Reactions of Cobalt and Nickel Complexes with Fluoroalkenes and Perfluorobutadiene

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Abstract

Organofluorine compounds are highly desirable products owing to the unique physical and chemical properties imparted by fluorine. Fluorocarbons are useful molecules that are used in multiple industries such as refrigeration, agrochemicals, pharmaceuticals, insecticides, high-value fluoropolymers and reagents in catalysis. As ligands, they are privileged in the relative inertness of the C–F bonds and their electrophilicity, which makes them ideal candidates for coordination chemistry with late, electron rich metals.

Chapter 2 describes the preparation of new Ni metallacyclopentene complexes with phosphite and bis(phosphine) ligands and investigates the reaction of the latter with Lewis acidic trimethylsilyltriflate, TMSOTf (Tf = SO_2CF_3). As phosphine ligands react with the perfluoro-butadiene (PFB) substrate, the phosphite complex Ni((κ^2-C_4F_6)[P(O-*i*-Pr)$_3$]$_2$ (**2-1**) was prepared from Ni(cod)$_2$ /2 P(O-*i*-Pr)$_3$ and excess PFB. Reaction of **2.1** with bis(phosphine) dppe [1,2-bis(diphenylphosphine)ethane] proceeded slowly with release of P(O-*i*-Pr)$_3$ and formation of electron-rich Ni(κ^2-C_4F_6)(dppe) (**2-2**) that undergoes fluoride abstraction using TMSOTf. The major product is proposed to be a dienyl complex resulting from ring contraction and cycloreversion.

In **Chapter 3** we investigate reactions of fluoroalkenes with cobalt hydrides containing phosphine and phosphite ligands in order to see if their reactivity can be controlled by the ligands' steric and electronic properties. The four cobalt compounds used were CoH[P(O^{i}Pr)$_3$]$_4$ (**3-1**), CoH[P(O-*o*-tol)$_3$]$_n$ (**3-2**), CoH(triphos)(CO) (**3-3**); [triphos = bis(diphenylphosphinoethyl)-phenylphosphine], and CoH(PPh$_3$)$_3$(N$_2$) (**3-4**). In light of previous reports of tetrafluoroethylene insertion into Co carbonyl hydrides, we were surprised that analogous reactivity was not observed except for **3-4**. Instead, reactions with hexafluoropropene gave a mixture of alkene cobalt fluoride and cobalt alkenyl complexes.

In **Chapter 4** we summarize our contributions to knowledge and compare our results to those from the current state of the art.

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Abbreviations and Symbols

Atm . . . . . Atmosphere

bipy . . . . . 2,2’-Bipyridyl

Bu. . . . . Butyl

C6H6. . . . . Benzene

ca. . . . . Approximately

CFC. . . . . Chlorofluorocarbon

CFC(s) . . . . . Chlorofluorocarbon(s)

Cp . . . . . Cyclopentyl (esp. when referring to the phosphine PCp_3)

Cp . . . . . η^5-Cyclopentadienyl

Cy . . . . . .Cyclohexyl

d. . . . . Day(s)

dcppe . . . . . 1,2-Bis(dicyclopentylphosphino)ethane

DFT. . . . . Density Functional Theory

DMF. . . . . Dimethylformamide

dppb . . . . . 1,4-Bis(diphenylphosphino)butane)

dppe . . . . . 1,2-Bis(diphenylphosphino)ethane

dppf . . . . . 1,1’-bis(diphenylphosphino)ferrocene

dppp . . . . . 1,3-Bis(diphenylphosphino)propane

equiv. . . . . Equivalent

Et. . . . . Ethyl

FC(s) . . . . . .Fluorocarbon(s)

h. . . . . Hour(s)

HCC . . . . . Hydrochlorocarbon

HCFC . . . . . Hydrochlorofluorocarbon

HCFC. . . . . Hydrochlorofluorocarbon(s)

HCFO. . . . . Hydrochlorofluoroolefin

HF. . . . . Hydrofluoric acid

HFCB. . . . . Hexafluorocyclobutene

HFO. . . . . Hydrofluoroolefin

HFP. . . . . Hexafluoropropene

L. . . . . Ligand

M. . . . . .Metal

M-C. . . . . Metal-carbon bond

Me. . . . . Methyl

M-R. . . . . .Metal-alkyl bond

$M–R^f$. . . . . Metal-perfluoroalkyl bond

NHC . . . . . *N*-Heterocyclic carbene

NMR. . . . . Nuclear Magnetic Resonance

Ph. . . . . Phenyl

Pr. . . . . Propyl

PTFE. . . . . Polytetrafluoroethylene

RT. . . . . Room temperature

TFE . . . . . Tetrafluoroethylene

Tol. . . . . Toluene

Triphos . . . . . Bis(2-diphenylphosphinoethyl)phenylphosphine

Tripod . . . . . .1,1,1-Tris(diphenylphosphinomethyl)ethane

UV-Vis. . . . . Ultraviolet-visible spectrometry

VDF. . . . . Vinylidene difluoride

Chapter 1. Introduction

1.1 C-F Bonds

1.1.1. Fluorine in 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 that are tightly held by the nucleus and are therefore quite unreactive (fluorine is only a very weak H-bond acceptor, for example). The C-F bond is highly polarized (δ- at fluorine and δ+ at carbon) due to the electronegativity difference between carbon and fluorine (2.5 vs 4)[1]. This polarity suppresses lone pair donation from fluorine and in general, fluorine is a weak coordinator. In pharmaceutical and agrochemical compounds, fluorine affects the polarity of the parent molecule and, with a van der Waals radius like hydrogen (1.47 vs. 1.20 Å), does not usually change the metabolic pathways that the mirrored non-fluorinated molecules undergo[2]. The C-F bond polarity allows for the modulation of lipophilicity of biologically active molecules as well as control of fluorocarbon boiling points.[3,4]

1.1.2. C-F bond properties

Although C-F bonds are rarely found in nature, they are the strongest bonds to carbon of any element. The major overlap of π-orbitals of carbon with non-bonding electrons of fluorine is one reason for this stability[5]**.** This overlap, coupled with the least electronegative hybridization of carbon (low s-character) and the high electronegativity of fluorine, leads to thermodynamic stabilization. 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. The bond energies, depending on the number of fluorine present on carbon, are between 130 and ~ 545 kJ/mol, which is because of the major overlap of the π-orbitals of carbon with the non-bonding electrons of fluorine. This effect is multiplied when additional fluorines are present[6].

1.1.3. Using C-F bonds for organic compounds

C-F containing organic is not the smallest building block of organic chemistry, but HF (hydrofluoric acid)[7], which mostly comes from processing the mineral fluorite (CaF2) into anhydrous HF, is considered as the smallest one[8]. While researchers reluctant to use this substance because of its high corrosivity and toxicity, alternative effective fluoride and fluoroalkyl (R^F) transfer reagents have been developed for late-stage fluorination and perfluoroalkylation[9].

The high electronegativity of fluorine has a considerable effect on the fluorocarbon molecule's dipole moment and the acidity or basicity of other groups, as has been observed in inorganic chemistry. C-H bonds close to the fluorinated group also become more acidic; for instance, fluorinated homologues of imidazole have a pKa of 2.4 while imidazole has a pKa of 7. In addition, in spite of the short C-F bond length, there is little steric strain in polyfluorinated compounds, and van der Waals interactions between hydrogens and oxygens do not lead to massive changes in the molecular volume. However, the fluorine substituents in polyfluorinated compounds can shield the carbon skeleton from possible attacking reagents.

1.2 Organofluorine Compounds

1.2.1 Fluoroorganic compound properties

The importance of fluorinated compounds spurred extensive research on their development. However, there are some limits on industrial strategies to access these compounds. For example, some of these compounds' industrial synthesis still relies on Swarts fluorination strategies developed in the 1890s[10]. Fluorination of organic polyhalides with antimony trifluoride (or zinc and mercury fluorides) in the presence of a trace of a pentavalent antimony salt:

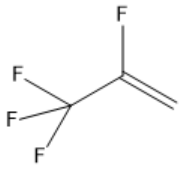
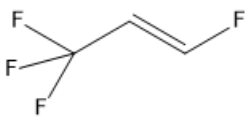
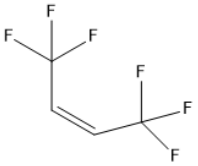
$$ClHC{=}CClCHCl_2 + SbF_3 \xrightarrow{SbCl_5} ClHC{=}CClCF_3 + SbCl_3.$$ [10]

The development of these strategies come from the strength of the C-F bond, oxidation potential and the low nucleophilicity of fluoride in media in which it is soluble, and it also requires caustic or highly reducing or oxidizing conditions or high temperatures[11-23]. Alternatively direct fluorination of hydrocarbons can be affected by high oxidation state metal fluorides such as CoF_3 in the Fowler-Flutech process.[24]

Fluoroorganic compounds have high thermal and chemical stability because of the significantly strong C-F bond (average bond energy around 480 kJ/mol) compared to other bonds in organic chemistry, and other carbon-halogen bonds (e.g., C–Cl bond is around 320kJ/mol). Moreover, the chemical and physical of properties of organofluorines present several remarkable behaviors that are different from those of all other substituents encountered in organic molecules.

1.2.2 Applications of organofluorine compounds

Organofluorine compounds have been used in many applications such as refrigerants, surfactants and water treatment agents, foam-blowing agents, polymers, liquid crystalline materials, pharmaceuticals, and agrochemicals.[25,26] Fluorine often brings unusual and surprising characteristics to the various molecular frames in which it is included. In this thesis we focus on fluoroalkenes that are utilized largely by the fluoropolymer industry[27] and more recently as the 4th generation of low global warming potential (GWP) refrigeration and inert blowing agents[28] (**Scheme1.1**). Increased molecular repulsion (large van der Waals radius) between adjacent molecules tends to give fluorocarbons high volatility, which is essential for refrigeration applications.

Low GWP refrigerant	**Low GWP refrigerant**	**GWP agent**
HFO-1234-yf 	HFO-1234ze 	HFO-1336mzz(z) 

Scheme 1.1: Selection of important hydrofluoro-olefins (HFOs).

1.2.3 ASHRAE Nomenclature and Safety Designations

Most patents and marketing materials describe small fluorinated molecules using a system of nomenclature devised by the American Society of Heating, Refrigerating, and AirConditioning Engineers (ASHRAE). In most marketing materials, major OEMs typically

substitute a brand name in place of the “R-” abbreviation as a way to distinguish their own products from those of competing manufacturers. **Figure 1.1** shows the ASHRAE refrigerant numbering system.

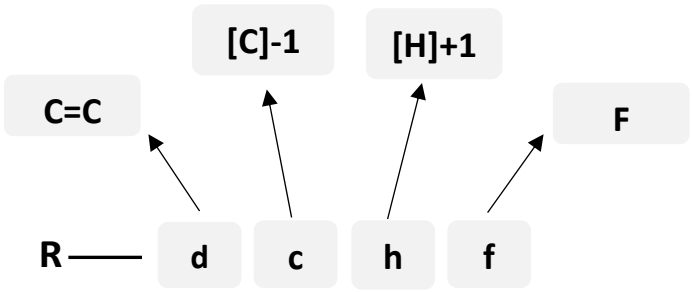


Figure 1.1. ASHRAE refrigerant numbering system.

Higher haloalkanes (C3 and beyond) are more complex and possess far too many constitutional isomers for their nomenclature to be assigned simply on the basis of rudimentary symmetry arguments; therefore, different letters are suffixed to the R-number which describe specific C1 fragments present in the molecule. These fragments are described in Table 2, along with their associated letter designations.

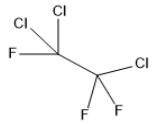
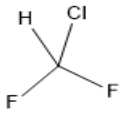
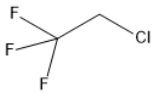
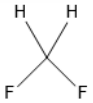
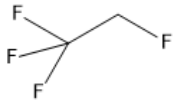
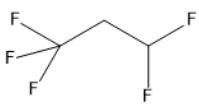
Table 1.1. Halocarbon Molecular Fragments and Their Corresponding Letter designations.

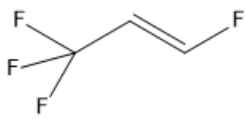
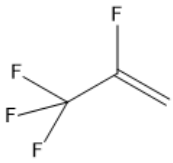
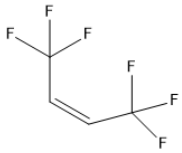
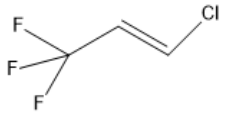
Fragment	Designation
CCl2	a
CClF	b
CF2	c
CHCl	d
CHF	e
CH2	f
CCl3	j
CCl2F	k
CClF2	l
CF3	M
CHCl2	N
CH2Cl	O
CHF2	P
CH2F	Q
CHClF	R

CH3	S
C	T
CCl	X
CF	Y
CH	Z

1.2.4 Different kinds of fluorocarbons

Fluorocarbons (FCs) are effective as surfactants, solvents, refrigerants, and monomers for fluoropolymers[29,30,31]**.** For refrigerants, there are three classes of fluorocarbons that have been used: chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs). Because of global warming and ozone depletion, many countries have banned using CFCs and HCFCs since 1995.[32,33] Hydrofluoroalkenes (HFAs) have recently been shown to possess greatly reduced global warming potential when compared to saturated HFCs[34]. Examples of important CFCs, HCFCs, HFCs and HFOs/HCFOs are shown in **Scheme 1.2**.

