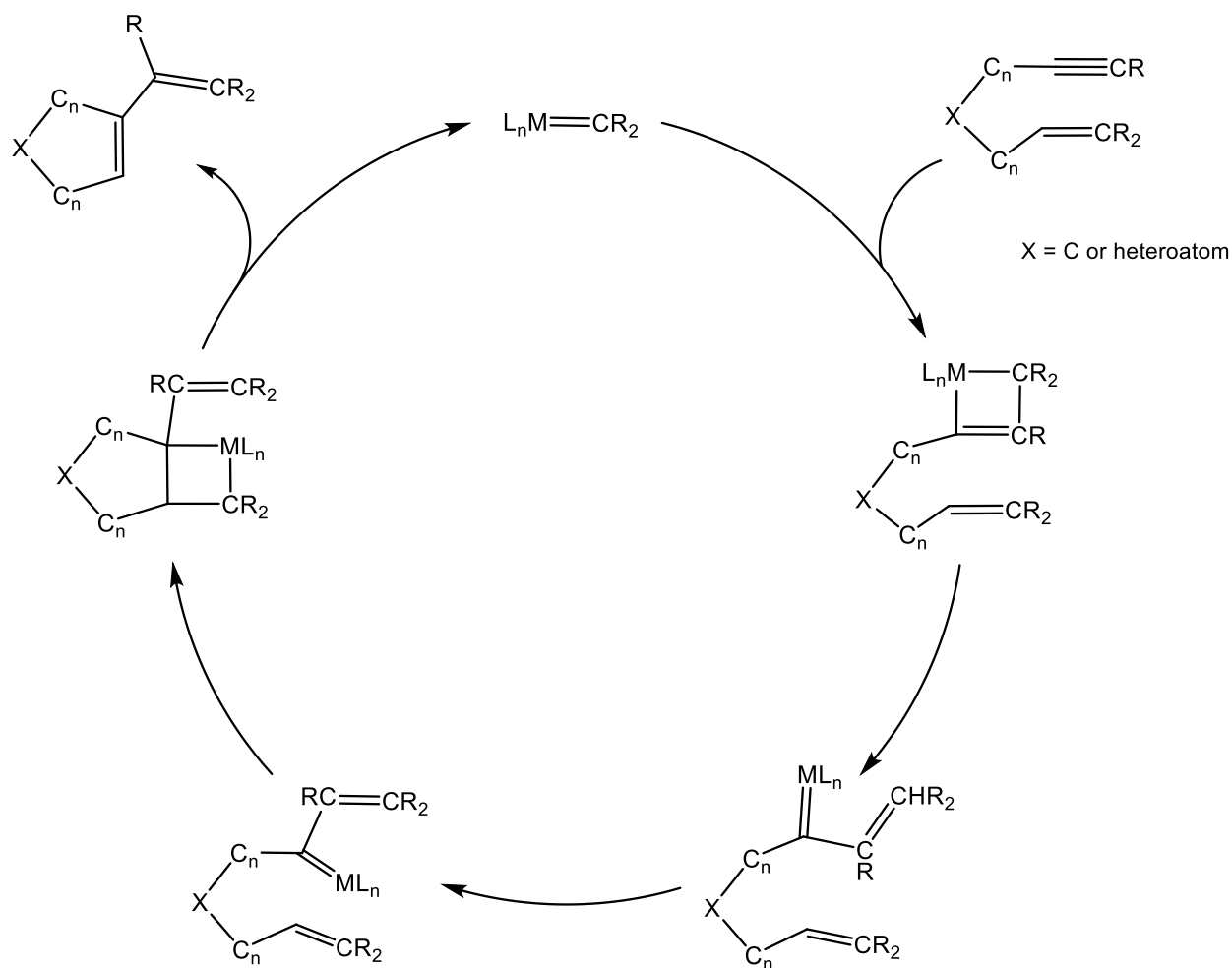
- (1) Fustero, S.; Simón-Fuentes, A.; Barrio, P.; Haufe, G. *Chem. Rev.* **2015**, *115*, 871–930.
- (2) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003.
- (3) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293–1326.
- (4) Yuan, J.; Hughes, R. P.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2010**, *29*, 1942–1947.
- (5) Ojima, I. *Fluorine in Medicinal Chemistry and Chemical Biology*; Blackwell: Chichester, U.K., 2009.
- (6) Im, J.; Walshe-Langford, G. E.; Moon, J.-W.; Löffler, F. E. *Environ. Sci. Technol.* **2014**, *48*, 13181–13187.
- (7) Lee, G. M.; Leung, A. S. C.; Harrison, D. J.; Korobkov, I.; Hughes, R. P.; Baker, R. T. *Organometallics* **2017**, *36*, 2853–2860.
- (8) Giffin, K. A.; Pua, L. A.; Piotrkowski, S.; Gabidullin, B. M.; Korobkov, I.; Hughes, R. P.; Baker, R. T. *J. Am. Chem. Soc.* **2017**, *139*, 4075–4086.
- (9) Leclerc, M. C.; Da Gama, J. G.; Gabidullin, B. M.; Baker, R. T. *J. Fluor. Chem.* **2017**, *203*, 81–89.
- (10) Fuller, J. T.; Harrison, D. J.; Leclerc, M. C.; Baker, R. T.; Ess, D. H.; Hughes, R. P. *Organometallics* **2015**, *34*, 5210–5213.
- (11) Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics* **2015**, *34*, 5683–5686.
- (12) Harrison, D. J.; Daniels, A. L.; Guan, J.; Gabidullin, B. M.; Hall, M. B.; Baker, R. T. *Angew. Chem. Int. Ed.* **2018**, *57*, 5874–5878.
- (13) Daniels, Alex L., Guan, J., Gabidullin, B. M., Hall, M. B., Baker, R. T. **2019**, submitted for publication.
- (14) Maples, P. K.; Green, M.; Stone, F. G. A. *J. Chem. Soc. Dalt. Trans.* **1973**, *0*, 2069.
- (15) Koroniak, H.; Palmer, K. W.; Dolbier, W. R.; Zhang, H.-Q. *Magn. Reson. Chem.* **1993**, *31*, 748–751.

- (16) Stucky, B. G. D.; Folkers, J. B.; Kistenmacher, T. J. *Acta Cryst* **1967**, 23, 1064.
- (17) Krysan, D. J.; Mackenzie, P. B. *J. Org. Chem.* **1990**, 55, 4229–4230.

Chapter 3 – Investigating the Reactivity of Terminal Alkynes with Ni(0) Difluorocarbene Complexes

3.1 Introduction

Acetylenes are frequently utilized reagents in many valuable synthetic pathways including cyclopropanation,¹ alkyne polymerization,²⁻⁴ and most notably, enyne metathesis.⁵⁻⁷ The enyne metathesis reaction is an atom-economical bond reorganization of an alkene and an alkyne to form a 1,3-diene, either intra- or intermolecularly, as shown in Scheme 3.1.⁸ While enyne metathesis is in the same mechanistic family as alkene metathesis, it has not been as thoroughly studied or advanced.⁹ Much like alkene metathesis, however, enyne metathesis is also catalyzed by metal carbenes, and many complexes are able to facilitate both reactions.

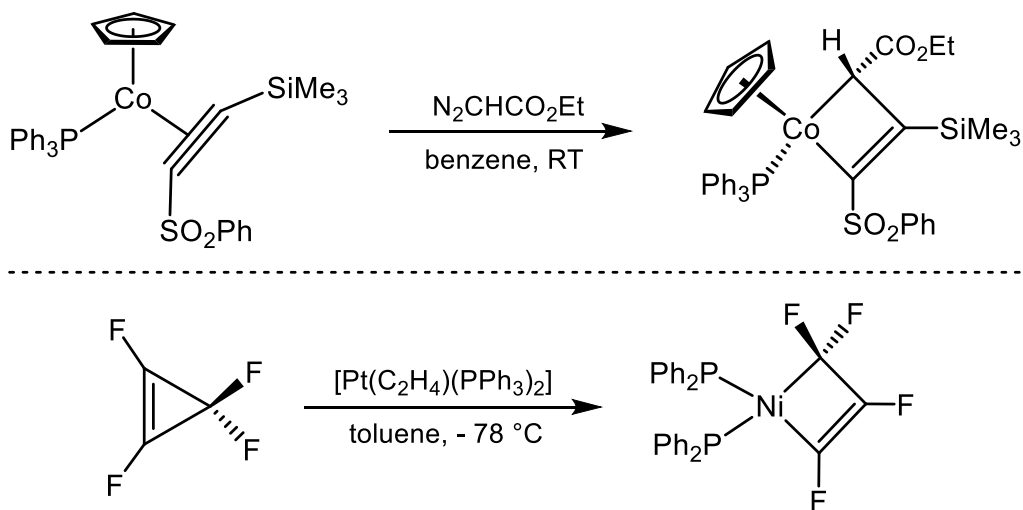


Scheme 3.1. Enyne metathesis mechanism.

Metallacyclobutene complexes are proposed to be crucial intermediates or transition states in these C–C and other C–E bond-forming reactions,⁹ (E = N,O,S) yet a more complete understanding of their stability and the mechanistic roles they play requires further investigation. For instance, the carboamination of diaryl-acetylenes with a titanium complex is proposed to proceed via the formation of a metallacyclobutene intermediate.¹⁰ The reactivity of metallacyclobutenes, however, makes elucidation of structural characteristics via isolation highly dependent on factors such as the metal, ancillary ligand, and employed acetylene substituents. Use

of appropriate combinations of these factors thus offers an opportunity for further study of the formation and reactivity of these unsaturated metallacycles.

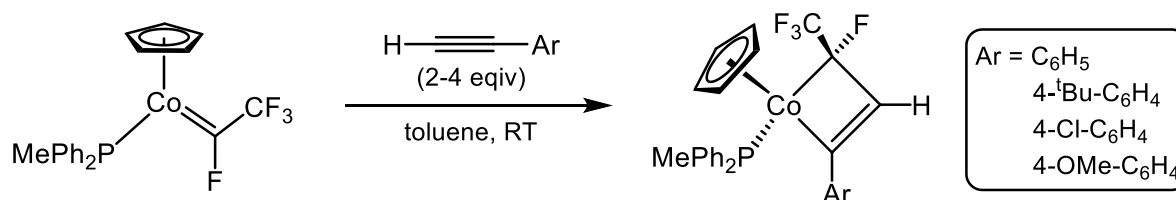
There have been several notable instances of the isolation of metallacyclobutene complexes. A significant advance was made by O'Connor with the preparation of a cobaltacyclobutene complex, $\text{Cp}(\text{PPh}_3)\text{Co}[\kappa^2\text{-C}(\text{SO}_2\text{Ph})=\text{C}(\text{SiMe}_3)\text{CH}(\text{CO}_2\text{Et})]$, through reaction of a cobalt-alkyne compound with an ethyl diazoacetate carbene source.^{11,12} Furthermore, a report by Hughes demonstrated the synthesis of perfluorinated metallacyclobutenes via oxidative addition of perfluorocyclopropene to $\text{Pt}(0)$ and $\text{Ir}(0)$ complexes.^{13,14} Both examples are shown in Scheme 3.2.