CFC-12  Chlorofluorocarbon 1ST Generation	**CFC-113**  Chlorofluorocarbon 1st Generation	
HCFC-22  Hydrochlorofluoro-carbon 2nd Generation	**HCFC-133a**  Hydrochlorofluoro-carbon 2nd Generation	
HFC-23  Hydrofluorocarbon 3rd Generation	**HFC-134a**  Hydrofluorocarbon 3rd Generation	**HFC-245fa**  Hydrofluorocarbon 3rd Generation

HFO-1234ze	HFO- 1234yf	HFO-1336mzz(z)	HCFO-1233ze
			
Hydrofluoroolefin 4th Generation	Hydrofluoroolefin 4th Generation	Hydrofluoroolefin 4th Generation	Hydrochlorofluoro-olefin 4th Generation

Scheme 1.2. Examples of important CFCs, HCFCs, HFCs and HFOs/HCFOs.

1.2.5 Chlorofluorocarbons

Chlorofluorocarbons (CFCs) were used as non-toxic refrigerants for decades until it was found that their atmospheric release damaged the earth's ozone layer. Following the Montreal Protocol, CFCs were replaced by hydrochlorofluorocarbons (HCFCs), and then by hydrofluorocarbons (HFCs). HFCs do not contain C-Cl bonds and they degrade in the troposphere, so they have no ozone-depleting potential, but they contribute significantly to global warming. Several events rapidly generated the development of new areas of fluorine chemistry, which are still in use today. The chemistry of fluorine was mostly concerned with inorganics before the new functional molecules during the first decades of the 20th century and following the works of H. Moissan. Concerning the CFCs saga, following the synthesis of these new refrigerants by T. Midgley, the halogen exchange fluorination method using anhydrous hydrogen fluoride remained the major tool for industrial production of numerous fluoroorganics, including (trifluoromethyl) arenes.[35]

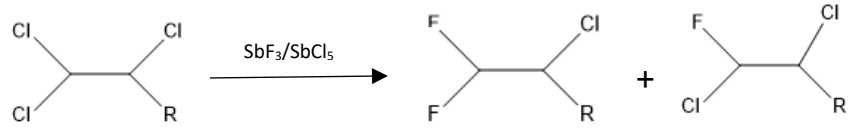
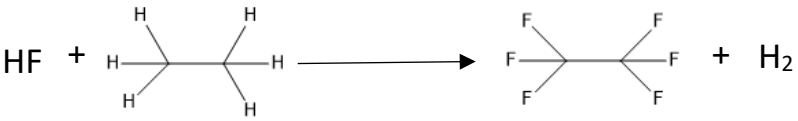
1.2.6 Synthesis of CFCs and HFCs

For the industrial synthesis, CFCs were made originally using the Swarts process in which chlorine atoms are replaced by fluorine in the presence of a Lewis acid such as SbF_5 or SbF_3Cl_3 (**Scheme 1.3**)[36]. Method 2 or "burning" with F_2 is a process that replaces all the hydrogen atoms in a substrate with fluorine atoms to provide perfluorinated compounds.[37,38,39] Electrochemical

fluorination is also a valuable method for the introduction of fluorine atoms into organic molecules as it can be performed in a one-step procedure under mild conditions. Electrolytic fluorination has found great applications in the field of perfluoroorganic compounds.[40]

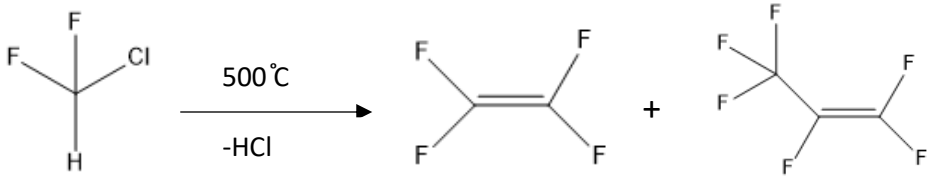
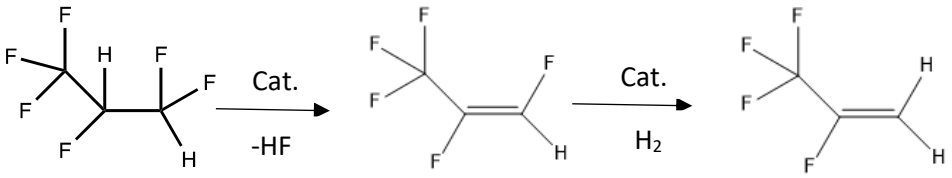
1.2.7 C2 and C3 fluorocarbons on large industrial scales

Many C2 and C3 fluorocarbons can be generated on large scales. Pyrolysis of chlorodifluoromethane at ~500 °C affords some popular fluorinated monomers such as hexafluoropropene (HFP), and tetrafluoroethylene (TFE) (**Scheme 1.4**). The 4th generation refrigerant, 1,1,1,2-tetrafluoropropene, is prepared by a stepwise process of dehydrofluorination (loss of HF) at elevated temperature followed by hydrodefluorination of the fluoroalkene intermediate.

Method 1: Swarts fluorination **R: alkyl, aryl**	
Method 2: Fluorination: "burning" with F_2	
Method 3: Electrochemical fluorination	

Scheme 1.3. Early methods used for the formation of C-F bonds.

Most current ways to synthesize FCs, need harsh conditions like use of toxic reagents and high pressures and temperatures. Moreover, some fluorinated compounds are destructive to the environment, humans, and animals because of their persistence and toxicity[41] (cf., perfluorooctanoic acid (PFOA) used in production of stain-resistant fluoropolymers like Teflon).

Synthesis of TFE and HFP	
Synthesis of R-1234yf	

Scheme 1.4. Modern synthesis of some common C2 and C3 fluorocarbons.

1.2.8 Other methods used to make hydrofluorocarbons

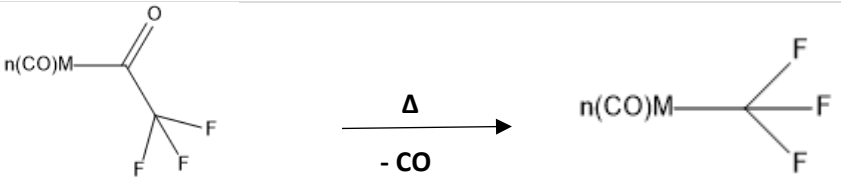
One process to synthesize hydrofluorocarbons uses Cr(III)-based heterogeneous catalysts. For example, 1,1,1,2-tetrafluoroethane (HFC-134a), one of the most popular refrigerants, can be prepared by fluorination of trichloroethylene using HF in the gas phase in the presence of CrF_3/O_2.[42] Some by-products including 1,2-dichlorofluoroethylene (HCFO-1121), 2-chloro, 1,1,1-trifluoroethane (HCFC-133), and pentafluoroethane (HFC-125) can be separated by distillation**.** Alternatively, HFC-125 can be prepared by hydrofluorination of tetrafluoroethylene using the same chromium oxyfluoride catalyst.

1.3 Metal Organofluorine complexes (M-R^F)

1.3.1. History of M–R^F complexes

Organometallic complexes containing M–C_{RF} bonds (R^F = CF_3, CF_2CF_3, etc.) have been studied since the 1950's. The McClellan[43] and Stone groups[44] reported formation of the M–CF_3 bond via thermal decarbonylation of $(CO)_5$Mn-C(O)CF_3 by Ethyl[45]. At the same time, Hieber and Beck followed similar syntheses of the cobalt analogues $(CO)_4$CoC(O)CF_3[46] (**Scheme 1.5**). This decarbonylation reaction requires an open coordination site for the formed CF_3 group and therefore mainly occurs with metal carbonyls that have thermally labile CO ligands. Chee and

Robertson reported a non-carbonyl example using $PtCl(COCF_3)(PMePh_2)_2$ which required more forcing conditions such as high temperature (exceeding 200 °C).[47]

M = Co, Mn N = 4 (Co), 5 (Mn) Δ = 20℃ (Co), 100℃ (Mn)	

Scheme 1.5. Hieber and Beck's route to M-CF_3 complexes.

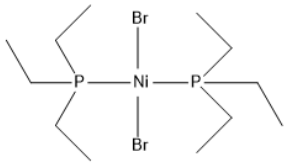
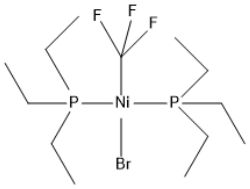
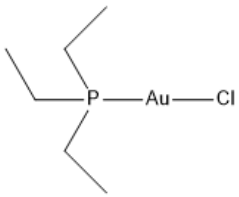
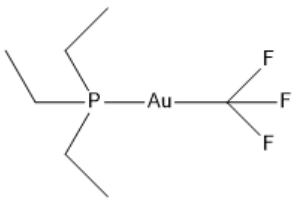
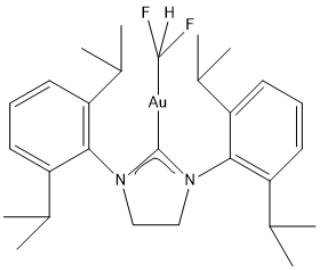
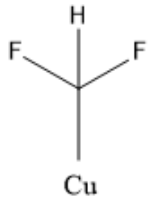
In addition, Wilkinson and Parshall reported examples of organometallic fluorine compounds in the 1960s by using perfluorinated alkenes and dienes.[48] Research related to M-R^F complexes slowed after this early rush of publications most likely due to the obvious stability and unreactive nature of these complexes compared to non-fluorinated metal-alkyls, which profited from the activation of α/β-C–H bond activation, reactivity of the M–C bond, and useful catalytic transformations like polymerization and cross-coupling that did not appear to occur with M–R^F examples. Fluorine and fluorinated ligands show noticeable bonding effects because of the coexistence of an important inductive electron withdrawing effect coupled with π-donation of electron density back to its neighbors. The evident difference in reactivity between fluorinated and non-fluorinated alkyl ligands is reflected in their bond dissociation energies (BDEs).[49,50]

1.3.2. M-R^F bonds with early metals and late metals

For early metals, (Ti) electrostatic interactions appear to be leading for the unusual lengthened M-C bond because of highly electropositive CF_3 carbon and repulsion of the electropositive metal. In opposition, more negative carbon (-0.96 for CH_3 vs. +0.79 for CF_3) of Ti–CH_3 makes this bond shorter.[51] On the other hand, late metals such as Ni, Cu and Pd have multiple interactions that lead to dramatically shortened M-C bonds for M-CF_3 when compared to their M-CH_3 counterparts. Middle to late metal M–R^F bonds are shortened because of the presence of strong F-C π-backbonding into p-orbitals on carbon. The other thing is that unlike typical CR_3 ligands, CR^F_3 ligands can participate in retro-dative bonding with the parent metal and this interaction increases from left to right across the same period[52] .

1.3.3. Transmetalation Reactions of M-CF_3 compounds

M-CF_3 compounds are commonly used synthons for the preparation of transition metal CF_3 complexes. In the earliest studied compounds, researchers used fluoroalkyls of Zn, Hg and Cd to synthesis various organometallic complexes, although the use of Hg and Cd has continued to wane because of their associated toxicity.[53-64] **Scheme 1.6** shows transmetalation strategies for the synthesis of M-R^F complexes reported by Morrison et al. (1981 and 1989) and Shen et al. (2015). In the earliest research, the focus was on the use of Ag, Zn and Mg to synthesize new M-R^F complexes. The use of $(DMPU)_2Zn(CF_2H)_2$ in the presence of either Cu or Ni, for the preparation of Ar-CF_2H compounds was recently reported by Mikami et al. and Vicic et al.[65-77]

Morrison et al. 1981 Yield: 67%		$Cd(CF_3)_2$. glyme CH_2Cl_2	
Morrison et al. 1989 Yield: 65%		$Cd(CF_3)_2$. glyme CH_2Cl_2	
Shen et al. 2015		CuI MeCN	

Scheme 1.6: Transmetalation strategies for the synthesis of M-R^F.

1.3.4. C–F bond activation, a synthetic way to fluorinated organic molecules

Novel synthetic ways to fluorinated organic molecules can be provided by C–F bond activation of fluorinated ligands facilitated by transition metals.[68,69,70] For the first time, Reger and Dukes

reported the weakening of the Cα –F bond using a strong Lewis acid (SbF5) for the synthesis of a metal difluorocarbene from a d^4 Mo–CF_3 complex. The reactivity of Mo–CF_3 can be explained by having a longer Cα–F bond distance than the average sp^3 carbon–fluorine bond.[71.] Selective activation of the Cα–F bond was further demonstrated on a longer fluoroalkyl chain complex and also for perfluorometallacyclopropane complexes.