Scheme 3.2. Important examples of early isolation of metallacyclobutene complexes.

Recently, Baker *et al.* reported the formation of a series of cobaltacyclobutenes derived from varied terminal aryl-acetylenes and ancillary ligand substitution.¹⁵ Reactions of $\text{CpCo}=\text{CF}(\text{CF}_3)(\text{PPh}_2\text{Me})$ with *para*-substituted aryl-acetylenes yielded the desired cobaltacyclobutenes, $[\text{Cp}(\text{PPh}_2\text{Me})\text{Co}\{\kappa^2\text{-C}(\text{Ar})=\text{CHCF}(\text{CF}_3)\}]$, as shown in Scheme 3.3. Studies

indicate a limited substrate scope as both alkyl-acetylenes and disubstituted acetylenes did not afford the desired products. Moreover, the scope showed little substrate dependence on reactivity, as a variety of electronically distinct aryl-acetylenes all gave the metallacyclobutene product with similar rates.



Scheme 3.3. Previous report of fluorinated cobaltacyclobutene complexes.

The effects of changing the ancillary phosphine ligand were also investigated. When PPh₂Me was replaced with less basic PPh₃, a multitude of products were formed, all in <20% yields. It was proposed that the metallacyclobutene product was initially formed, followed by rapid PPh₃ loss leading to a highly reactive 16-electron intermediate that led to multiple by-products. As noted in the introduction, formation of these metallacyclobutenes is proposed to occur via direct attack of the fluorocarbene carbon on the acetylene carbon without previous π -coordination of the latter. For the complex in Scheme 3.3, computational studies suggested that the reaction proceeds through a Co(II) 1,4-diradical intermediate, as opposed to a potential Co(III) zwitterionic intermediate (See Introduction Section 1.4.3.4).¹⁵

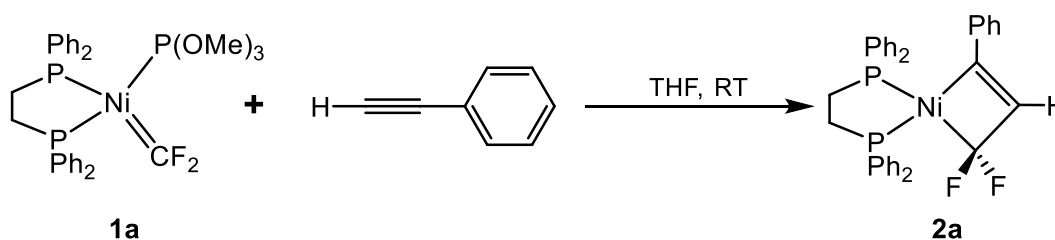
The analogous Co=CF₂ compound was found to be less reactive towards acetylenes than Co=CF(CF₃), requiring elevated temperatures and longer reaction times to yield any cobaltacyclobutenes, which were also shown to be less thermally stable. As the more electron-rich nickel difluorocarbene complex **1a** has been shown to have a great affinity for reaction with small

fluorinated olefins,¹⁶ it was envisioned that its reaction with terminal aryl-acetylenes may result in more stable metallacyclobutenes, allowing further investigation of their reactivity.

3.2 Results & Discussion

3.2.1 Reactivity of **1a** with Terminal Acetylenes

Beginning with terminal aryl-acetylenes, a solution of **1a** in THF was charged with one equivalent of phenylacetylene, resulting in a dark red solution. After leaving the reaction mixture for 24 h at room temperature, the crude ¹⁹F NMR spectrum showed some unreacted **1a**, as well as several new products. A doublet of triplets resonance at -89.6 ppm (³J_{FH} = 48 and ³J_{FP} = 40 Hz) was assigned to a single regioisomer of the expected Ni(II) metallacyclobutene complex **2a**, as shown in Scheme 3.4 and confirmed by the ¹H-decoupled ¹⁹F NMR spectrum.



Scheme 3.4. Reaction of **1a** with phenylacetylene to yield **2a**.

Further inspection of the ¹⁹F NMR spectrum revealed two additional major products consisting of a doublet of triplets at -100.1 (³J_{FH} = 60 and ³J_{FP} = 7 Hz) and a doublet at -106.4 ppm (³J_{FH} = 54 Hz) assigned to nickelacyclohexadiene **3a**, and the difluorinated cyclopentadiene **4a**, respectively (Figure 3.1). Further analysis of the product integrals shows a clear preference for the formation of **2a**, with a product ratio of 7.4:1.6:1 for **2a**, **3a**, and **4a**.

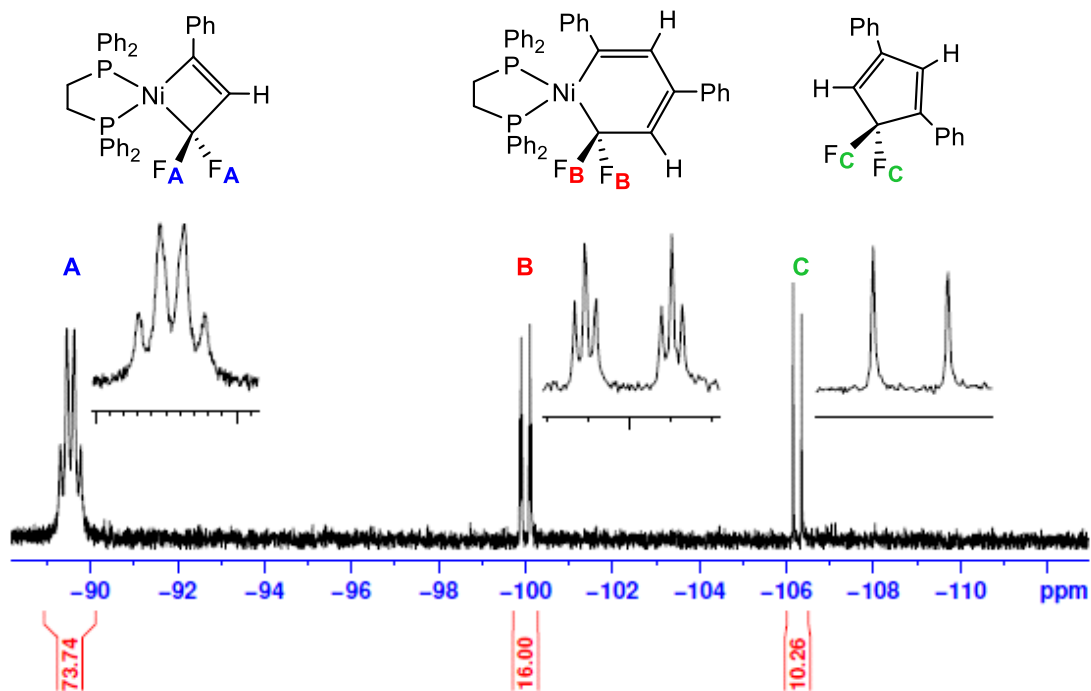
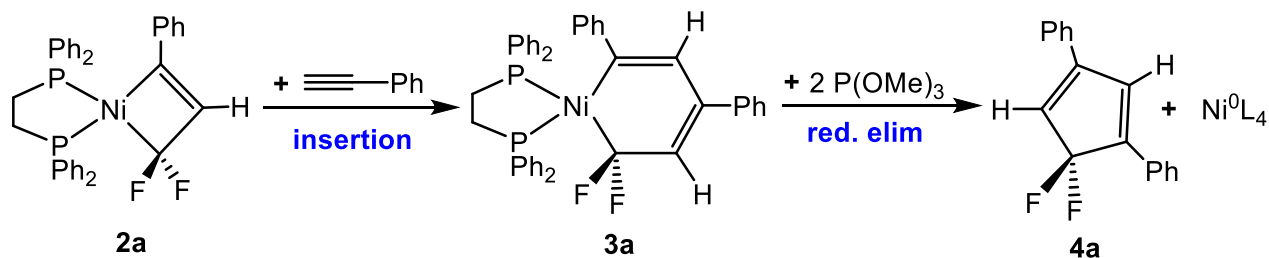


Figure 3.1. ^{19}F NMR (282 MHz, THF) spectrum of the reaction of **1a** with phenylacetylene showing the three major products, **2a**, **3a**, and **4a**.

The successive formation of these products is proposed to occur via regioselective insertion of a second equivalent of the acetylene into the Ni–C_{Ph} bond of **2a** to give **3a**, which then undergoes reductive elimination to **4a** and Ni(0) as shown in Scheme 3.5. Investigation of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed two triplets at 162.7 and 40.9 ppm with $^2J_{\text{PP}} = 25$ Hz, assigned to zerovalent Ni(dppe)[P(OMe)₃]₂, further supporting this reaction pathway.



Scheme 3.5. Further reactivity of **2a**.

More detailed NMR monitoring of this reaction afforded additional information. In particular, the first-formed intermediate consists of a very broad ^{19}F NMR resonance at -86.2 ppm (Figure 3.2). After 24 h, a second equivalent of acetylene was added and the ^{19}F NMR spectrum after another 24 h showed the disappearance of **1a** and the broad intermediate, affording **3a** and **4a**. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture revealed a triplet at 53.3 ppm with $^3J_{\text{PF}} = 7$ Hz, indicative of the dppe phosphine coupling to the CF_2 group in **3a**. Addition of a second equivalent of $\text{P}(\text{OMe})_3$ then drove the reaction completely to **4a** after another 24 h. The corresponding ^{31}P NMR spectra are shown in Fig. 3.3.

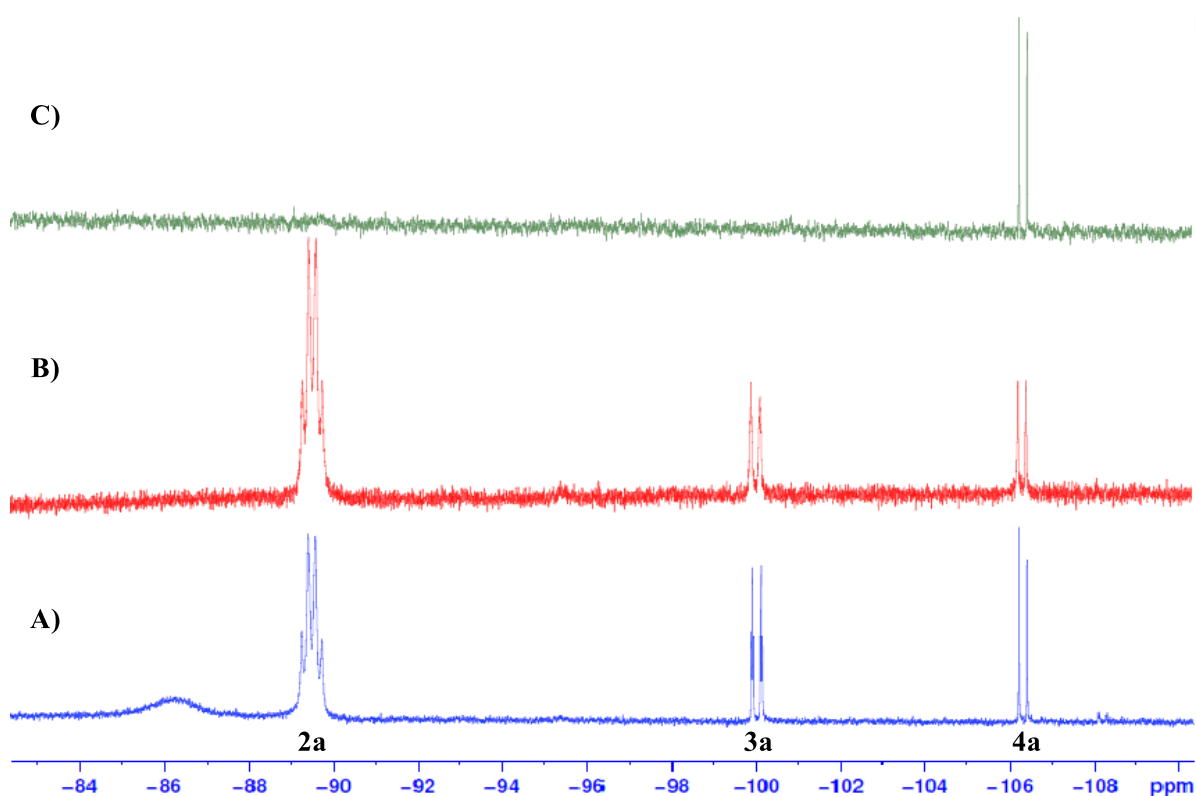


Figure 3.2. ^{19}F NMR (282 MHz, THF) spectra of the reaction of **1a** with 1.5 equiv. of phenyl acetylene: A) After 24 h; B) After 48 h, with 3 total equiv. of phenylacetylene; C) After 72 h, with 2 total equiv. of $\text{P}(\text{OMe})_3$.

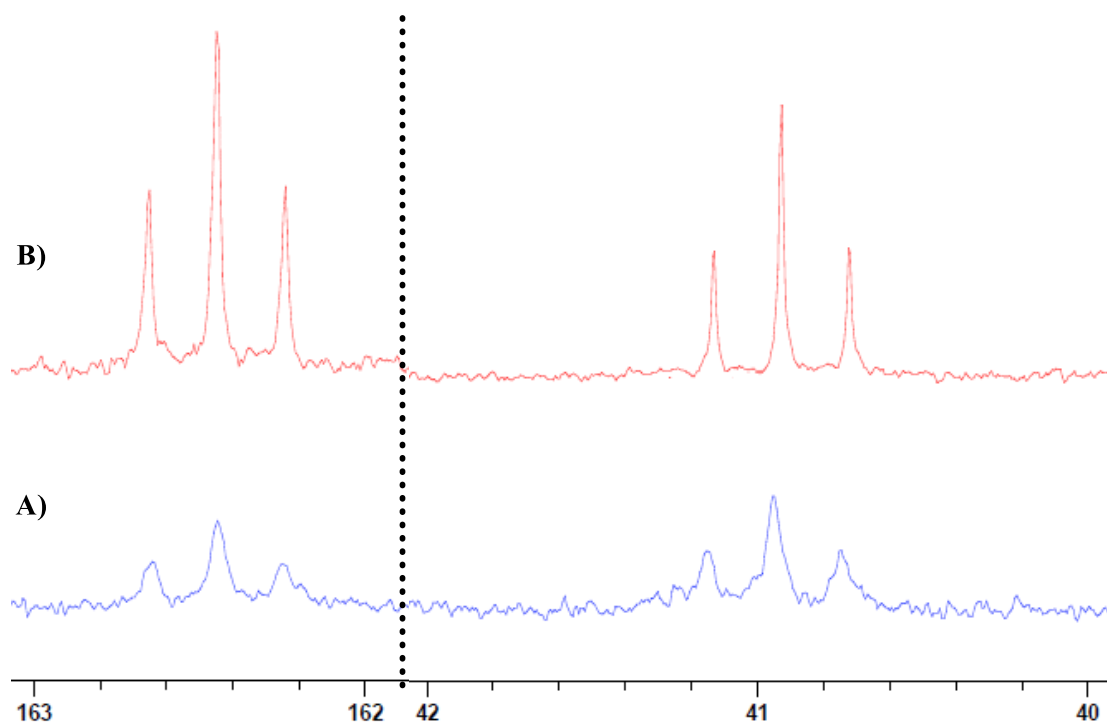


Figure 3.3. Stack ^{31}P NMR spectra plot showing growth of $\text{Ni}(\text{dppe})[\text{P}(\text{OMe})_3]_2$ in the reaction of **1a** with phenyl acetylene: A) After 48 h B) After 72 h, with excess $\text{P}(\text{OMe})_3$ (2 equiv). The region between 42 and 162 ppm are omitted for clarity.

In an attempt to isolate **4a**, the reaction solution was evaporated *in vacuo*, redissolved in C_6D_6 , and subsequently filtered through a short column of silica in order to remove any small amounts of nickel products remaining. Attempts to characterize **4a** using gas chromatography-mass spectrometry proved unsuccessful, presumably due to its poor volatility; similar reported compounds have boiling points near $350\text{ }^\circ\text{C}$. Instead, more in-depth NMR analysis of the sample was performed.

As previously stated, in order to drive the reaction toward **4a**, several equivalents of phenylacetylene were required, along with a slight excess of $\text{P}(\text{OMe})_3$. Because of this, attempts to analyze the ^1H NMR proved extremely difficult due to phenylacetylene overwhelming the aromatic region and overlapping with many potential product peaks of **4a**. However, closer

examination of the ^1H NMR spectrum revealed a triplet at 6.5 ppm. This resonance is assigned to the C–H proton on the carbon next to the CF_2 group with $^3J_{\text{HF}} = 54$ Hz. This coupling corresponds exactly with the doublet observed in the ^{19}F NMR spectrum. Furthermore, upon running a $^1\text{H}\{^{19}\text{F}\}$ NMR experiment, the triplet collapses into a singlet, as shown in Figure 3.4.

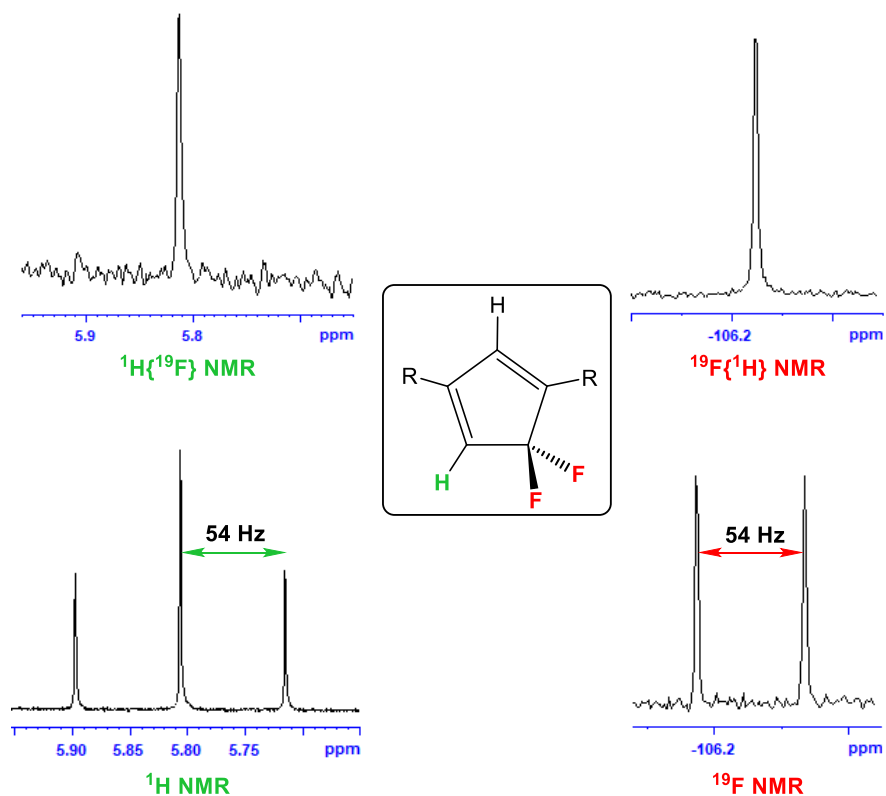
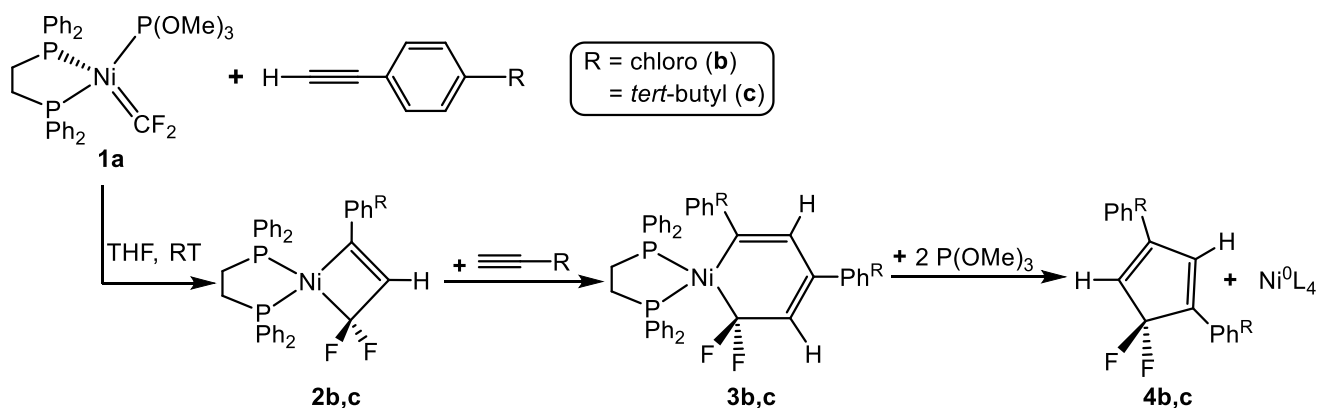


Figure 3.4. ^1H , $^1\text{H}\{^{19}\text{F}\}$, ^{19}F , and $^{19}\text{F}\{^1\text{H}\}$ NMR (THF) spectra of **4a** displaying the loss of fluorine and proton couplings respectively when decoupling, and the shared 54 Hz coupling constant.