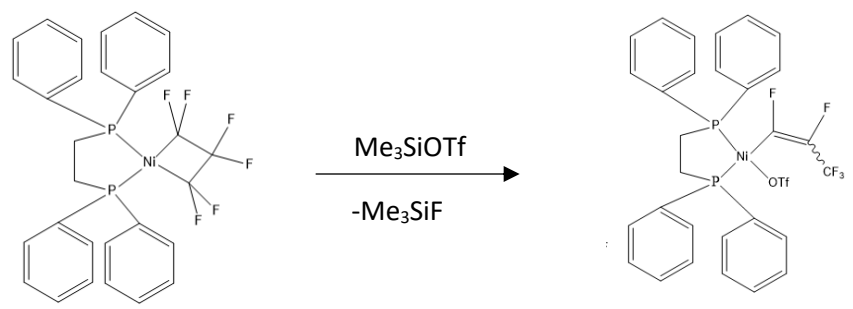
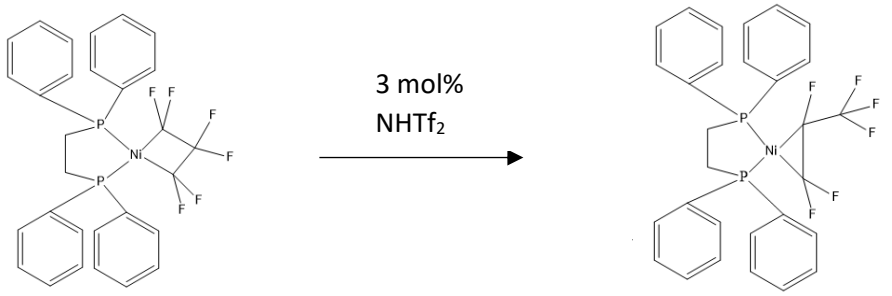
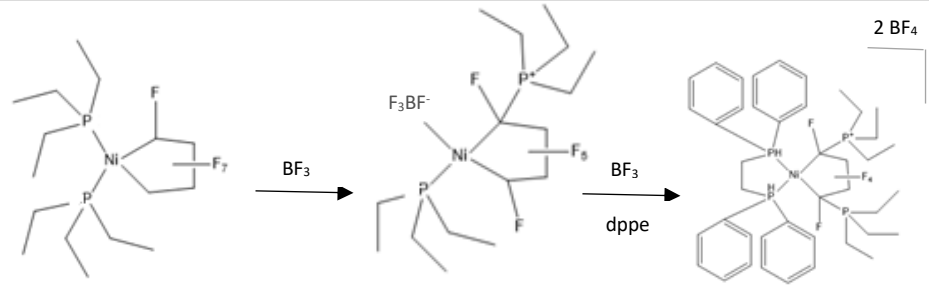
1.3.5. Some important C–F bond activation reactions

Following pioneering work by Burch et al.[73], Baker's group reported fluoride abstraction reactions from both metallacyclopentanes[74] and -butanes.[75]. For the latter fluoride abstraction occurred at the β-position when CpCo(C_3F_6)((PPh_2Me) was treated with stoichiometric Me_3SiOTf or a catalytic amount of $HNTf_2$, yielding the *trans*-vinyl and isomerization/ring contraction metallacyclopropane. Similar results were later published with the Ni(C_3F_6)(dppe) complex[76] (**Scheme 1.7).**

Burch and coworkers reported Cα–F bond activation of Ni$(CF_2)_4(PEt_3)_2$ by treatment with 1 equivalent of BF_3. They showed that phosphine ligand migration to the 'carbene' carbon generates a phosphine-functionalized metallacycle. Furthermore, addition of a second equivalent of BF_3 yielded a second Cα–F activation and dppe was used to displace the weakly coordinating tetrafluoroborate ligands (**Scheme 1.7**).[73]

1.3.6 Nickel in Organometallic Chemistry

Nickel plays an important role in organometallic chemistry. Nickel has 10 d-electrons in a neutral Ni(0) species and can exist in several oxidation states. Ni(0)[77] and Ni(II)[78] are the most common oxidation states , but Ni(I), Ni(III) and Ni(IV)[79] have also been reported.[80,81,82] **Scheme1.8** shows examples of nickel complexes in a variety of coordination geometries and oxidation states. Reactions using nickel frequently proceed through either a 16 or 18 electron species. For example, the oxidative addition of a substrate to a 14 electron Ni(0) complex (like the 14-electron bis-NHC nickel(0) complex [Ni(Mes2Im)2]) forms a stable 16 electron square planar Ni(II) complex, which is well suited for subsequent reductive elimination.

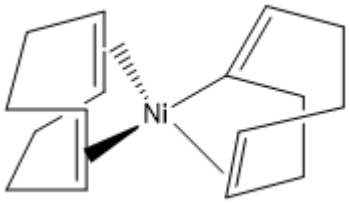
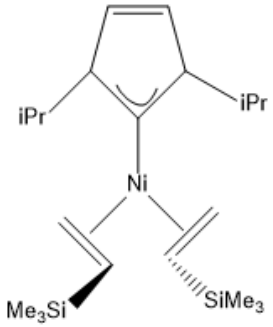
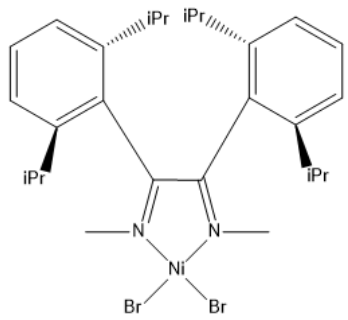
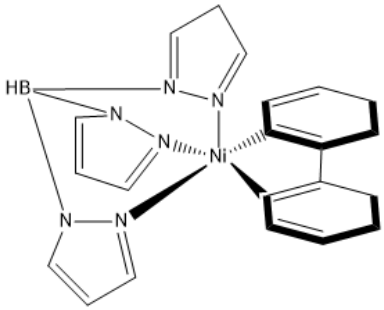
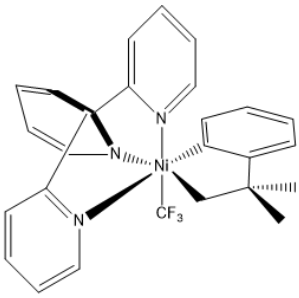
Cβ–F bond activation in Ni(C_3F_6)(dppe) using a Lewis acid	
Cβ–F bond activation in Ni(C_3F_6)(dppe) using a Bronsted acid	
Cα–F abstraction in a bis(phosphine) nickel perfluorocyclopentane.	

Scheme 1.7: C–F bond activation reactions in nickel perfluorometallacycles.

1.3.7 Using Cu(I) for fluoroalkylation

In 1965[83] Cu(I)–CF_3 intermediates were invoked in the stoichiometric trifluoromethylation of aryl iodides by McLoughlin and then followed up in a literature reaction in 1969[84]**.** Many prominent researchers have expanded this important and useful reaction since that time[85]. In 2008, Vicic[86] presented the first crystallographically characterized NHC-supported Cu(I)–CF_3 trifluoromethylating reagent and a year after that, in 2009**,** Amii[87] reported the first copper-catalyzed aryl trifluoromethylation by using trifluoromethyl trimethylsilane (TMS-CF_3), known as Ruppert's or Ruppert-Prakash reagent. Additionally, reductive elimination from a Pd(II) center is the first example of a stoichiometric, selective coupling reaction that was reported by Grushin. He also reported the important methodology, that could be used with a wide variety of linear fluoroalkanes, by using 2 equivalents of KOtBu with 1 equivalent of CuCl to generate

K(DMF)[Cu(OtBu)$_2$] as the base in the reaction media[88] (**Scheme 1.9**). Another reaction by the same author used the same procedure for the synthesis of Cu-CF_2CF_3 from HCF_2CF_3. Of all the fluoroalkanes tested, only fluoroform and pentafluoropropane gave the desired Cu complexes.[8]

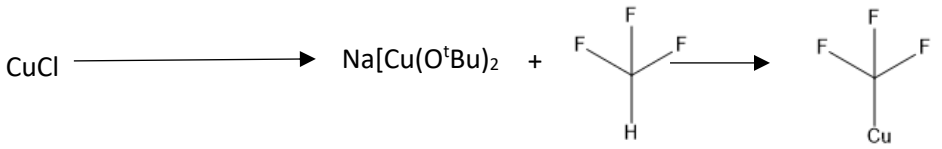
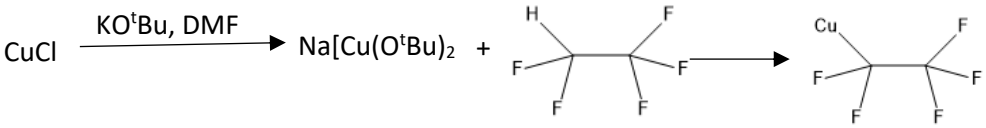
Ni(0) Tetrahedral	**Ni(0) Trigonal planar**
	
Ni(II) Square planar	**Ni(III) Square pyramidal**
	
Ni(IV) Octahedral	
	

Scheme 1.8. Isolable nickel complexes in different oxidation states and geometries

1.4 Fluoroolefins

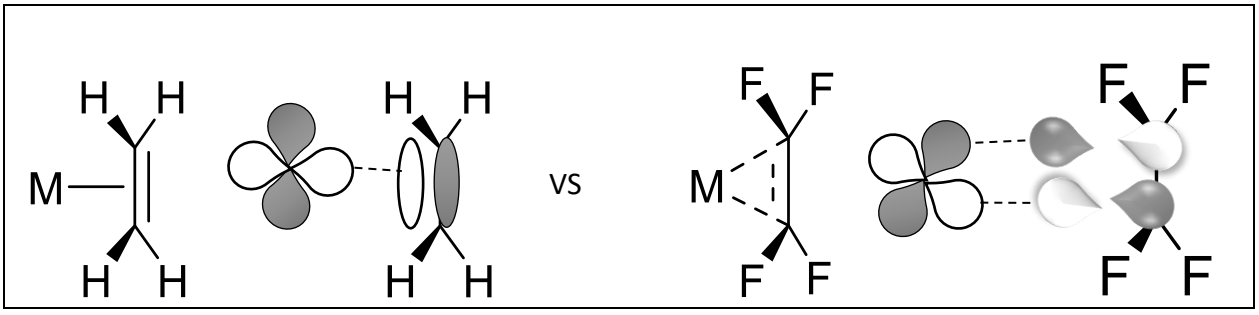
1.4.1. Fluoroolefin compounds' properties and history

Fluoroolefin compounds include at least one vinylic C–F bond and the high electronegativity of fluorine influences the electron density within the π-bond. The coordination chemistry of fluoroolefins is almost exclusively studied on metals of group 7 or later because their metals are better at π-backbonding. There are more examples of the coordination chemistry of tetrafluoroethylene (TFE) compared to other hydrofluoroolefins, likely due to limited availability of the latter.

Grushin et al. 2011	
Grushin et al. 2013	

Scheme 1.9: Metalation of hydrofluoroalkanes.

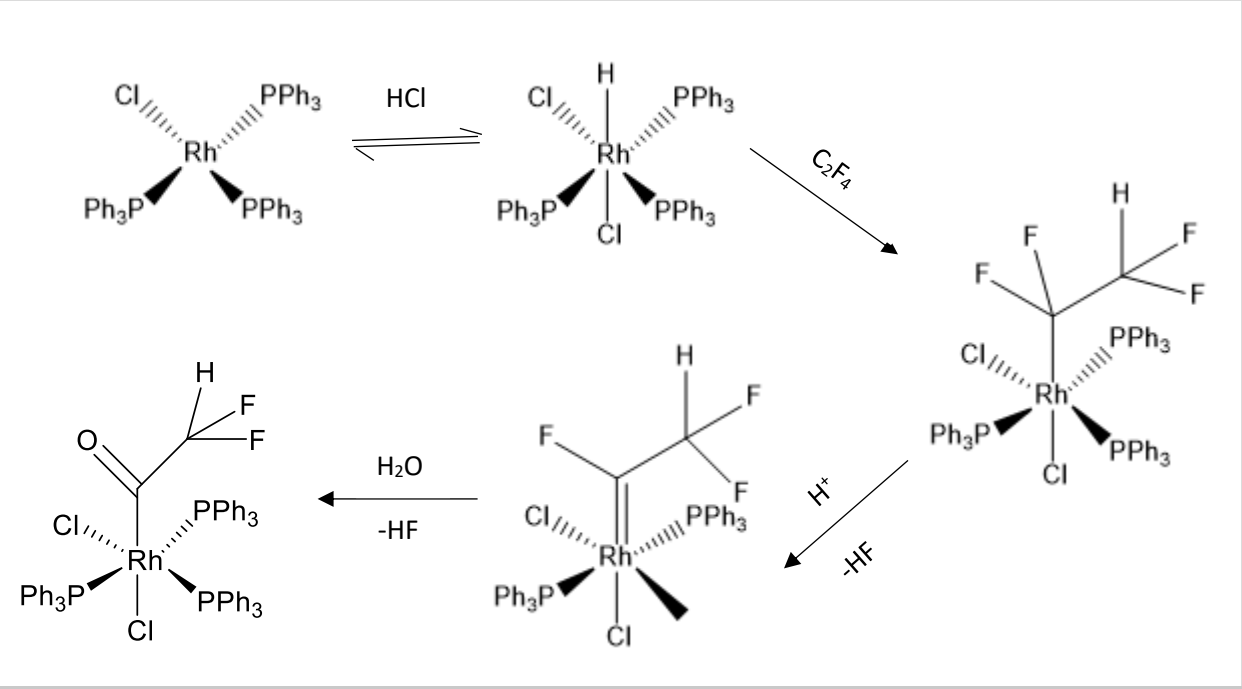
Much of the early work in this field was pioneered by Wilkinson[90] on iron and Stone[91] on nickel. Because of the high reducing power, these late metals were able to form perfluorinated metallacyclopentanes for the first time by reducing tetrafluoroethylene. Jones and coworkers prepared simple fluoroolefin adducts as early as 1965 working with monovalent rhodium and iridium[92]. **Scheme 1.10** compares the coordination chemistry of ethylene vs TFE with the latter dominated by π-back-bonding from a filled metal d orbital to the alkene π* orbital.[93]



Scheme 1.10: Coordination chemistry of TFE vs ethylene.

1.4.2 Insertion of TFE into an in-situ generated metal-hydride

For the first time, in 1967[94], Wilkinson proposed that the simple adduct of metals with fluoroolefins can be described as π-Lewis acid/base pairs in their simplest form **(Scheme 1.11).** While it was possible to get a π-adduct with TFE from Wilkinson's complex in the absence of acid, the 2H-tetrafluoroethyl fragment was found in the presence of HCl. The resulting complex was unstable in the presence of excess acid due to protonation of the C-F bond.

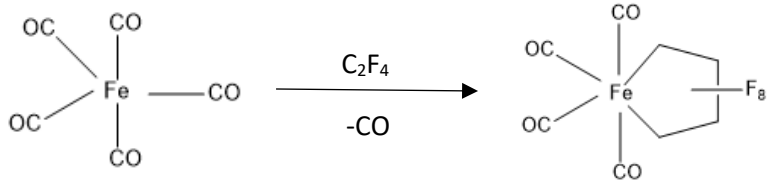
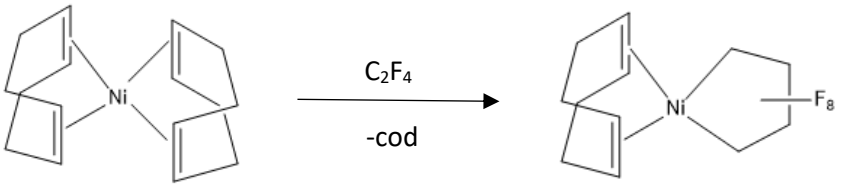
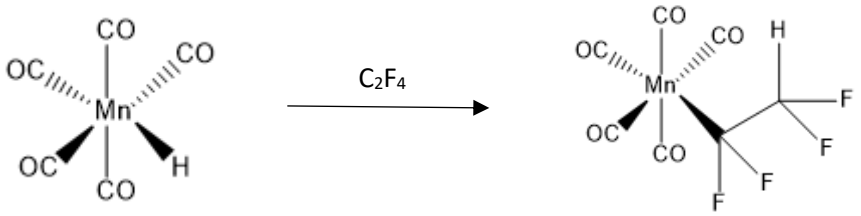
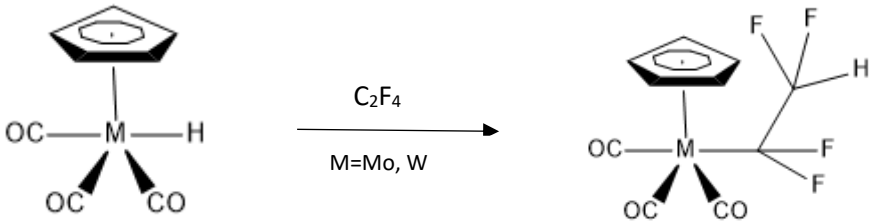
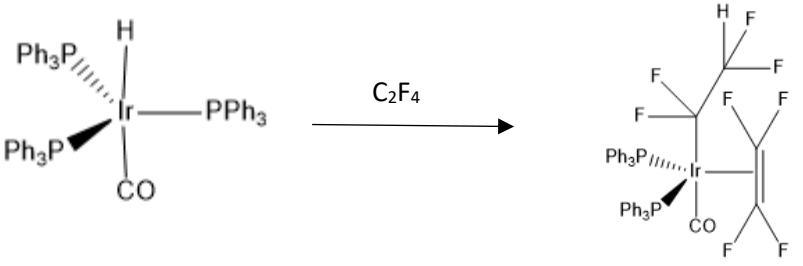
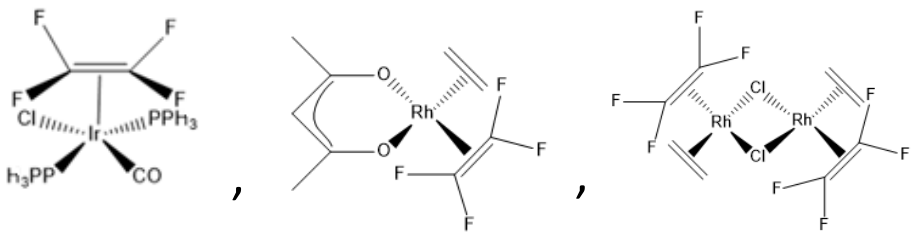


Scheme 1.11: Insertion of TFE into an *in-situ* generated Rh(III) hydride, C-F bond protonolysis, and hydrolysis.

1.4.3 Fluoroolefin insertion into reactive metal-hydride bonds

In 1961, Stone[95,96] reported the insertion of TFE into the reactive metal hydride bond in $MnH(CO)_5$. Fluoroolefins are susceptible to nucleophilic attack due to their electrophilic nature.[97] This reaction was followed by other examples like the rhenium analog, and cyclopentadienyl molybdenum and tungsten tricarbonyl hydrides. TFE can also insert into a metal–metal bond; for example, dicobalt octacarbonyl reacts with TFE to yield the ethanediyl-bridged complex, $(CO)_4Co(\mu\text{-}\eta^2\text{-}C_2F_4)Co(CO)_4$[98] (**Scheme 1.12**). For non- fluorinated olefins, the fluoroalkyl forms a

stable covalent bond and does not insert again, as was also demonstrated later by Roper on monovalent iridium.[99]

First report of d^6 perfluorometallacycle **Wilkinson 1959**	
First report of d^8 perfluorometallacycle **Stone 1970**	
Insertion of TFE into metal hydrides **Stone 1961**	
Insertion of TFE into metal hydrides **Stone 1963**	
Insertions of TFE into metal hydrides. **Roper 1990**	
TFE adducts of group 9 metals **Jones 1965**	

Scheme 1.12: Some fluoroolefin reactions with metal complexes.

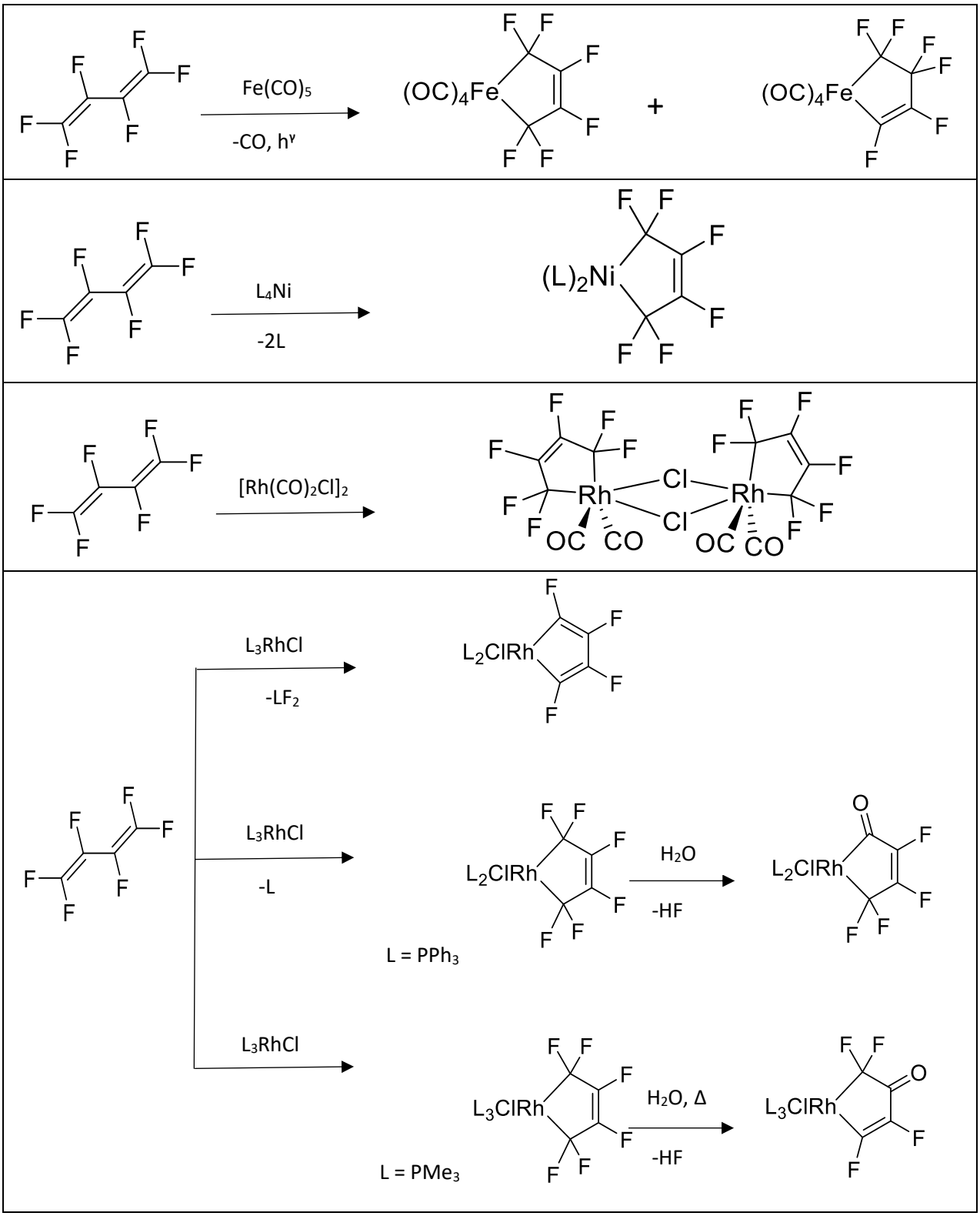
1.5. Fluorinated Dienes

1.5.1. Fluorinated dienes in transition-metal chemistry

A recent review by Lentz and Moritz outlines the structure, synthesis, and reactivity of transition-metal complexes derived from fluorinated dienes. The inability of coordination catalysts to induce polymerization or metathesis of fluoroalkenes was already published in the late 1950s.[100,101] Recently, increasing interest in activating the unreactive C-F bond by transition-metal catalysis has resulted in a renaissance of fluoro-organometallic chemistry and catalysis.[102,103]

1.5.2. Perfluorobutadiene

Early work states that "rather air-sensitive products are formed from perfluorobutadiene with iron and cobalt carbonyls", but no details were given.[104] Scheme 1.13 shows that iron, nickel, and rhodium complexes react with perfluorobutadiene to form metallacyclopentenes. One of these products available either thermally from $Fe_3(CO)_{12}$ or photochemically from $Fe(CO)_5$ was later identified as $Fe(\eta^1,\eta^1\text{-}C_4F_6)(CO)_4$ based on spectroscopic and microanalytical data.[105] This complex is thermally stable and sublimes with no tendency to lose carbon monoxide. Small amounts of an isomeric side product were detected by spectroscopic means. Similar structures were allocated to the nickelacyclopentenes synthesized from isocyanide complexes and a diarsine by ligand substitution[106,107]. Reacting perfluorobutadiene with $[Rh(CO)_2Cl]_2$ afforded a dimeric product proposed to include planar metallacycles as shown in **Scheme 1.13**. The authors reported, however, that the diene is released by addition of external ligands like PPh_3 or pyridine[108] and the extra fluorenes react with the free ligands. In another report, the product from $RhCl(PPh_3)_3$ as assigned an apparent stoichiometry of $RhCl(C_4F_4)(PPh_3)_2$. Hughes disproved this expectation 25 years later by showing that the reported data fit more accurately with the hydrolysis product.[109] A more stable isomer was isolated and characterized using PMe_3.

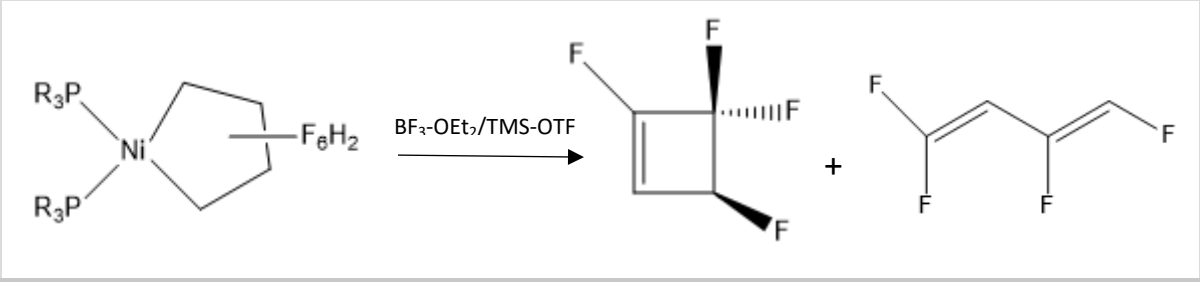


Scheme 1.13. Iron, nickel, and rhodium complexes of perfluorobutadiene forming metallacyclopentenes.

1.6. Fluorometallacycle Reactivity and Functionalization

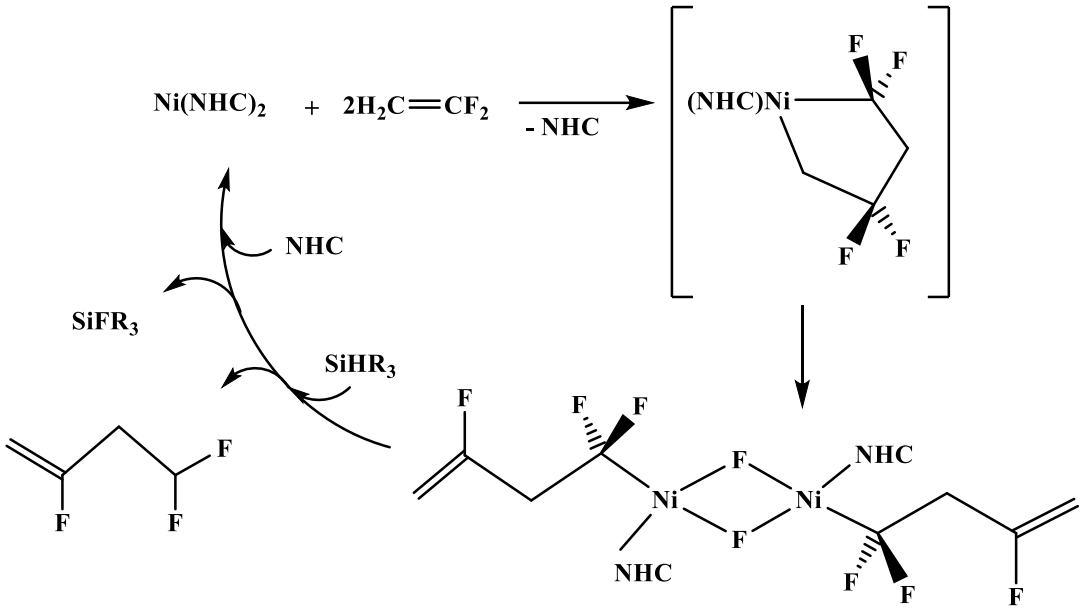
1.6.1 Reactivity of substituted fluorometallacycles

A variety of fluorometallacycles have been studied extensively by the Baker and Ogoshi labs over the last decade. **Scheme 1.14** shows that inclusion of hydrogen substituents (derived from trifluoroethylene, CH_2=CHF) alters the metallacycle's reactivity with Lewis acids. Reactions of the head-to-tail hydrofluoronickelacycles with BF_3•OEt_2 results in a double fluoride activation**,** to give 1,1,2,3-tetrafluorocyclobutene as the major organic product with a minor amount of (Z,E)-1,1,3,4-tetrafluorobutadiene. When the analogous reaction was done with the Lewis acid TMS-OTf the opposite selectivity was observed, giving the butadiene as the major organic product (Tf = SO_2CF_3).