The same sample was used to obtain a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum which suffered from the same problems as the ^1H NMR. However, a triplet at 104.6 ppm was observed with a coupling constant of 232 Hz, which matches well with that expected for a one bond carbon-fluorine coupling ($^1J_{\text{CF}}$). A ^{13}C DEPT experiment showed the disappearance of the triplet, supporting its assignment as the quaternary CF_2 carbon in the cyclic **4a** product. Finally, an HMQC experiment was run, but

the long-lived evolution of fluorine coupling over the course of the experiment led to difficulty assigning possible correlations. However, several key pieces of spectroscopic evidence clearly match the assignment of **4a**, providing support for the proposed mechanistic pathway.

Since **1a** demonstrated the ability to react with phenylacetylene, we investigated electronic effects of aryl-acetylenes with both electron-donating and -withdrawing substituents. A solution of **1a** in THF was charged with 1.5 equivalents of 4-chlorophenylacetylene or 4-*tert*-butylphenylacetylene, resulting in a dark red solution. After allowing the reaction to sit at room temperature for 24 h, the crude ^{19}F NMR revealed conversion to the analogous products, **2b,c**, **3b,c** and **4b,c** as shown in Scheme 3.6.



Scheme 3.6. Reaction of **1a** with 4-chlorophenylacetylene or 4-*tert*-butylphenylacetylene.

The ^{19}F NMR spectrum of the 4-chlorophenylacetylene reaction mixture contained similar multiplet resonances corresponding to **2b**, **3b**, and **4b** at -90.1, -100.6 and -107.0 ppm as shown in Figure 3.5. Also, observation of the $^{19}\text{F}\{^1\text{H}\}$ NMR showed these peaks losing multiplicity to become a triplet, triplet, and singlet respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction mixture at this time revealed a triplet of triplets at 114.3 ppm ($^1J_{\text{CF}} = 237$, $^2J_{\text{CP}} = 12$ Hz) which is indicative of the CF_2 moiety of **3b** from coupling to the two adjacent fluorines and the phosphine.

Furthermore, two triplets at 133.6 and 134.3 ppm were found ($^2J_{CF} = 7$ Hz) and assigned to the β -CH carbon in both **2b** and **3b**. These carbon NMR resonances are shifted slightly to the right out of the traditional aromatic region to make them visible despite the excess of 4-chlorophenylacetylene. This corroborates our earlier observation with the reaction of phenylacetylene, where we could only locate the carbon and proton resonances because the rest were shifted to the left and buried.

More in-depth analysis of the $^{19}\text{F}\{^1\text{H}\}$ NMR integrals shows a clear favourability for **3b**, with a 1:2.5:1 ratio of the products **2b**, **3b**, and **4b**. This suggests that electron-withdrawing substituents may destabilize the metallacyclobutene, promoting the second acetylene insertion. Consistent with this hypothesis, the observed product ratio from reaction of **1a** with 4-*tert*-butylphenylacetylene was 12:1.4:1 for **2c**, **3c** and **4c**, clearly favouring the initial nickelacyclobutene product (Figure 3.6).

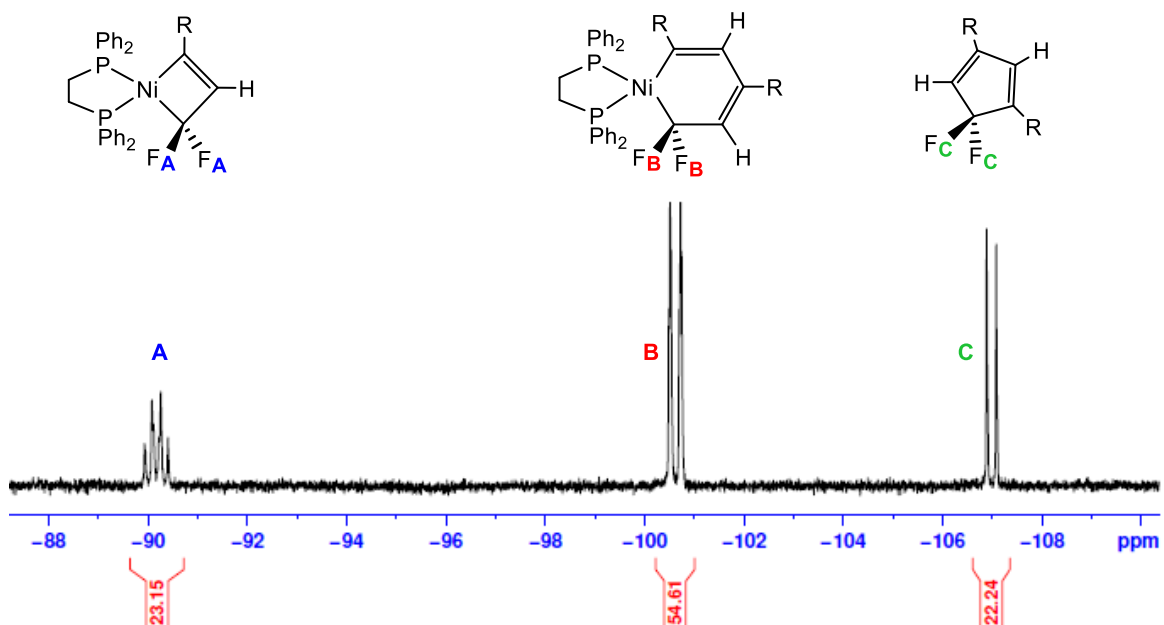


Figure 3.5. ^{19}F NMR spectrum (282 MHz, THF) of the reaction of **1a** with 4-chlorophenylacetylene.

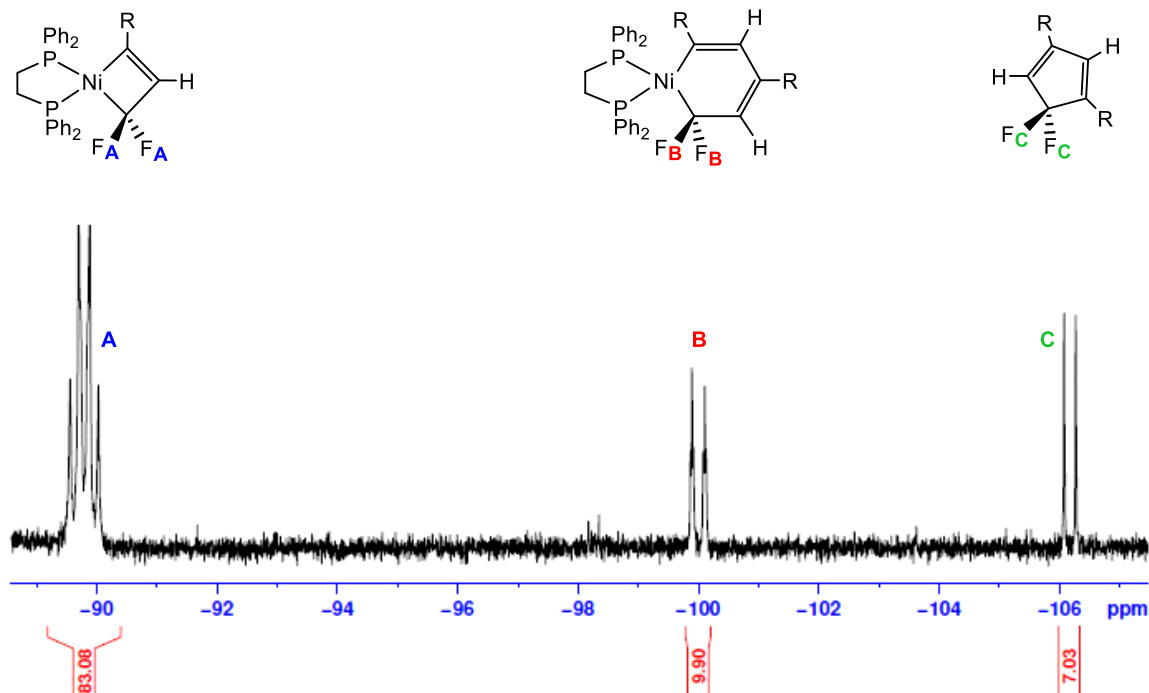


Figure 3.6. ^{19}F NMR spectrum of the reaction of **1a** with 4-*tert*-butylphenylacetylene.

A similar result was obtained with **1a** and 1.5 equiv. of electron-rich 1-hexyne, albeit over a longer reaction time. After allowing the reaction mixture to sit at room temperature for 48 hours, the ^{19}F NMR spectrum showed a very broad resonance at -87.6 ppm which gave rise after 5 days to a doublet of triplets at -89.5 ppm ($^3J_{FH} = 51$ and $^3J_{FP} = 41$ Hz), assigned to the metallacyclobutene product, **2d**. This led to the assignment of the broad resonance (and that observed with 4-chlorophenylacetylene in Figure 3.2) as a long-lived intermediate towards the initial cycloaddition reaction (see Conclusions below). Further observation of the ^{19}F NMR spectrum showed the presence of **3d** and **4d**, although in very minor amounts. After continual monitoring for several days indicated no further reaction, attempts to gently heat the solution mixture to drive the reaction were made, resulting in rapid decomposition of **2d**.

3.2.2 Influence of Ancillary Ligands on Ni=CF₂ Reactivity with Aryl-acetylenes

The previous section summarized the substituent effect of electron-donating/withdrawing groups on formation of different partially fluorinated metallacyclobutenes and hexadienes. It was found that substrates featuring more electron-donating substituents favored the formation of the metallacyclobutene, presumably due to stabilization of the metallacycle. Indeed, electron-withdrawing groups had the opposite effect, destabilizing the metallacyclobutene and making it more susceptible to a second acetylene insertion to form the metallacyclohexadiene product. In order to further investigate this trend in the stability and reactivity of the metallacyclobutene products, we varied the ancillary ligand electronics on the nickel difluorocarbene precursor.