Scheme 1.14. Reactivity of trifluoroethylene-derived nickel metallacycles with Lewis acids.

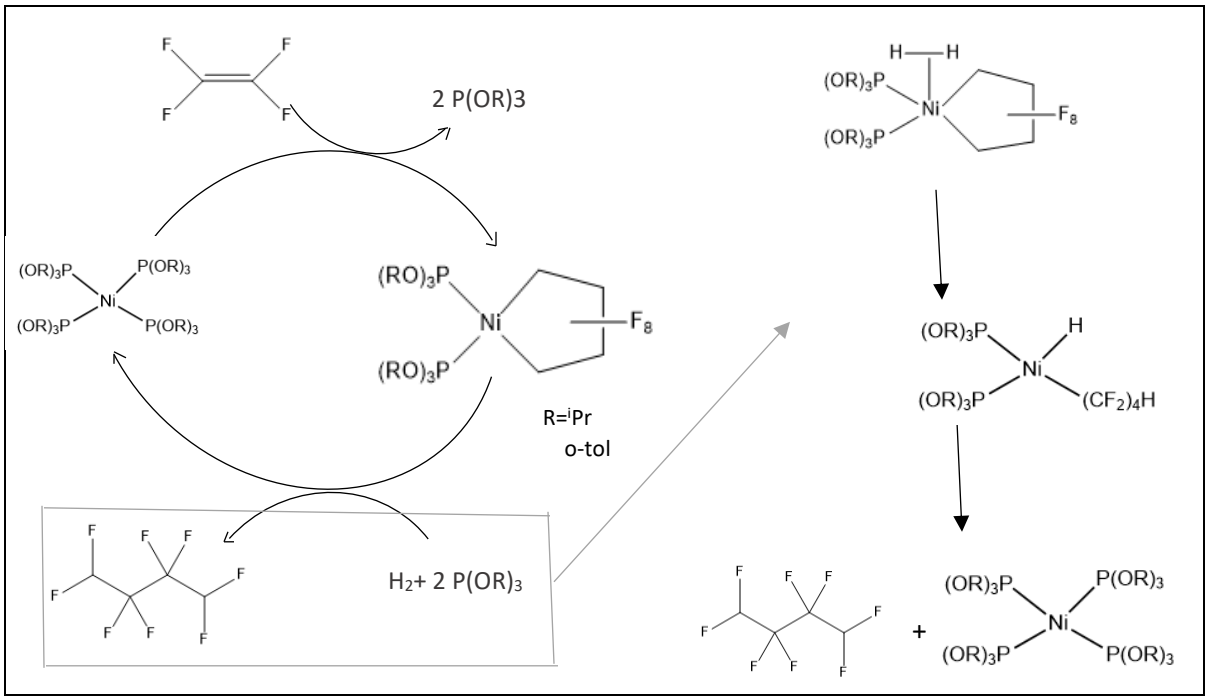
Another example of fluorometallacycle Cβ-F bond activation was discovered by Sicard[110] using the bulky NHC ligand 1,3-di(1-adamantyl)imidazolidene (IAd; **Scheme 1.15**). β-fluoride elimination from the metallacyclopentane intermediate gave the butenyl-nickel fluoride-bridged dimer. Addition of a silane converted Ni-F to Ni-H and subsequent reductive elimination yielded the new HFO in a catalytic hydrodefluorodimerization process.



Scheme 1.15. Reaction steps for Ni-NHC complex-catalyzed VDF hydrodefluorodimerization.[110]

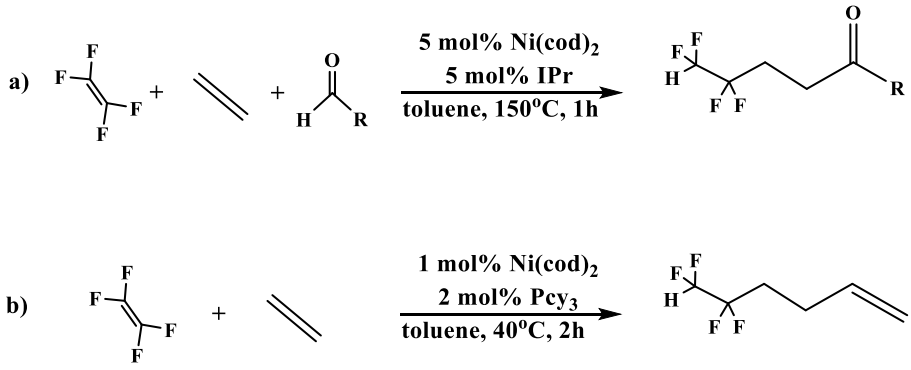
1.6.2 Fluoroalkene homologation

Baker et al. developed a catalytic method for the hydrodimerization of TFE using hydrogen gas[111] (**Scheme 1.16**). The metallacycle functionalization was proposed to proceed through a dihydrogen complex intermediate, followed by protonation of the α-carbon and formation of a nickel hydride. Finally reductive elimination gives the product HFC, regenerating zerovalent nickel. In a later study the same group showed that the low-coordinate NHC nickel metallacycle discussed above greatly increases the rate of Ni–C^F bond hydrogenolysis (7 psig and 25 °C vs. 700 psig and 100 °C).[112]



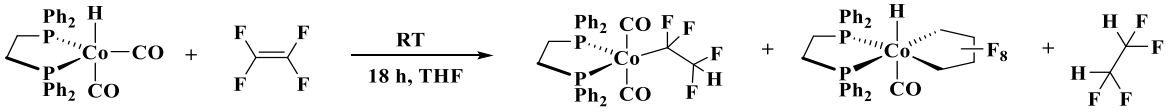
Scheme 1.16. Catalytic hydrodimerization of tetrafluoroethylene using [Ni].

Using catalytic $Ni(cod)_2$ and the bulky NHC ligand IPr, the Ogoshi group achieved a cross-trimerization of aldehydes, ethylene and TFE (**Scheme 1.17a**).[113,114] The mixed ethylene/TFE metallacycle reacts with enones in to yield the cross-trimerization product. A similar reaction could be used in the ethylene/TFE co-trimerization to give 5,5,6,6-tetrafluoro-1-hexene (**Scheme 1.17b**).[115]



Scheme 1.17. Ni-catalyzed selective cross-trimerization reactions.[114,115]

Finally, a Baker group study of Co-H reactivity with TFE yielded the first examples of metal hydride perfluorometallacycles (**Scheme 1.18**).[116] The 18e- count of these complexes may prevent the usually facile C-H reductive elimination. These complicated reactions of P-ligated Co(I) carbonyl hydrides with TFE begin with loss of one CO ligand and insertion of TFE into the Co-H bond. The resulting Co-CF_2CF_2H complex can then lose CO, coordinate a second TFE, and rearrange to the Co-H metallacycle. In a competing reaction, the Co-CF_2CF_2H complex can react with the Co-H starting material to give hydrogenated TFE.



Scheme 1.18. Reaction of dppe Co carbonyl hydride with TFE.[116]

1.7. Scope of this Thesis

In Chapter 2 we prepare unsaturated metallacyclopentenes from low valent Ni precursors and perfluorobutadiene and then compare their reactivity with the known saturated analogs. In Chapter 3 we build on previous work on Co carbonyl hydride reactions with TFE. Here we investigate reactions of cobalt hydrides containing phosphine and phosphite ligands with several fluoroalkenes with the aim of accessing additional coordination sites through ligand dissociation. This could then allow for β-F elimination and a new fluoroalkene functionalization reaction. Chapter 4 presents our conclusions and future outlook.

1.8. References

1. Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36* (4), 255–263.

2. Fujiwara, T.; O'Hagan, David. *J. Fluorine Chem*. **2014**, *167*, 16-29.

3. Böhm, H.-J.; Banner, D.; Bendels, S.; Kansy, M.; Kuhn, B.; Müller, K.; Obst-Sander, U.; Stahl, M. *ChemBioChem* **2004**, *5*, 637–643.

4. Hagmann, W. K. *J. Med. Chem*. **2008**, *51*, 4359–4369.

5. Lemal, D. M. *J. Org. Chem*. **2004**, *69*, 1–11.

6. Hughes, R. P. *Adv. Organomet. Chem*. **1990**, *31*, 183.

7. D. O'Hagan, D. B. Harper. *J. Fluorine Chem*., **1999**, *100*, 127.)

8. (a) Aigueperse, J.; Mollard, P.; Devilliers, D.; Chemla, M.; Faron, R.; Romano, R.; Cuer, J. P. In *Ullmann's Encyclopedia of Industrial Chemistry*, John Wiley & Sons, Inc., 2000. (b) Harsanyi, A.; Sandford, G. *Green Chem*. **2015**, *17*, 2081–2086.

9. (a) Stavber, S. *Molecules* **2011**, *16*, 6432-6464. (b) Liu, X.; Xu, C.; Wang, M.; Liu, Q. *Chem. Rev.* **2015**, *115*, 683-730.

10. Swarts, F. *Bull. Acad. Belg.* **1892**, *24*, 456.

11. Booth, H. S.; Mong, W. L.; Burchfield, P. E. *Ind. Eng. Chem*., **1932**, *24*, 328.

12. Rây, P. C. *Nature*, **1933**, *132*, 173.

13. Bigelow, L. A.; Pearson, J. H. *J. Am. Chem. Soc.,* **1934**, *56*, 2773.

14. Henne, A. L.; Hubbard, D. M. *J. Am. Chem. Soc.,* **1936**, *58*, 404.

15. Henne, A. L.; Renoll, M. W. *J. Am. Chem. Soc.,* **1938**, *60*, 1060.

16. Henne, A. L.; Ladd, E. C. *J. Am. Chem. Soc.,* **1938**, *60*, 2491.

17. Simons, J. H.; Francis, H. T.; Hogg, J. A. *J. Electrochem. Soc.,* **1949**, *95*, 53.

18. Tewksbury, C. I.; Haendler, H. M. *J. Am. Chem. Soc*., **1949**, *71*, 2336.

19. Musgrave, W. K. R.; Smith, F. *J. Chem. Soc.*, **1949**, 3021.

20. Musgrave, W. K. R.; Smith, *J. Chem. Soc.,* **1949**, 3026.

21. Haszeldine, R. N.; Smith, F. *J. Chem. Soc*., **1950**, 3617.

22. Miller, W. T.; Koch, S. D. *J. Am. Chem. Soc.,* **1957**, *79*, 3084.

23. Fuller, G.; Stacey, M.; Tatlow, J. C.; Thomas, C. R. *Tetrahedron,* **1962**, *18*, 123.

24. Burford III, W. B.; Fowler, R. D.; Hamilton Jr., H. C.; Anderson, C. E.; Weber, C. E.; Sweet, R. G. *Ind. Eng. Chem.* **1947**, *39*, 319-329.

25. O'Hagan, D. *J. Fluorine Chem*. **2010**, *131*, 1071–1081.

26. Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, *H. Chem. Rev*. **2014**, *114*, 2432–2506.

27. (a) Kim, C. U.; Lee, J. M.; Ihm, S. K. *J. Fluorine Chem.* **1999**, *96*, 11. (b) Kim, C. U.; Lee, J. M.; Ihm, S. K. *J. Appl. Polym. Sci*.**1999**, *73*, 777-793.

28. Emani, M. S.; Roy, R.; Mandal, B. K. *Indian J. Sci. Res*. **2017**, *14*, 175-181.

29. Dolbier Jr., W. R. *J. Fluorine Chem.* **2005**, *126*, 157-163.

30. Siqing, W. *Chem. Prod. Tech*. **2010**, *5*, 005.

31. Singh, R. R.; Pham, H. T.; Wilson, D. P.; Thomas, R. H.; Shankland, I. *U.S. Patent* 7,534,366, **2009**.

32. 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.

33. Pinnock, S.; Hurley, M. D.; Shine, K. P.; Wallington, T. J.; Smyth, T. J. *J. Geophys. Res. Atmos*. **1995**, *100*, 23227-23238.

34. Yang, L.; da Rocha, S. R. *J. Phys. Chem. B*. **2014**, *118*, 10675-10687.

35. Midgley, T.; Henne, A. L. *Ind. Eng. Chem*. **1930**, *22*, 542.

36. Wang, Z. Reagents, Swarts reaction in *Comprehensive Organic Name Reactions and Reagents*, John Wiley and Sons, New York; **2010**.

37. Furin, G. G. *Adv. Heterocyclic Chem.,* Katritzky, A. R., Ed. **2006**, *90*, 239.

38. Lagow, R; Margrave, J. *Prog. Inorg. Chem.* **1979**, *26*, 161-210.

39. Hutchinson, J.; Sandford, G. *Top. Curr. Chem*. **1997,** *193*, 1–43.

40. Sandford, G. *J. Fluorine Chem*. **2007**, *128*, 90–104.

41. Ritter,S. K. *Chem. Eng. News*, **2010**, *88*, 12–17.

42. Renfre, M. M.; Lewis, E. E. *Ind. Eng. Chem.,* **1946**, *38*, 870.

43. McClellan, W. R. *J. Am. Chem. Soc*. **1961**, *83*, 1598–1600.

44. Kaesz, H. D.; King, R. B.; Stone, F. G. A. Z. *Naturforsch*. **1960**, *15*, 763–764.

45. Coffield, T. H.; Kozikowski, J.; Closson, R.D. Abstr. I.C.C.C. Conference, vol. Special Publication No. 13, *The Chemical Society, London*, **1959**, p. 126.

46. Hieber, W.; Beck, W.; Lindner, E. *Z. Naturforsch. B*, **1961**, *16b*, 229–231.

47. Bennett, M. A.; Chee, H.; Robertson, G. B. *Inorg. Chem*. **1979**, *18*, 1061.

48. (a) Hoehn, H. H.; Pratt, L.; Watterson, K. F.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2738–2745. (b) Parshall, G. W.; Wilkinson, G. *J. Chem. Soc.* **1962**, 1132.

49. Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc*. **1990**, *112*, 2057-2066.

50. (a) Lumsden, S. E. A.; Durgaprasad, G.; Muthiah, K. A. T.; Rose, M. J. *Dalton Trans*. **2014**, *43*, 10725–10738. (b) Welch, K. D.; Dougherty, W. G.; Kassel, W. S.; Dubois, D. L.; Bullock, R. M. *Organometallics*, **2010**, *29*, 4532–4540. (c) Van Putten, R.; Uslamin, E. A.; Garbe, M.; Liu, C.; Gonzalez-de-Castro, A.; Lutz, M.; Junge, K.; Hensen, E. J. M.; Beller, M.; Lefort, L.; Pidko, E. A. *Angew. Chem. Int. Ed.* **2017**, *56*, 7531–7534.

51. Hall M. B.; Fenske, R. F. *Inorg. Chem*. **1972**, *11*, 768.

52. (a) Goodman, J.; Grushin, V. V.; Larichev, R. B.; Macgregor, S.A.; Marshall, W. J.; Roe, D. C. *J. Am. Chem. Soc.* **2009**, *131*, 4236. (b) Goodman, J.; Grushin, V. V.; Larichev, R. B.; Macgregor, S. A.; Marshall, W. J.; Roe, D. C. *J. Am. Chem. Soc*. **2010**, *132*, 12013.

53. Treichel, P. M.; Stone, F. G. A. *Adv. Organomet. Chem.,* **1964**, *1*, 143.

54. Morrison, J. A.; Gerchman, L. L.; Eujen, R.; Lagow, R. J. *J. Fluorine Chem.*, **1977**, *10*, 333.

55. Lagow, R. J.; Morrison, J. A. *Adv. Inorg. Chem. Radiochem*. **1983**, *27*, 293.

56. Krause, L. J.; Morrison, J. A. *Inorg. Chem*. **1980**, *19*, 604.

57. Krause, L. J.; Morrison, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 2995.

58. Zissis, J.-P.; Moreau, P.; Commeyras, A. *J. Fluorine Chem*. **1981**, *19*, 71.

59. Nair, H. K.; Morrison, J. A. *J. Organomet. Chem*. **1989**, *376*, 149.

60. Ontiveros, C. D.; Morrison, J. A.; Hani, R.; Geanangel, R. A. *Inorg. Synth.* **1986**, *24*, 55-58.

61. Tyrra, W. E.; Naumann, D. *J. Fluorine. Chem*. **2004**, *125*, 823.

62. Naumann, D.; Roy, T.; Caeners, B.; Hütten, D.; Tebbe, K.-F.; Gilles, T. Z. Anorg. *Allg. Chem*. **2000**, *626*, 999.

63. Naumann, D.; Wessel, W.; Hahn, J.; Tyrra, W. *J. Organomet. Chem.* **1997**, *547*, 79.

64. Loizou, D. C.; Castillo, J.; Oki, A. R.; Hosmane, N. S.; Morrison, J. A. *Organometallics* **1992**, *11*, 4189.

65. Aikawa, K.; Nakamura, Y.; Yokota, Y.; Toya, W. Mikami, K. *Chem. Eur. J*. **2015**, *21*, 96.

66. Serizawa, H.; Ishii, K.; Aikawa, K.; Mikami, K. *Org. Lett*. **2016**, *18*, 3686.

67. Xu, L.; Vicic, D. *J. Am. Chem. Soc*. **2016**, *138*, 2536.

68. Campbell, M. G.; Hoover, A. J.; Ritter, T. *Top. Organomet. Chem.* **2015,** *52,* 1.

69. LaBerge, N. A.; Love, J. A. *Top. Organomet. Chem.* **2015,** *52,* 55.

70. Ohashi, M.; Ogoshi, S. *Top. Organomet. Chem.* **2015,** *52,* 197.

71. Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153* (1), 67–72.

73. Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7* (7), 1642–1648.

74. Giffin, K. A.; Korobkov, I.; Baker, R. T. *Dalton Trans*. **2015**, *44* (45), 19587–19596.

75. Harrison, D. J.; Lee, G. M.; Leclerc, M. C.; Korobkov, I.; Baker, R. T. *J. Am. Chem. Soc*. **2013**, *135* (49), 18296–18299.

76. Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics* **2015**, *34* (24), 5683–5686.

77. Elsby, M. R.; Johnson, S. A. *J. Am. Chem. Soc*. **2017**, *139*, 9401-9407.

78. Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169-1204.

79. Camasso, N. M.; Sanford, M. S. *Science* **2015**, *347*, 1218-1220.

80. Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299.

81. Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc*. **2009**, *131*, 16573-16579.

82. Schultz, J. W.; Fuchigami, K.; Zheng, B.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2016**, *138*, 12928-12934.

83. McLoughlin, V. C. R.; Thrower, J. *U.S. Patent* 3,408,411, **1968**.

84. McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *25*, 5921.

85. Selected Reviews: (a) Burton, D. J.; Lu, L. *Top. Curr. Chem.* **1997**, *193*, 45. (b) McClinton, M. A.; McClinton, D. A. *Tetrahedron* **1992**, *32*, 6555. (c) Burton, D. J.; Yang, Z. Y. *Tetrahedron* **1992**, *48*, 189.

86. (a) Dubinina, G. G.; Furutachi, H.; Vicic, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 8600. (b) Dubinina, G. G.; Ogikubo, J.; Vicic, D. A. *Organometallics* **2008**, *27*, 6233.

87. Oishi, M.; Kondo, H.; Amii, *H. Chem. Commun*. **2009**, 1909.

88. Zanardi, A.; Novikov, M. A.; Martin, E.; Benet-Buchholz, J.; Grushin, V. V. *J. Am. Chem. Soc*., **2011**, *133*, 20901.

89. Lishchynskyi, A.; Grushin, V. V. *J. Am. Chem. Soc*., **2013**, *135*, 1258.

90. Watterson, K. F.; Wilkinson, G. *Chem. Ind.* **1959**, 991.

91. Cundy, C. S.; Green, M.; Stone, F. G. A.; *J. Chem. Soc. A.* **1970**, 1647-1653.

92. Parshall, G. W.; Jones, N.; *J. Am. Chem. Soc*. **1965**, *87*, 5356.

93. Sicard, A. uOttawa MSc thesis, **2016**.

94. Baird, M. C.; Mague, J. T.; Wilkinson, G. *J. Chem. Soc. A*. **1967**, 1347-1360

95. Manuel, T. A.; Stafford, S. L.; Stone, F. G. A.*; J. Am. Chem. Soc.* **1961**, *104* (2), 2–3.

96. King, R. B.; Treichel, P. M.; Stone, F. G. A.; *Proc. Chem. Soc*. **1961**, 69.

97. Treichel, P. M.; Pitcher, E.; Stone, F. G. A.; Pitcher, E. *Inorg. Chem*. **1962**, *1* (3), 511– 517.

98. Beveridge, A. D.; Clark, H. C. *J. Organomet. Chem*. **1967**, *11*, 601.

99. Burrell, A. K.; Roper, W. R. *Organometallics* **1990**, *9*(6), 1905-1910.

100. For fluoropolymers see: (a) Ameduri, B.; Boutevin, B. *Well Architectured Fluoropolymers: Synthesis, Properties and Applications*, Elsevier, Amsterdam, **2004**; (b) Hougham, G.; Cassidy, P. E.; Johns, K.; Davidson, T. (Ed.), *Fluoropolymers 1: Synthesis,* Kluwer/Plenum, New York, **1999**.

101. For metathesis of fluorinated substrates see (a) Fomine, S.; Tlenkopatchev, M. A. *Appl. Catal. A* **2009**, *355*, 148; (b) Elsheikh, M. Y.; Bonnet, P. PCT *Int. Appl*., **2008**, 13pp; (c) Macnaughtan, M. L.; Johnson, M. J. A.; Kampf, J. W. *Organometallics* **2007**, *26*, 780; (d) Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem. Int. Ed*., **2001**, *40*, 3441.

102. For reviews on fluoro-organometallic chemistry see (a) Hughes, R. P. *Eur. J. Inorg. Chem*. **2009**, 4591; (b) Lentz*,* D. *J. Fluorine Chem*. **2004**, *125*, 853; (c) Stone, F. G. A. *J. Fluorine Chem*. **1999**, *100*, 227; (d) Hughes, R. P.; Curnow, O. J.; Zheng, X.; Mairs, E. N.; Rheingold, A. L. *ACS Symp. Ser*. **1994**, *555.*; (e) Stone*,* F. G. A. *Pure Appl. Chem*., **1972**, *30*, 551; (f) Bruce, M. I.; Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 747; (g) Rausch, M. D. *New York Acad. Sci*., **1966**, *28*, 611.

103. For recent work on C–F bond activation see (a) Teltewskoi, M.; Panetier, J. A.; Macgregor, S. A.; Braun, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 3947; (b) Kuhnel M. F.; Lentz, D. *Angew. Chem. Int. Ed.* **2010**, *49*, 2933; (c) Zheng, T.; Sun, H.; Chen, Y.; Li, X.; Durr, S.; Radius, U.; Harms, K. *Organometallics* **2009**, *28*, 5771; (d) Johnson, S. A.; Erin, E. T.; Cruise, S. J. *Organometallics* **2009**, *28*, 3842; (e) Doster M. E.; Johnson, S. A. *Angew. Chem, Int. Ed*. **2009**, *48*, 2185; (f) Braun, T.; Salomon, M. A.; Altenhoner, K.; Teltewskoi, M.; Hinze, S. *Angew. Chem. Int. Ed*. **2009**, *48*,

1818; (g) Wang, F.; Hu, J. *Chin. J. Chem.* **2009**, *27*, 93; (h) Fuchibe, K.; Kaneko, T.; Mori, K.; Akiyama, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 8070; (i) Nova, A.; Mas-Balleste, R.; Ujaque, G.; Gonzalez-Duarte, P.; Lledos, A. *Dalton Trans*. **2009**, 5980; (j) Gu, W.; Haneline, M. R.; Douvris, C.; Ozerov, O. V. *J. Am. Chem. Soc*. **2009**, *131*, 11203; (k) Reade, S. P.; Acton, A. L.; Mahon M. F.; Whittlesey, M. K. *Chem. Eur. J*. **2009**, *13*, 1774; (l) Deacon, G. B.; Forsyth, C. M.; Junk P. C.; Wang, J. *Chem. Eur. J.* **2009**, *15*, 3082; (m) Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc*. **2009**, *131*, 1847; (n) Adonin, N. Y.; Prikhod'ko, S. A.; Bardin V. V.; Parmon, V. N. *Mendeleev Commun*., **2009**, *19*, 260; (o) Meier, G. Braun, T. *Angew. Chem. Int. Ed*. **2009**, *48*, 1546; (p) Ali, M.; Liu, L.-P.; Hammond G. B.; Xu, B. *Tetrahedron Lett,* **2009**, *50*, 4078.

104. Hoehn, H. H.; Pratt, L.; Waterson, K. F.; and Wilkinson, G. *J. Chem. Soc*., **1961**, 2738 115.

105. Roundhill, D. M.; Lawson, D. N.; Wilkinson, G. *J. Chem. Soc. A*, **1968**, 845.

106. Browning, J.; Green, M.; Stone, F. G. A.; *J. Chem. Soc. A*, **1971**, 453.

107. Green, M.; Shakshooki, S. K.; Stone, F. G. A.; *J. Chem. Soc. A*, **1971**, 2828.

108. Roundhill, D. M.; Lawson, D. N.; Wilkinson, G.; *J. Chem. Soc*. A, **1968**, 845.

109. Hughes, R. P.; Rose, P. R.; Rheingold, A. L. *Organometallics,* **1993**, *12*, 3109.

110. Sicard, A. J. University of Ottawa PhD thesis, 2018.

111. Baker, R. T.; Beatty, R. P.; Farnham, W. B.; Wallace, R. D. *US patent,* 5,670,679, **1997**.

112. Andrella, N. O.; Sicard, A. J.; Gorelsky, S. I.; Korobkov, I.; Baker, R. T. *Chem. Sci*. **2015**, *6* (11), 6392–6397.

113. Ohashi, M.; Shirataki, H.; Kikushima, K.; Ogoshi, S. *J. Am. Chem. Soc.* **2015**, *137*, 6496-6499.

114. Ohashi, M.; Kawashima, T.; Taniguchi, T.; Kikushima, K.; Ogoshi, S. *Organometallics* **2015**, *34*, 1604-1607.

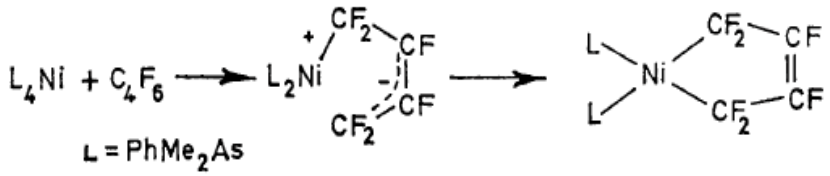
115. Kawashima, T.; Ohashi, M.; Ogoshi, S.; *J. Am. Chem. Soc.* **2017**, *139*, 17795-17798.