The reaction of **1a** with 2 equivalents of CuCl and P(OMe)₃ in benzene has been shown previously to give Ni=CF₂[P(OMe)₃]₃, **1b** in 80% yield.¹⁶ Since it was previously determined that electron-donating substrates will stabilize the metallacyclobutene, 4-*tert*-butylphenylacetylene was chosen as the substrate to see if use of a Lewis acidic phosphite would destabilize the metallacyclobutene as opposed to more basic dppe. A solution of **1b** in THF was charged with 1.5 equivalents of 4-*tert*-butylphenylacetylene and allowed to react at room temperature overnight. The crude ¹⁹F NMR spectrum of the reaction mixture showed conversion only to the six-membered metallacyclohexadiene and organic product **3e** and **4e**. All of **1b** was consumed with no indication of metallacyclobutene formation. While the electron-donating substituent stabilized the metallacyclobutene in the reaction with **1a**, use of a nickel complex with a less electron-donating ancillary ligand results in a more reactive metallacyclobutene. Similar products **3f** and **4f** were obtained from **1b** and 4-chlorophenylacetylene whereas with 1-hexyne, only the reductive elimination product **4g** was observed.

Turning then to more electron-rich phosphines than dppe, we attempted to make a dmpe analogue of the Ni=CF₂ precursor based on known literature procedures (dmpe = 1,2-bis(dimethylphosphino)ethane). The nickel precursor needed to synthesize **1a** is a relatively simple and efficient reaction, performed by reacting Ni(CF₃)[OC(O)CF₃](PPh₃)₂ with dppe in a solution of Et₂O to furnish the Ni(CF₃)[OC(O)CF₃](dppe) product. To synthesize the dmpe analogue of **1a**, a 50 mL diethyl ether solution containing 1.23 g of Ni[OC(O)CF₃](CF₃)(PPh₃)₂ was added to 0.27 mL of dmpe in 25 mL of Et₂O, resulting in an orange solution with observation of a precipitate as expected. The reaction mixture was stirred for 16 h overnight, and subsequently filtered and dried to collect 0.558 g of a red-orange solid. The ¹⁹F NMR spectrum (see experimental section), however, showed two products: the desired **1a** analog, Ni(CF₃)[OC(O)CF₃](dmpe), and a five-coordinate bis(dmpe) salt assigned as [Ni(CF₃)(dmpe)₂]⁺(O₂CCF₃)⁻. Multiple attempts to purify the product via extraction into hexane or diethyl ether were made; however, the solubility of the products was too similar for any effective isolation.

As the inseparable bis(dmpe) salt was thought to be unlikely to react in the subsequent synthetic step, an attempt to synthesize the Ni=CF₂ complex was made. The analogous literature procedure outlined in Chapter 2 (See Experimental Section 2.3.2) was followed as it more consistently provided an isolable solid product. However, attempts to isolate the Ni=CF₂ product proved unsuccessful as it was consistently being collected as a thick viscous oil that proved difficult to work with. Furthermore, analysis of the oily product via ¹⁹F NMR spectroscopy showed other unidentified impurities. Multiple synthetic attempts were made with no improvements. Since the problems associated with this synthetic procedure outweighed the potential electron-donating benefits, an alternative electron-donating phosphine ligand was sought out.

The dipe ligand [dipe = 1,2-bis(diisobutylphosphino)ethane] was chosen as an alternative as it was thought that the small methyl groups on the dmpe ligand were leading to unwanted side reactions. The synthesis of the Ni=CF₂ precursor Ni(CF₃)[OC(O)CF₃](dipe) was performed by adding a cold 10 mL solution containing 0.460 g of dipe dropwise to a stirring 60 mL cold solution of Et₂O containing a 1 g suspension of Ni(CF₃)[OC(O)CF₃](PPh₃)₂. The yellow solution was stirred for 15 minutes after which a homogeneous solution was observed. The solution was placed in the freezer at -30 °C overnight, and yellow crystals were formed. The solution was filtered to collect 0.61 g of yellow crystals after drying (83 % yield). The ¹⁹F NMR spectrum revealed a doublet of doublets and a singlet at -29.3 and -74.9 ppm and the ³¹P NMR spectrum showed resonances at 51.5 and 45.2 ppm (²J_{PP} = 38 Hz).

The subsequent reduction reaction to give the desired Ni=CF₂ carbene was performed according to Chapter 2, Experimental Section 2.3.2 to yield the desired compound Ni=CF₂[P(OMe)₃](dipe) **1c**. While the synthesis of **1c** proceeded much more cleanly than the attempted dmpe reaction described previously, **1c** could only be isolated as a thick oily solid in small amounts that proved difficult to work with.

A solution of **1c** in 0.3 mL of THF was charged with 4-chlorophenylacetylene resulting in a dark red solution. The solution was allowed to react at room temperature for 24 hours. Analysis of the crude ¹⁹F NMR spectrum showed conversion to only the metallacyclobutene product **2h**. Continual monitoring of the reaction mixture via ¹⁹F NMR showed no further reactivity or conversion to the other products. The reaction mixture was filtered and evaporated *in vacuo* and re-dissolved in C₆D₆ in order to attempt to more fully characterize the complex, however, the subsequent ¹⁹F NMR spectrum showed **2h** as an extremely broad resonance with poor multiplicity

signal and attempts to take a ^1H NMR revealed no further information. Presumably **2h** was unstable and decomposed upon filtration.

3.3 Conclusion

The study of base-metal perfluorometallacycles has been of great interest over the past decade. Specifically, metallacyclobutenes are proposed to be crucial intermediates in many industrially relevant catalytic processes. The Baker group has previously demonstrated the efficient synthesis of a variety of Co fluorometallacyclobutene systems with a $\text{CpCo}=\text{CF}(\text{CF}_3)(\text{PPh}_2\text{Me})$ complex through reaction with terminal acetylenes.¹⁵ It was also found that replacement of the ancillary phosphine with a less basic one resulted in a destabilized metallacycle that was easily subjected to decomposition pathways. Analogous reaction attempts with the $\text{Co}=\text{CF}_2$ system showed a greater barrier for reactivity. This chapter summarized our efforts to use the electron-rich $\text{Ni}=\text{CF}_2[\text{P}(\text{OMe})_3](\text{dppe})$ **1a** for reaction with terminal acetylenes to study the formation of metallacyclobutenes.

Reaction of **1** with 1.5 equivalents of 4-R-phenylacetylenes or 1-hexyne resulted in the formation of the expected metallacyclobutene products ($\text{R} = \text{H}, \text{Cl}, ^t\text{Bu}$). Contrary to the previously reported Co system, the metallacyclobutenes were able to undergo a second insertion of acetylene to yield a six-membered nickelacyclohexadiene, and furthermore, a subsequent reductive elimination to give a difluorinated cyclopentadiene. Ogoshi *et al.* previously observed a novel instance of 5- to 7-membered ring expansion as a key intermediate process during investigations of oxidative cyclization of TFE and simple alkenes with Ni(0) precursors.¹⁷ The work presented

here represents not only the first example of a fluorinated metallacyclohexadiene, but also the first observed 4- to 6-membered ring expansion of fluorinated metallacyclobutenes.

The electronics of the acetylene substrate played a dramatic role in the selectivity of product formation. Substrates featuring more electron-donating substituents resulted in a more stabilized metallacyclobutene that was less inclined to undergo a second insertion reaction. Alternatively, those with more electron-withdrawing substituents formed metallacyclobutenes more prone to the second insertion to favor the formation of the nickelacyclohexadiene. The reaction could be effectively manipulated to push the progress forward by adding more acetylene and P(OMe)₃. Studies into varying the ancillary ligand electronics further supported these findings. Reaction of the less acidic **1b** resulted in no observation of metallacyclobutene, and only nickelacyclohexadiene and difluorinated cyclopentadiene. Furthermore, reaction of **1c** had the opposite effect where it more selectively synthesized the metallacyclobutene due to a higher degree of stabilization. Overall, the original Ni=CF₂ complex **1a** proved to be an adequate complex for efficient facilitation of cycloaddition reactions with terminal acetylenes.

3.4 Experimental

3.4.1 Materials and Methods

Unless otherwise stated, all reactions were carried out under an atmosphere of oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, Et₂O and THF were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contours) solvent purification system. Benzene-d₆, toluene-d₈, and THF-d₈ were degassed by three freeze-pump-thaw cycles, and subsequently dried

by running through a column of activated alumina. All solvents were stored over activated (heated at $\sim 250\text{ }^{\circ}\text{C}$ for $>8\text{ h}$ under vacuum) 4 \AA molecular sieves. Glassware was oven-dried at $150\text{ }^{\circ}\text{C}$ for $>2\text{ h}$. All reagents were purchased from commercial suppliers unless otherwise stated. ^1H , $^1\text{H}\{^{19}\text{F}\}$, ^{19}F , $^{19}\text{F}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on either Bruker Avance and AvanceII 300 MHz, a 500 MHz or 600 MHz NMR spectrometer with respect to proton nuclei. ^1H NMR spectra were referenced to residual protons (C_6D_6 , $\delta 7.15$) with respect to tetramethylsilane at $\delta 0.00$. $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were referenced to an external sample of 80% CCl_3F in CDCl_3 at 0.00 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. The reagents phenylacetylene, 4-chlorophenylacetylene, 4-*tert*-butylphenylacetylene, 1-hexyne, trimethylphosphite, dmpe, and dipe, were all purchased from commercial suppliers.

3.4.2 Synthesis of Ni Difluorocarbene Complexes

Attempted synthesis of $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{dmpe})$. A 100 mL round bottom flask was charged with 50 mL diethyl ether solution and 1.23 g of $(\text{PPh}_3)_2\text{Ni}[\text{OC}(\text{O})\text{CF}_3](\text{CF}_3)$. To this solution was added 0.27 mL of dmpe in 25 mL of Et_2O , resulting in an orange solution suspension. The reaction mixture was stirred for 16 hours overnight, and subsequently filtered and dried to collect 0.558 g of a red-orange solid. The ^{19}F NMR however, showed conversion to two products: the desired $\text{Ni}(\text{CF}_3)[\text{OC}(\text{O})\text{CF}_3](\text{dmpe})$ product at $\delta -29.6$ (broad multiplet, 3F, CF_3) and -74.6 (singlet, 3F, O_2CF_3), and another major impurity assigned as $\text{Ni}(\text{CF}_3)(\text{dmpe})_2^+\text{O}_2\text{CCF}_3^-$ at $\delta -3.9$ (quintet, 3F, CF_3 , $^3J_{\text{FP}} = 29\text{ Hz}$) and -74.6 (singlet, 3F, $^-\text{O}_2\text{CCF}_3$). $^{31}\text{P}\{^1\text{H}\}$ showed $\delta 22.8$ (quartet, 2P, dppe, $^3J_{\text{FP}} = 29\text{ Hz}$) and 42.8 (singlet, 4P, bis-dppe). Multiple attempts to purify the product via extraction into hexane or diethyl ether were made, however, the solubility of the products was too similar for any effective isolation.