116. Ghostine, K., University of Ottawa MSc thesis, **2018.**

Chapter 2. Synthesis and Reactivity of Nickel Perfluorobutadiene Complexes

2.1 Introduction

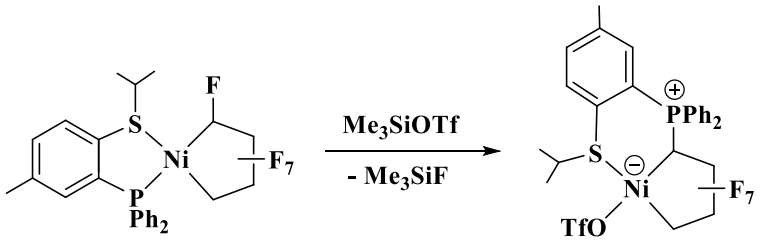
As noted in the introduction, Stone and co-workers showed that NiL_4 complexes react with perfluorobutadiene to give $L_2Ni(C_4F_6)$ metallacyclopentene complexes [L = $CNBu^t$, $AsMe_2Ph$ and L_2 = 1,2,-$(AsMe_2)$-C_6H_4].[1,2] Surprised that the diene interacts with nickel only in its cisoid form, they speculated that the reaction may proceed via a charged intermediate (**Scheme 2.1**). As the



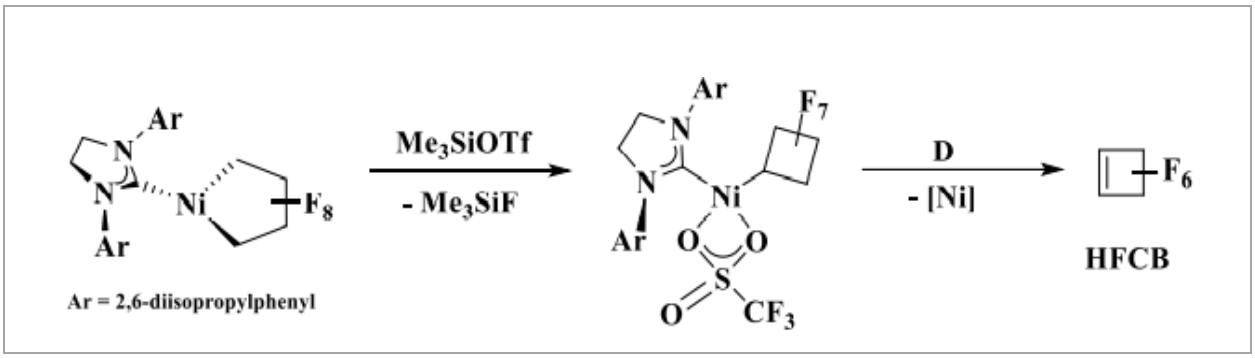
Scheme 2.1 Proposed reaction pathway for perfluorometallacyclopentene formation.

reactivity of such complexes has not been pursued in the 50 years since their report, we thought to prepare analogs with phosphite and phosphine complexes and investigate their reactivity with the Lewis acid Me_3SiOTf.

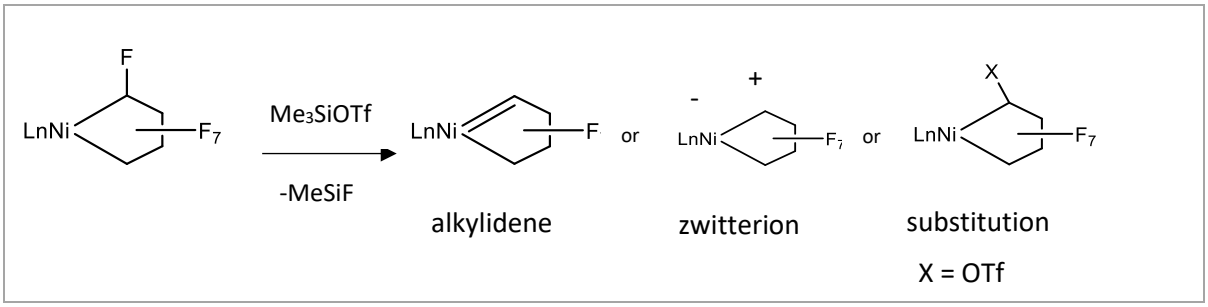
In previous work from Burch[3] and the Baker group,[4-7] fluoride abstraction from a C_α-F bond of Ni fluorometallacyclopentanes results in ligand migration (**Scheme 2.2**) or ring contraction (**Scheme 2.3**). When the latter reaction was conducted at low temperature, evidence was obtained for a C_α-OTf intermediate,[7] suggesting that the carbonium ion formulation is preferred over the originally proposed Ni carbene (**Scheme 2.4**).[3]



Scheme 2.2. Fluoride abstraction gives ligand migration to C_α.



Scheme 2.3. Fluoride abstraction reaction gives ring contraction.



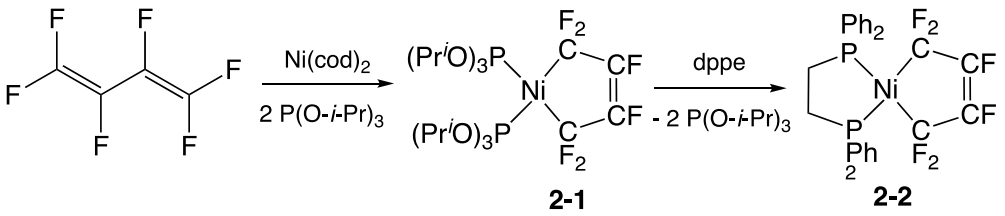
Scheme 2.4. Possible nickelacyclopentane with TMSOTf reaction intermediates.

In this chapter we prepare new Ni metallacyclopentene complexes with phosphite and bis(phosphine) ligands and investigate the reaction of the latter with TMSOTf (Trimethylsilyl trifluoromethanesulfana).

2.2. Results and Discussion

2.2.1 Preparation of Ni(C_4F_6)[P(O-*i*-Pr)$_3$]$_2$ (2-1)

Although we aim to prepare an electron-rich metallacyclopentene to investigate the fluoride abstraction reaction, electron-rich ligands will likely react with the fluorinated diene ligand so we first prepared the less electron-rich phosphite complex (**Scheme 2.5**). Reaction of a 1:2 solution of Ni(cod)$_2$ and P(O-*i*-Pr)$_3$ in benzene with excess hexafluoro-1,3-butadiene gave a yellow orange solution of Ni(1,4-C_4F_6)[P(O-*i*-Pr)$_3$]$_2$ (**2-1**). The ^{19}F NMR spectrum consisted of two resonances at -85.9 (tr mult, $^3J_{FP}$ = 43 Hz, 4F) and -148.9 ppm ('quint', $^3J_{FF}$ = 7.5 Hz, 2F) and the ^{31}P NMR showed a quintet of triplets resonance at 122.6 ppm ($^3J_{FP}$ = 43, $^4J_{FP}$ = 7 Hz) (**Figure 2.1**).



Scheme 2.5. Synthesis of nickelacyclopentene complexes **2-1** and **2-2.**

2.2.2 Preparation of Ni(C_4F_6)(dppe) (2-2)

As Lewis acids can also react with the P-O bond, we added the bis(phosphine) ligand dppe [1,2-bis(diphenylphosphino)ethane] to obtain the electron-rich metallacyclopentene. Reaction of **2.1** with one equiv of dppe proceeded slowly with release of 2 equiv of P(O-*i*-Pr)$_3$ and formation of Ni(1,4-C_4F_6)(dppe) (**2-2**). The ^{19}F NMR spectrum consisted of a triplet resonance at –85.1 ($^3J_{FP}$ = 32 Hz, 4F) for the Cα-Fs and a doublet of multiplets resonance at -146.3ppm for the Cβ-Fs ($^4J_{FP}$ = 11 Hz, 2F). The ^{31}P NMR showed a quintet of doublets resonance at 45.1 ppm ($^3J_{FP}$ = 32, $^4J_{FP}$ = 11 Hz) (**Figure 2.2**).

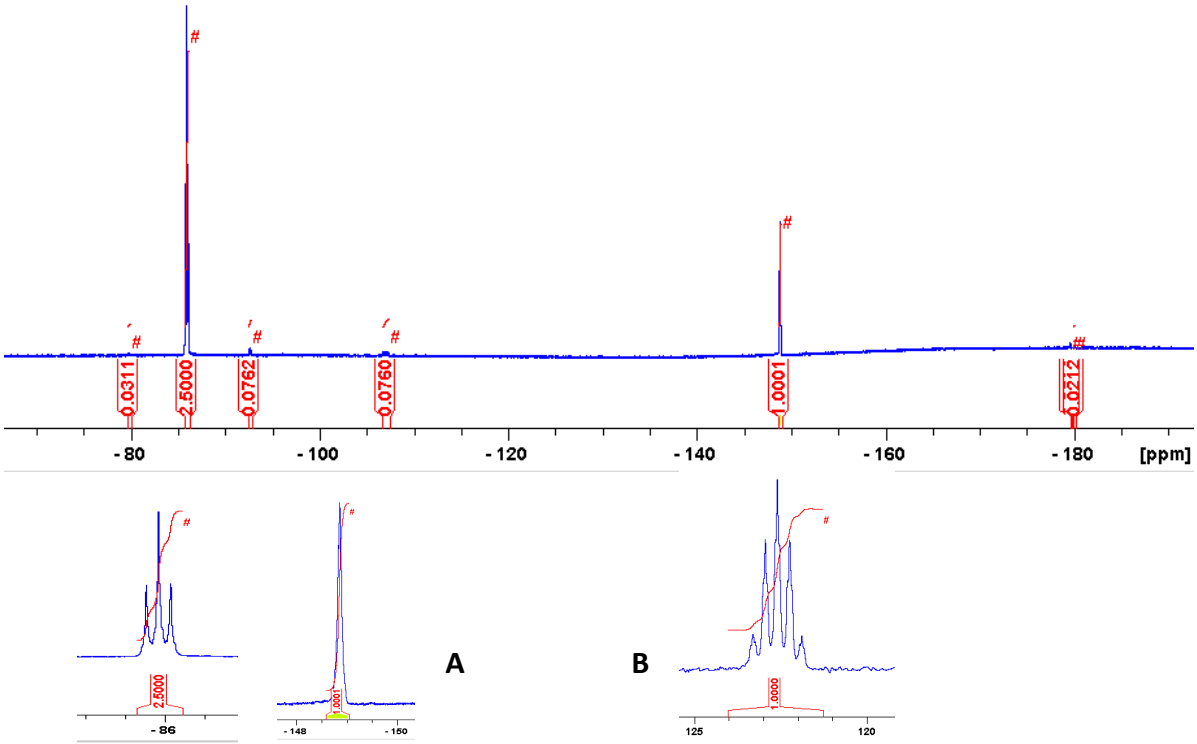


Figure 2.1. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **2-1** with insets (**A**) and ^{31}P{^{1}H} NMR spectrum (121 MHz, C_6D_6) (**B**).

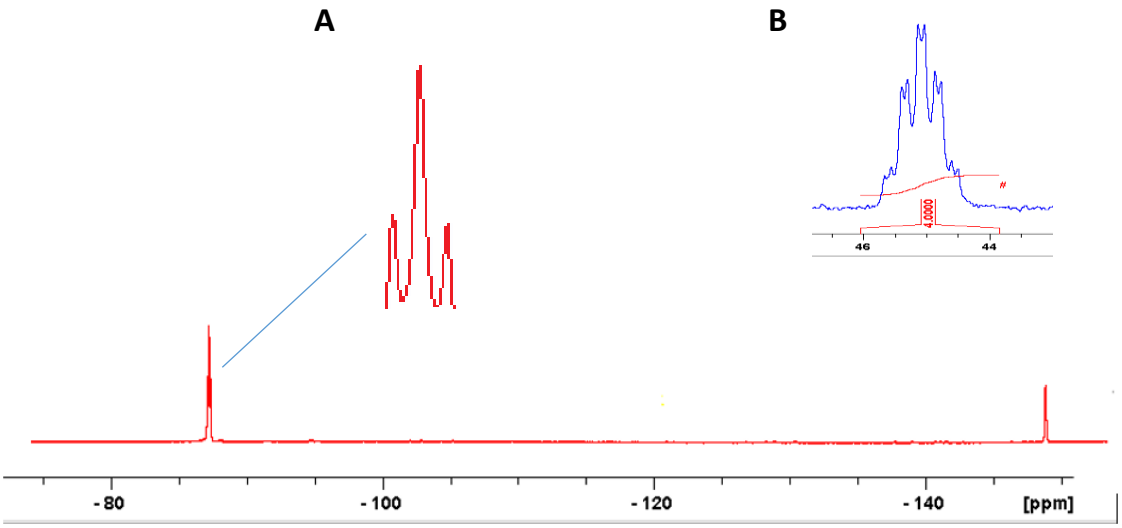


Figure 2.2. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **2.2** with insets (**A**) and $^{31}P\{^1H\}$ NMR spectrum (121 MHz, C_6D_6) (**B**).

2.2.3 Reaction of 2.2 with TMSOTf

Addition of 1 equiv of TMSOTf to a solution of **2-2** in C_6D_6 proceeded slowly. After 2 d formation of Me_3SiF was accompanied by two new ^{31}P NMR multiplet resonances (**Figure 2.3**) suggesting a decrease in symmetry of the resulting major product, **2-3**.