Attempted Synthesis of Ni=CF₂[P(OMe)₃](dmpe) (1b). Reaction was performed according to synthesis outlined in Chapter 2, Experimental Section 2.3.2 with the mixture of Ni(CF₃)[OC(O)CF₃](dmpe) and (dmpe)₂Ni(CF₃)⁺O₂CF₃⁻ outlined above. Analysis of the ¹⁹F showed the desired Ni=CF₂[P(OMe)₃](dmpe) complex at 92.3 ppm as a doublet of triplets (³J_{FP} = 44.7, ³J_{FP} = 63.0 Hz) along with multiple unidentifiable impurities. ³¹P NMR showed peaks at 19.0 (doublet of triplets, 2P, dmpe, ³J_{PP} = 30.4, ³J_{FP} = 44.7 Hz) and 166.8 ppm (triplet of triplets, 1P, P(OMe)₃, ³J_{PP} = 30.4, ³J_{FP} = 44.7 Hz).

Synthesis of Ni(CF₃)[OC(O)CF₃](dipe). A 100 mL round bottom flask charged with 60 mL of Et₂O and 1 g of (PPh₃)₂Ni[OC(O)CF₃](CF₃) was cooled to approximately -30 °C resulting in an orange suspension. While stirring, a cold solution of 0.460 g of dipe in 10 mL of Et₂O was added dropwise over 5 minutes, resulting in an immediate color change to yellow and a disappearance of the suspension. After 15 minutes, the solution was placed in the freezer at -30 °C overnight resulting in the formation of yellow crystals. The crystals were collected via filtration and dried resulting in the isolation of 0.61 g (83 % yield). ¹⁹F NMR (282 MHz, 23 °C, THF) -29.3 ppm (doublet of doublets, 3F, Ni-CF₃, ³J_{FP} = 6.5 Hz, ³J_{FP} = 46 Hz). ³¹P{¹H} NMR (121 MHz, 23 °C, THF) 51.5 (doublet of quartets, P, *trans*-P, ³J_{PF} = 6.5 Hz, ³J_{FP} = 38 Hz); 45.2 ppm (doublet of quartets, P, *cis*-P, ³J_{PF} = 46 Hz, ³J_{PP} = 38 Hz).

Synthesis of Ni=CF₂[P(OMe)₃](dipe) (1c). Reaction was performed according to synthesis outlined in Chapter 2, Experimental Section 2.3.2, resulting in the collection of 0.187 g of a dark red oil (80 % yield). Analysis of the ¹⁹F NMR spectrum showed near complete conversion to **1c**. ¹⁹F NMR (282 MHz, 23 °C, THF) -86.1 ppm (doublet of triplets, 3F, Ni-CF₃, ³J_{FP} = 41.5, ³J_{FP} = 67.5 Hz). ³¹P{¹H} NMR (121 MHz, 23 °C, THF) 38.7 (doublet of triplets, 1P, dipe, ³J_{PP} = 36, ³J_{PF} = 41.5 Hz); 162.4 ppm (triplet of triplets, 1P, P(OMe)₃, ³J_{PP} = 36, ³J_{PF} = 67.5 Hz).

3.4.3 Reactivity Studies of **1a**, **1b**, and **1c** with Phenylacetylenes

Reaction of 1a with Phenylacetylene. A solution of **1a** (15 mg, 0.02 mmol) in 0.3 mL of THF was charged with 4 μ L of phenylacetylene (1.5 equiv, 0.04 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ^{19}F NMR showed conversion to three major products: the metallacyclobutene **2a**, the metallacyclohexadiene **3a**, and the reductive elimination organic product **4a** in a 74:16:10 ratio.

Characterization of $[\text{dppe}]\text{Ni}[\kappa^2\text{-C(Ph)=CHCF}_2]$ (**2a**)

^{19}F NMR (282 MHz, 23 $^\circ\text{C}$, THF) -89.6 ppm (doublet of triplets, 2F, CF_2 , $^3J_{\text{FP}} = 40$, $^3J_{\text{FH}} = 48$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 23 $^\circ\text{C}$, THF) -89.6 ppm (triplet, 2F, CF_2 , $^3J_{\text{FP}} = 40$ Hz).

Characterization of $[\text{dppe}]\text{Ni}[\kappa^2\text{-C(Ph)=CHC(Ph)=CHCF}_2]$ (**3a**)

^{19}F NMR (282 MHz, 23 $^\circ\text{C}$, THF) -100.1 ppm (doublet of triplets, 2F, CF_2 , $^3J_{\text{FP}} = 7.5$, $^3J_{\text{FH}} = 54.5$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 23 $^\circ\text{C}$, THF) -100.1 ppm (singlet, 2F, CF_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 23 $^\circ\text{C}$, THF) 53.3 ppm (triplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $^3J_{\text{PF}} = 7.5$ Hz).

Characterization of 5-difluoro-1,3-diphenylcyclopentadiene (**4a**)

^{19}F NMR (282 MHz, 23 $^\circ\text{C}$, THF) -106.4 ppm (doublet, 2F, CF_2 , $^3J_{\text{FH}} = 54$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 23 $^\circ\text{C}$, THF) -106.4 ppm (singlet, 2F, CF_2).

Attempted Isolation of 3a and 4a for Further Characterization. A solution of **1a** (15 mg, 0.02 mmol) in 0.3 mL of THF was charged with 4 μ L of phenylacetylene (1.5 equiv, 0.035 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ^{19}F NMR spectrum revealed conversion to **2a**, **3a**, and minimal **4a**. An additional 1.5 equivalents of phenylacetylene (4 μ L) was added and the reaction mixture sat for a further 24 h. The crude ^{19}F NMR revealed further conversion to **3a** and **4a** with noticeable decrease of **2a**. After an additional phenylacetylene equivalent was added, and after 24 h again, the ^{19}F NMR spectrum showed near complete consumption of **2a**, however both **3a** and **4a** were present in near equal amounts. It proved near impossible to manipulate the reaction conditions to just get isolation of **3a**.

In order to attempt to instead isolate **4a**, 1 equivalent of trimethylphosphite (3 μ L) was added to the reaction mixture and allowed to sit for 24 h. The ^{19}F NMR spectrum showed near complete conversion to **4a**, with **2a** and **3a** barely visible in the baseline. The solution was shipped into the glovebox, evaporated *in vacuo*, and redissolved in C_6D_6 . The solution was filtered through a plug of silica and allowed adequate contact time to ensure decomposition of any leftover Ni species. This sample was used for ^1H , $^1\text{H}\{^{19}\text{F}\}$, $^{13}\text{C}\{^1\text{H}\}$, DEPT 135 ^{13}C , and HMQC NMR studies.

Reaction of 1a with 4-chlorophenylacetylene. A solution of **1a** (15 mg, 0.02 mmol) in 0.3 mL of THF was charged with of 4-chlorophenylacetylene (5 mg, 1.5 equiv, 0.035 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ^{19}F NMR spectrum showed conversion to three major products: the metallacyclobutene **2b**, the metallacyclohexadiene **3b**, and the reductive elimination organic product **4b** in a 23:55:22 ratio.

Characterization of [dppe]Ni[κ^2 -C(4-Cl-Ph)=CHCF₂] (**2b**)

¹⁹F NMR (282 MHz, 23 °C, THF) -90.1 ppm (doublet of triplets, 2F, CF₂, ³J_{FH} = 48, ³J_{FP} = 40 Hz).

¹⁹F{¹H} NMR (282 MHz, 23 °C, THF) -90.1 ppm (singlet, 2F, CF₂, ³J_{FP} = 40 Hz)

Characterization of [dppe]Ni[κ^2 -C(4-Cl-Ph)=CHC(4-Cl-Ph)=CHCF₂] (**3b**)

¹⁹F NMR (282 MHz, 23 °C, THF) -100.6 ppm (doublet of triplets, 2F, CF₂, ³J_{FH} = 59, ³J_{FP} = 77 Hz).

¹⁹F{¹H} NMR (282 MHz, 23 °C, THF) -100.6 ppm (singlet, 2F, CF₂, ³J_{FP} = 77 Hz).

³¹P{¹H} NMR (121 MHz, 23 °C, THF) 53.9 ppm (triplet, 1P, Ph₂PCH₂CH₂PPh₂, ³J_{PF} = 77 Hz).

Characterization of 5-difluoro-1,3-di(4-chlorophenyl)cyclopentadiene (**4b**)

¹⁹F NMR (282 MHz, 23 °C, THF) -107.0 ppm (doublet, 2F, CF₂, ³J_{FH} = 54 Hz).

¹⁹F{¹H} NMR (282 MHz, 23 °C, THF) -107.0 ppm (singlet, 2F, CF₂).

Reaction of 1a with 4-tert-butylphenylacetylene. A solution of **1a** (15 mg, 0.02 mmol) in 0.3 mL of THF was charged with 6.5 μ L of 4-tert-butylphenylacetylene (1.5 equiv, 0.035 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ¹⁹F NMR spectrum showed conversion to three major products: the metallacyclobutene **2c**, the metallacyclohexadiene **3c**, and the reductive elimination organic product **4c** in an 83:10:7 ratio respectively.

Characterization of [dppe]Ni[κ^2 -C(4-^tBu-Ph)=CHCF₂] (2c)

¹⁹F NMR (282 MHz, 23 °C, THF) -89.8 ppm (doublet of triplets, 2F, CF₂, ³J_{FH} = 49.5, ³J_{FP} = 41 Hz).

¹⁹F{¹H} NMR (282 MHz, 23 °C, THF) -89.8 ppm (triplet, 2F, CF₂, ³J_{FP} = 41 Hz).

Characterization of [dppe]Ni[κ^2 -C(4-^tBu-Ph)=CHC(4-^tBu-Ph)=CHCF₂] (3c)

¹⁹F NMR (282 MHz, 23 °C, THF) -100.0 ppm (doublet of triplets, 2F, CF₂, ³J_{FH} = 59.5, ³J_{FP} = 7.5 Hz).

¹⁹F{¹H} NMR (282 MHz, 23 °C, THF) -100.0 ppm (triplet, 2F, CF₂, ³J_{FP} = 7.5 Hz).

³¹P{¹H} NMR (121 MHz, 23 °C, THF) 53.2 ppm (triplet, 1P, Ph₂PCH₂CH₂PPh₂, ³J_{PF} = 7.5 Hz).

Characterization of 5-difluoro-1,3-di(4-tert-butyl)cyclopentadiene (4c)

¹⁹F NMR (282 MHz, 23 °C, THF) -106.2 ppm (doublet, 2F, CF₂, ³J_{FH} = 54.5 Hz).

¹⁹F{¹H} NMR (282 MHz, 23 °C, THF) -106.2 ppm (singlet, 2F, CF₂).

Reaction of 1a with 1-hexyne. A solution of **1a** (15 mg, 0.02 mmol) in 0.3 mL of THF was charged with 4 μL of 1-hexyne (1.5 equiv, 0.035 mmol, resulting in a dark red solution. The solution was allowed to react at room temperature for 24 hours. Analysis of the crude ¹⁹F NMR spectrum showed conversion to the metallacyclobutene, **2d**.

Characterization of [dppe]Ni[κ^2 -C(C₅H₁₁)=CHCF₂] (2d)

¹⁹F NMR (282 MHz, 23 °C, THF) -89.7 ppm (doublet of triplets, 2F, CF₂, ³J_{FH} = 52, ³J_{FP} = 40.5 Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 23 °C, THF) -89.7 ppm (triplet, 2F, CF_2 , $^3J_{\text{FP}} = 40.5$ Hz).

Reaction of 1b with 4-tert-butylphenylacetylene. A solution of **1b** (15 mg, 0.03 mmol) in 0.3 mL of THF was charged with 8.5 μL of 4-tert-butylphenylacetylene (1.5 equiv, 0.05 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ^{19}F NMR spectrum showed conversion to only the metallacyclohexadiene **3e**, and the reductive elimination organic product **4e** in a 52:48 ratio.

Characterization of $[\text{P}(\text{OMe})_3]_2\text{Ni}[\kappa^2\text{-C}(4\text{-}^t\text{Bu-Ph})=\text{CHC}(4\text{-}^t\text{Bu-Ph})=\text{CHCF}_2]$ (**3e**)

^{19}F NMR (282 MHz, 23 °C, THF) -102.1 ppm (doublet of triplets, 2F, CF_2 , $^3J_{\text{FH}} = 59$, $^3J_{\text{FP}} = 6.5$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 23 °C, THF) -102.1 ppm (triplet, 2F, CF_2 , $^3J_{\text{FP}} = 6.5$ Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, 23 °C, THF) 53.0 ppm (triplet, 1P, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $^3J_{\text{PF}} = 6.5$ Hz).

Characterization of 5-difluoro-1,3-di(4-tertbutyl)cyclopentadiene (**4e**)

^{19}F NMR (282 MHz, 23 °C, THF) -105.9 ppm (doublet, 2F, CF_2 , $^3J_{\text{FH}} = 55$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 23 °C, THF) -105.9 ppm (singlet, 2F, CF_2).

Reaction of 1b with 4-chlorophenylacetylene. A solution of **1b** (15 mg, 0.03 mmol) in 0.3 mL of THF was charged with 4-chlorophenylacetylene (7.0 mg, 1.5 equiv, 0.05 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ^{19}F NMR spectrum showed conversion to only the metallacyclohexadiene **3f**, and the reductive elimination organic product **4f** in a 74:26 ratio.

Characterization of $[P(OMe)_3]_2Ni[\kappa^2-C(4-Cl-Ph)=CHC(4-Cl-Ph)=CHCF_2]$ (**3f**)

^{19}F NMR (282 MHz, 23 °C, THF) -102.7 ppm (doublet of triplets, 2F, CF_2 , $^3J_{FH} = 59$, $^3J_{FP} = 7.5$ Hz).

$^{19}F\{^1H\}$ NMR (282 MHz, 23 °C, THF) -102.7 ppm (triplet, 2F, CF_2 , $^3J_{FP} = 7.5$ Hz).

$^{31}P\{^1H\}$ NMR (121 MHz, 23 °C, THF) 164.6 ppm (broad multiplet, 2P, $P(OMe)_3$).

Characterization of 5-difluoro-1,3-di(4-chloro)cyclopentadiene (**4f**)

^{19}F NMR (282 MHz, 23 °C, THF) -106.7 ppm (doublet, 2F, CF_2 , $^3J_{FH} = 55.5$ Hz).

$^{19}F\{^1H\}$ NMR (282 MHz, 23 °C, THF) -106.7 ppm (singlet, 2F, CF_2).

Reaction of 1b with 1-hexyne. A solution of **1b** (15 mg, 0.03 mmol) in 0.3 mL of THF was charged with 1-hexyne (5.5 μ L, 1.5 equiv, 0.05 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ^{19}F NMR showed conversion to only the reductive elimination organic product **4g**.

Characterization of 5-difluoro-1,3-di(pentyl)cyclopentadiene (**4g**)

^{19}F NMR (282 MHz, 23 °C, THF) -104.9 ppm (doublet, 2F, CF_2 , $^3J_{FH} = 55$ Hz).

$^{19}F\{^1H\}$ NMR (282 MHz, 23 °C, THF) -104.9 ppm (singlet, 2F, CF_2).

Reaction of 1c with 4-chlorophenylacetylene. A solution of **1c** (21 mg, 0.04 mmol) in 0.3 mL of THF was charged with 4-chlorophenylacetylene (8 mg, 1.5 equiv, 0.06 mmol), resulting in a dark red solution. The solution was allowed to react at room temperature for 24 h. Analysis of the crude ^{19}F NMR spectrum showed conversion to only the metallacyclobutene **2h**.

Characterization of $[\text{dipe}]_{\text{Ni}}[\kappa^2\text{-C(4-Cl-Ph)=CHCF}_2]$ (**2h**)

^{19}F NMR (282 MHz, 23 °C, THF) -93.0 ppm (doublet of triplets, 2F, CF_2 , $^3J_{\text{FH}} = 48.5$, $^3J_{\text{FP}} = 37$ Hz).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, 23 °C, THF) -93.0 ppm (singlet, 2F, CF_2 , $^3J_{\text{FP}} = 37$ Hz).

3.5 References

- (1) Liu, C. B.; Meng, W.; Li, F.; Wang, S.; Nie, J.; Ma, J. A. *Angew. Chem. Int. Ed.* **2012**, *51*, 6227-6230.
- (2) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907-915.
- (3) Sheng, Y.; Wu, Y.-D.; Leszczynski, J. *Organometallics* **2004**, *23*, 3189-3196.
- (4) Naumov, S.; Buchmeiser, M. *Organometallics* **2012**, *31*, 847-856.
- (5) Nadif, S. S.; Kubo, T.; Gonsales, S. A.; VenkatRamani, S.; Ghiviriga, I.; Sumerlin, B. S.; Veige, A. S. *J. Am. Chem. Soc.* **2016**, *138*, 6408-6411.
- (6) Solans-Monfort, X. *Dalton Trans.* **2014**, *43*, 4573-4586.
- (7) Galan, B. R.; Giessert, A. J.; Keister, J. B.; Diver, S. T. *J. Am. Chem. Soc.* **2005**, *127*, 5762-5763.
- (8) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice Hall New Jersey, 1997, Chapter 9.
- (9) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317-1382.
- (10) Zhao, G.; Basuli, F.; Kilgore, U. J.; Fan, H.; Aneetha, H.; Huffman, J. C.; Wu, G.; Mindiola, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 13575-13585.
- (11) Hemond, R. C.; Hughes, R. P.; Robinson, D. J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2239-2241.
- (12) Hughes, R. P.; King, M. E.; Robinson, D. J.; Spotts, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8919-8920.
- (13) O'Connor, J. M.; Ji, H.; Iranpour, M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 1586-1588.
- (14) O'Connor, J. M.; Ji, H. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 9846-9847.
- (15) Lee, G. M.; Leung, A. S.; Harrison, D. J.; Korobkov, I.; Hughes, R. P.; Baker, R. T. *Organometallics* **2017**, *36*, 2853-2860.
- (16) Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics* **2015**, *34*, 5683-5686.
- (17) Ohashi, M.; Kawashima, T.; Taniguchi, T.; Kikushima, K.; Ogoshi, S. *Organometallics* **2015**, *34*, 1604-1607.

Chapter 4 – Conclusions & Future Work

4.1 Conclusions & Future Work

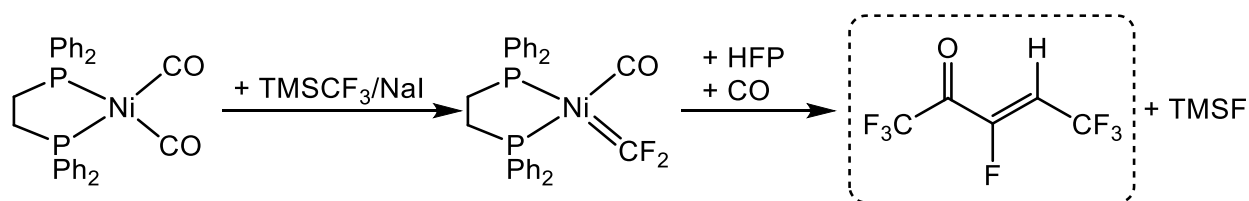
Reactions of simple olefins represent a highly sought pathway toward a wide array of organic products desired for their utility in multiple industries.¹ Within these reaction pathways are metallacycle complexes proposed to be key intermediates towards facilitating reaction.² The chemistry of metal-alkylidenes has been thoroughly developed over the past 30 years, however, analogous reactivity with metal fluorocarbenes remains an idealized objective.^{3,4} The Baker group has contributed a decade of efforts toward developing and understanding the formation and reactivity of base-metal perfluorometallacycle complexes.⁵⁻¹³ The electron-rich Ni(0) difluorocarbene complex **1** has been shown to efficiently undergo cycloaddition with TFE to furnish a perfluorometallacyclobutane.¹³ The work of this thesis has aimed to expand on the established reactivity of **1** with a broader scope of substrates.

Chapter 2 focused on examining the reactivity of **1** with a variety of fluoroalkenes to investigate if metathesis products were being produced. Reaction of **1** with vinylidene fluoride, perfluoro(methyl vinyl ether), and trifluoroethylene, resulted in the formation of several fluorinated metallacycles. The effect of an electron-rich difluorocarbene on the selectivity of metallacycle formation can be compared to that of a more π -acidic system when examining previously reported reactivity of $\text{Ni}=\text{CF}(\text{CF}_3)[\text{P}(\text{O}^i\text{Pr})_3]_3$. Upon reaction with vinylidene fluoride, both $\text{Ni}=\text{CF}_2$ and $\text{Ni}=\text{CFCF}_3$ form the same regioisomers of the metallacyclobutane with the H's on the β -C. In contrast, reaction of $\text{Ni}=\text{CF}(\text{CF}_3)$ with perfluoro(methyl vinyl ether) gave metathesis products and both metallacyclobutane regioisomers, whereas the same reaction with **1** gave only **Ni-met^F-2**, in which the OCF_3 moiety is on the α -C, demonstrating a greater regioselectivity. Both regioisomers were also proposed to result from treatment of trifluoroethylene with $\text{Ni}=\text{CF}(\text{CF}_3)$ with the CHF moiety on the α -C or β -C, in an approximate 1:3 ratio. Both regioisomers were unstable, however, affording observed C–F bond activation and 2,1-F shift products, respectively. In this work, $\text{Ni}=\text{CF}_2$ (**1a**) and trifluoroethylene selectively give the regioisomer with the CHF on the α -C, which also undergoes the 2,1-F shift, presumably forming the $\text{CFH}=\text{CF}(\text{CF}_3)$ alkene complex. Further reaction of the latter with excess TrFE provides a single isomer of the *cis*-head-to-tail metallacyclopentane isomer **Ni-met^F-5**. This result reinforces the superior regioselectivity enforced by the dppe ligand, as all other previously used tertiary phosphorus ligands afforded at least three isomers in this reaction. Also, this result provides additional support that the presence of a CHF moiety in a metallacyclobutane greatly destabilizes it, resulting in further reactivity.

While reaction of **1** with CTFE also yielded a single metallacyclobutane isomer, **Ni-met^F-6**, subsequent α -Cl elimination resulted in the formation of a nickel-chloride tetrafluoroallyl complex **Ni-alk^F-2**, demonstrating the capacity of metallacycle products to facilitate further

reaction. Although additional work is required to understand and potentially avoid the observed F replacement by H, the reactivity of **Ni-met^F-6** at the α -C will be revealing, as all fluorinated metallacyclobutanes reported to date typically react by β -C-F activation.

Most interesting, the reaction of **1** with HFP which was hoped to yield metathesis products, instead yielded the trifluoromethyl nickel perfluoroalkenyl complex, **Ni-alk^F-1**. The unexpected formation of **Ni-alk^F-1** represents an exciting pathway that could potentially be utilized for the formation of valuable fluorinated organics. For instance, reaction of the known Ni(0) starting material Ni(dppe)(CO)₂ with TMSCF₃/NaI could be used for direct generation of fluorocarbene complex Ni=CF₂(dppe)(CO). If this species undergoes a similar F-transfer from HFP to the carbene carbon, migration of the resulting perfluoroalkenyl group to the coordinated CO, followed by reductive elimination, could potentially afford the new fluorinated α,β -unsaturated ketone CF₃C(O)CF=CH(CF₃) in a catalytic process (Scheme 4.1).



Scheme 4.1. Potential application of novel Ni=CF₂/HFP reactivity.

The mechanism of fluorometallacyclobutane formation via cycloaddition reactions of nucleophilic metal fluorocarbenes and fluoroalkenes has been previously investigated with DFT, which identified a low energy open-shell 1,4-diradical mechanism. This work featured new reactivity with HFP in which transfer of fluoride to the CF₂ carbon creates two different kinds of Ni-bound sp³ carbons. While a reasonable reaction pathway for this reaction has been proposed,

future work should investigate potential transition states for this reaction as well as Ni–Cl formation from the CTFE-derived metallacyclobutane **Ni-met^F-6**.

Chapter 3 concentrated on expanding previously reported reactivity of acetylenes with Co=CF(CF₃) complexes.⁷ Electron rich Ni=CF₂[P(OMe)₃](dppe) (**1a**) was envisioned to provide more stable metallacyclobutene products for potential future reactivity studies. Indeed, reactions of **1a** with 4-R-phenylacetylenes yielded the expected difluorometallacyclobutenes, which were then found to undergo a second acetylene insertion, affording difluorometallacyclohexadienes (R = H, Cl, ^tBu). Moreover, the six-membered metallacyclohexadiene products were found to undergo reductive elimination to yield difluoro-diaryl-cyclopentadienes. Further analysis of the product ratios for each individual acetylene revealed a clear trend in which more electron-donating substrates stabilize the metallacyclobutene resulting in less of the metallacyclohexadiene and substituted cyclopentadiene products.

Further investigation of the influence of electronics around the metal center were investigated by varying the ancillary ligand of the Ni(0) difluorocarbene. It was found that π -acidic phosphite ligands in Ni=CF₂[P(OMe)₃]₃ generated more reactive metallacyclobutenes, which in some cases were not even observed, yielding exclusively metallacyclohexadienes and difluorocyclopentadienes. Furthermore, use of the more electron-rich Ni=CF₂[P(OMe)₃](dipe) resulted in even more stable metallacyclobutenes. Although these systems proved difficult to manipulate in order to selectively synthesize one of the three products for isolation and full characterization, detailed NMR analysis provided several characteristic resonances to support the proposed product formation. In future work, the perfluorometallacycles should be characterized by X-ray diffraction to effectively compare the structure to previously reported Co complexes and

fully characterize the first example of a fluorinated metallacyclohexadiene. Furthermore, the ability to isolate the metallacyclobutene complex would be valuable for future studies using other substrates (CO, alkenes, isonitriles) for the second insertion reaction.

Ogoshi *et al.* previously observed a novel instance of 5- to 7-membered ring expansion as a key intermediate process during investigations of oxidative cyclization of TFE and simple alkenes with Ni(0) precursors.¹⁴ The proposed catalytic cycle is terminated via β -H elimination and subsequent reductive elimination to reform the Ni(0) catalyst. The reformation of the starting Ni(0) oxidation state is critical for development of a catalytic cycle. O'Connor *et al.* reported a similar hydrocarbon system in which a cobalt metallacyclobutene undergoes acetylene insertion to form a η^4 -metallacyclohexadiene intermediate which is followed by reductive elimination to afford a Co- η^5 -metallacyclopentadiene complex.¹⁵ This reaction ultimately suffers from the final product still being bound to the metal center, whereas our system undergoes reductive elimination from a six-membered nickelacyclohexadiene to furnish a difluorocyclopentadiene. Additionally, the Ni(0) complex Ni(dppe)[P(OMe)₃]₂ is reformed, which makes potential extension to catalytic applications a possibility.

The 4- to 6-membered ring expansion described here is the first example for fluorinated metallacycles and represents a unique route to substituted difluorocyclopentadienes. Development of alternative routes to fluorinated metallacyclohexadienes of different degree of fluorination and substitution could prove greatly beneficial. Bleeke *et al.* reported the formation of an iridium-cyclohexadiene complex when reacting CO₂ or N₂O with the iridium metallabenzene complex, Ir(κ^2 -C₅H₅)(PEt₃)₃.¹⁶ The reaction is proposed to proceed stepwise by nucleophilic attack of an iridabenzene R ring carbon on the electrophilic carbon of CO₂, followed by iridium-oxygen bond

formation. We envision potentially reacting other nucleophilic type reagents with some of our metallacyclobutene products to potentially yield more nickelacyclohexadienes of varying fluorination patterns based on the metallacyclobutene starting material.

The most intriguing results in this chapter are the strong electronic dependence on the formation of metallacycles. A greater understanding of the reaction profile would benefit from in-depth kinetic studies of the reaction with respect to each individual reaction component. Furthermore, DFT studies on the energies of metallacyclobutenes and metallacyclohexadienes of varied substitution (both in the substrate and ancillary ligand framework) may provide more support towards the intrinsic stability of the observed complexes.

Overall, the scope of this thesis entailed examining the potential reactivity of $\text{Ni}=\text{CF}_2[\text{P}(\text{OMe})_3](\text{dppe})$ with a broader substrate scope. In the midst of these reactivity studies it was found that not only does $\text{Ni}=\text{CF}_2[\text{P}(\text{OMe})_3](\text{dppe})$ provide unprecedented regioselectivity to metallacycle products, it is also capable of facilitating novel transformations. This work lays a solid foundation upon which future investigations into the formation and functionalization of fluorinated metallacycles can be pursued.

4.2 References

- (1) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907-915.
- (2) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85-93.
- (3) Harrison, D. J.; Daniels, A. L.; Guan, J.; Gabidullin, B. M.; Hall, M. B.; Baker, R. T. *Angew. Chem. Int. Ed* **2018**, *57*, 5772-5776.
- (4) Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2001**, *40*, 3441-3444.
- (5) Harrison, D. J.; Daniels, A. L.; Guan, J.; Gabidullin, B. M.; Hall, M. B.; Baker, R. T. *Angew. Chem.* **2018**, *130*, 5874-5878.
- (6) Andrella, N. O.; Sicard, A. J.; Gorelsky, S. I.; Korobkov, I.; Baker, R. T. *Chem. Sci.* **2015**, *6*, 6392-6397.
- (7) Harrison, D. J.; Gorelsky, S. I.; Lee, G. M.; Korobkov, I.; Baker, R. T. *Organometallics* **2012**, *32*, 12-15.
- (8) Fuller, J. T.; Harrison, D. J.; Leclerc, M. C.; Baker, R. T.; Ess, D. H.; Hughes, R. P. *Organometallics* **2015**, *34*, 5210-5213.
- (9) Harrison, D. J.; Lee, G. M.; Leclerc, M. C.; Korobkov, I.; Baker, R. T. *J. Am. Chem. Soc.* **2013**, *135*, 18296-18299.
- (10) Leclerc, M. C.; Bayne, J. M.; Lee, G. M.; Gorelsky, S. I.; Vasiliu, M.; Korobkov, I.; Harrison, D. J.; Dixon, D. A.; Baker, R. T. *J. Am. Chem. Soc.* **2015**, *137*, 16064-16073.
- (11) Lee, G. M.; Harrison, D. J.; Korobkov, I.; Baker, R. T. *Chem. Commun.* **2014**, *50*, 1128-1130.
- (12) Lee, G. M.; Leung, A. S.; Harrison, D. J.; Korobkov, I.; Hughes, R. P.; Baker, R. T. *Organometallics* **2017**, *36*, 2853-2860.
- (13) Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics* **2015**, *34*, 5683-5686.
- (14) Ohashi, M.; Kawashima, T.; Taniguchi, T.; Kikushima, K.; Ogoshi, S. *Organometallics* **2015**, *34*, 1604-1607.
- (15) O'Connor, J. M.; Fong, B. S.; Ji, H.-L.; Hiibner, K.; Rheingold, A. L. *J. Am. Chem. Soc.* **1995**, *117*, 8029-8030.
- (16) Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205-1228.