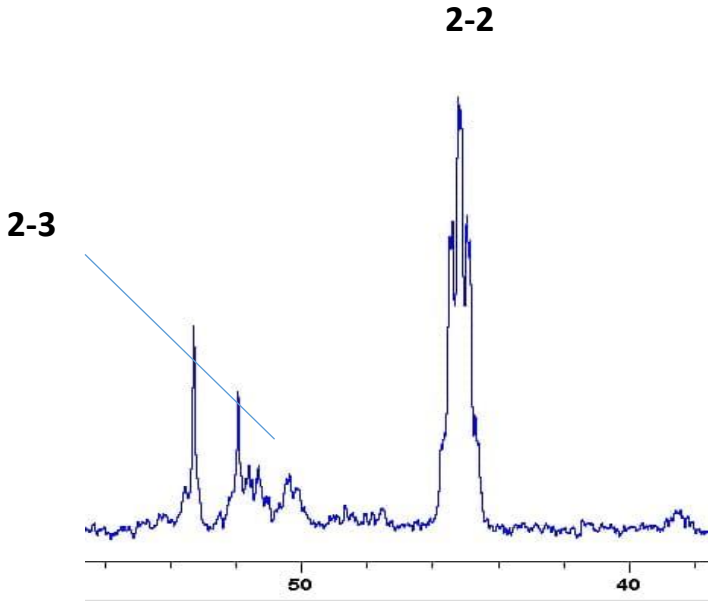


Figure 2.3 New ^{31}P NMR resonances arising from reaction of **2-2** with TMSOTf in C_6D_6.

The ^{19}F NMR spectrum of this reaction mixture shows resonances due to Me_3SiF at -76.1 ppm and the OTf^- anion at -77.2 ppm. In addition to **2.2,** there are nine new resonances, five of which are associated with major product **2.3** (**Figure 2.4**). Resonances 2,3 and 5 can be associated with a perfluorovinyl group ($^3J_{FF}$ = 107 and 71 Hz for *trans*- and *cis*-Fs, respectively) which could be obtained easily by a ring contraction followed by retrocyclization (**Scheme 2.6**). As resonances 1 and 2 are primarily coupled to the dppe ^{31}P nuclei with no strong coupling between them, we tentatively assign the structure of **2.3** to the η^2-dienyl complex (**Scheme 2.7**).[8]

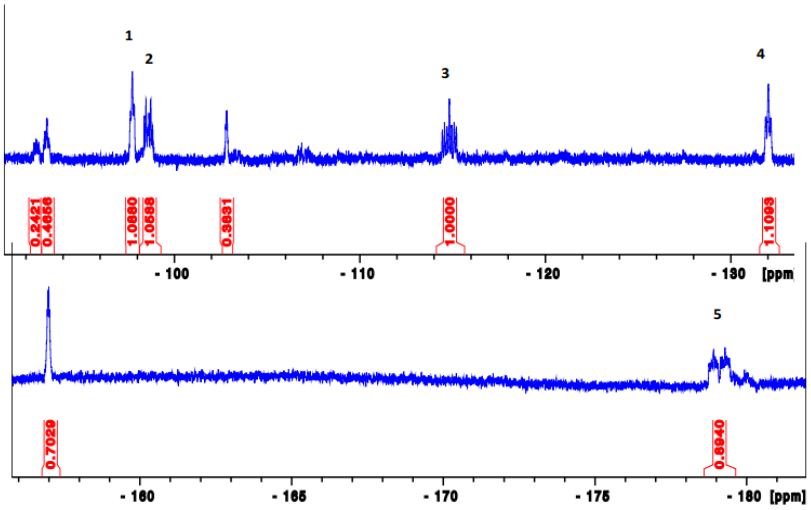
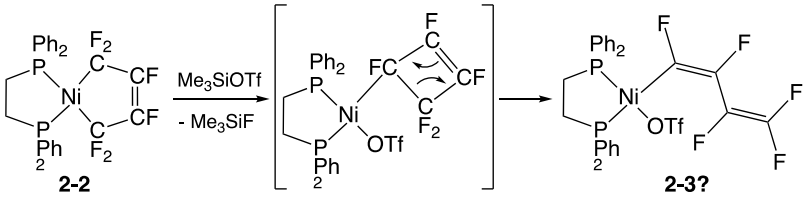
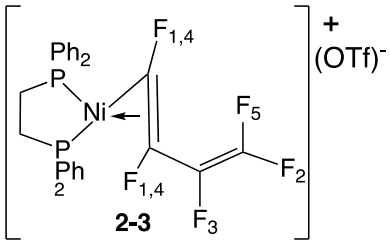


Figure 2.4 New ^{19}F NMR resonances arising from reaction of **2-2** with TMSOTf in C_6D_6.



Scheme 2.6. Proposed reaction scheme to form **2.3**



Sheme 2.7. Proposed structure of **2.3**

2.1. Conclusions

The goal of this chapter was to investigate fluoride abstraction from perfluoronickelacyclopentenes in order to compare the results with those already known for the corresponding metallacyclopentanes. In order to prevent reaction between electron-rich phosphines and the perfluorobutadiene, we first prepared the phosphite complex and then replaced the phosphite ligands with the chelating bis(phospine) dppe ligand. In previous work from Burch[3] and the Baker group,[4-7] fluoride abstraction from a C_α-F bond of Ni fluorometallacyclopentanes resulted in ligand migration or ring contraction. For the fluoronickelacyclopentene investigated here, we propose that ring contraction is followed by retrocyclization to afford a dienyl complex. Although the ^{19}F NMR spectrum is more consistent with an η^2-dienyl complex, additional work is needed to isolate and fully characterize product **2.3**.

2.2. Experimental Section

2.4.1 General

An MBraun glove box and Schlenk techniques were used to carry out the experiments under nitrogen. A J. C. Meyer solvent purification system was used to dry the benzene and hexanes using activated alumina columns. Stirring over activated alumina (ca. 10 wt.%) was used to dry the benzene-d_6 (C_6D_6) overnight, followed by filtration. Activated 4 Å molecular sieves (heated at ca. 250 ^oC for >10 h under vacuum) were added to all solvents stored in the glovebox. All glassware was heated in an oven for >2 h at 150 ^oC. $Ni(cod)_2$ was prepared according to the new literature method[9] and commercial chemicals used were 1,2-bis(diphenylphosphino)ethane (DPPE, 99%, Aldrich), triisopropylphosphite [$P(O^iPr)_3$, 95%, Strem], trimethylsilyltriflate (TMSOTf, 99%, Aldrich) and perfluorobutadiene (Synquest). A 300 MHz Bruker Avance instrument was used to record the ^{19}F and $^{31}P\{^1H\}$ NMR spectra at room temperature (21-23 ^oC) and ^{19}F and ^{31}P NMR shifts are reported relative to 1,3- bis(trifluoromethyl)benzene (BTB) at -63.5 ppm and phosphoric acid (85 % aqueous solution) at 0 ppm.

2.4.2 Synthesis of Ni(C_4F_6)[P(O-*i*-Pr)$_3$]$_2$ (2-1)

To a solution of 100 mg Ni(cod)$_2$ (0.36 mmol) in 10 mL benzene was added 151 mg of triisopropylphosphite (0.727mmol) giving a yellow-orange solution. Using a gas-tight syringe, 10 mL of hexafluoro-1,3-butadiene was then added. The resulting product (**2-1**) was characterized by ^{19}F and ^{31}P NMR spectroscopy. ^{19}F NMR (282 MHz, C_6D_6): –85.1 (tr, $^3J_{FP}$ = 32 Hz, 4Cα-F), -146.3 ppm (d mult, $^4J_{FP}$ = 11 Hz, 2 Cβ-Fs). ^{31}P NMR (121 MHz, C_6D_6) 45.1 ppm (quint d, $^3J_{FP}$ = 32, $^4J_{FP}$ = 11 Hz).

2.4.3 Synthesis of Ni(C_4F_6)(dppe) (2-2)

To a benzene solution of 154.41 mg of **2-1** was added 145 mg of dppe (0.36 mmol) giving a slightly darker orange solution. After the ^{31}P NMR spectrum indicated completion of the reaction, the solvent was removed and washed with hexane to remove any remaining phosphite or dppe. ^{19}F NMR (282 MHz, C_6D_6): –85.1 (tr, $^3J_{FP}$ = 32 Hz, 4Cα-F), -146.3 ppm (d mult, $^4J_{FP}$ = 11 Hz, 2 Cβ-Fs). ^{31}P NMR (121 MHz, C_6D_6) 45.1 ppm (quint d, $^3J_{FP}$ = 32, $^4J_{FP}$ = 11 Hz).

2.4.4 Reaction of 2-2 with TMSOTf

To a solution of **2-2** in benzene was added 80.7 mg TMSOTf (0.36 mmol) and the reaction mixture was monitored by NMR spectroscopy after 2 d. ^{19}F NMR (282 MHz, C_6D_6) Major product (**2.3**): -97.7 (tr mult, 28 Hz, 1F), -98.6 (d tr mult, 71, 27.5 Hz, 1F), -114.8 (ddd, 107, 73, 33.5 Hz, 1F), -132.0 (tr mult, 38 Hz, 1F), -179.1 ppm (dddd, 107, 40.5, 26, 13.5, 1F). ^{31}P NMR (121 MHz, C_6D_6) 51.4, 50.6 ppm (mult, 1P). Minor product, ^{19}F NMR (282 MHz, C_6D_6): -92.6 (mult), -93.1 (mult), -102.8 (mult), -157.0 (mult).

2.5. References

1. Browning, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 453.

2. Green, M.; Shakshooki, S. K.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2828.

3. Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7*, 1642.

4. Giffin, K. A.; Harrison, D. J.; Korobkov, I.; Baker, R. T. *Organometallics*, **2013**, *32*, 7424.

5. Giffin, K. A.; Korobkov, I.; Baker, R. T. *Dalton Trans.,* **2015**, *44*, 19587.

6. 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.

7. Andrella, N. O.; Sicard, A. J.; Gorelsky, S. I.; Korobkov, I.; Baker, R. T. *Chem. Sci* **2015**, *6*, 6392.

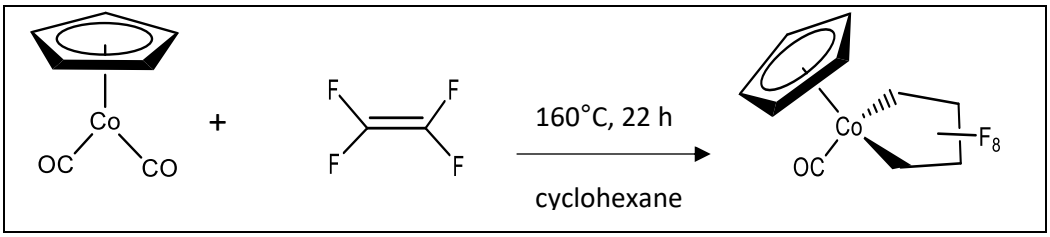
8. Sravani, C.; Venkatesh,S.; Vijayakrishna, K.; Sivaramakrishna, A. *Appl. Organomet. Chem.* **2014**, *28,* 733.

9. Sicard, A. J.; Baker, R. T. *Org. Proc. Res Devel.* **2020**, *24*, 2950.

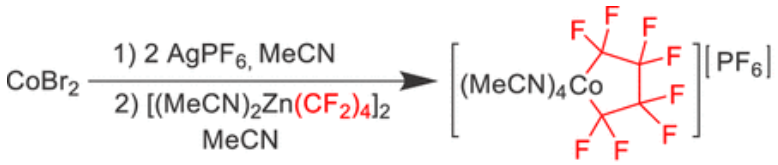
Chapter 3. Fluoroalkene Reactions with Cobalt Hydride Complexes

3.1. Introduction

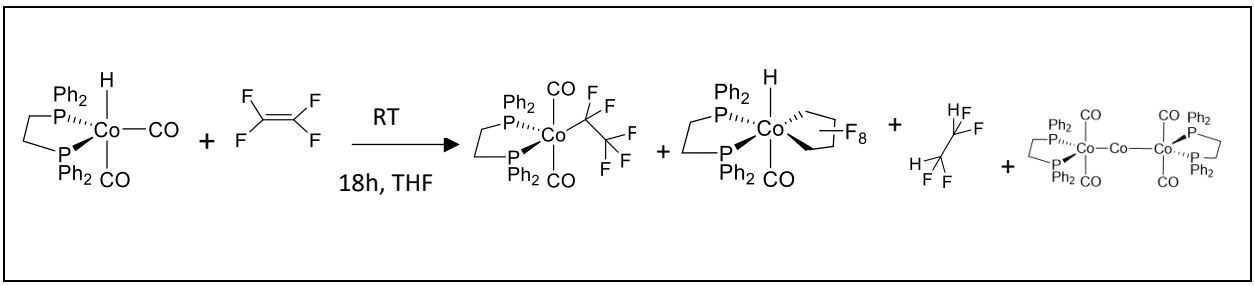
Cobalt perfluorometallacycles have not been widely studied since the preparation of CpCo(1,4-C_4F_8)(CO) by Stone in 1961 (**Scheme 3.1**)[1] with the only other example reported recently by Teng and Vicic (**Scheme 3.2**).[2] As discussed in Chapter 1, K. Ghostine from the Baker group showed that reactions of cobalt carbonyl phosphine hydrides with TFE afforded a mixture of the insertion product and Co hydride metallacycle.[3] Unfortunately, these reactions suffered from a competing reaction that yielded a zerovalent dimer $[Co(dppe)(CO)_2]_2$ (not shown) and hydrogenated TFE (**Scheme 3.3**).



Scheme 3.1. Synthesis of CpCo(1,4-C_4F_8)(CO).



Scheme 3.2: Synthesis of Co(1,4-C_4F_8)$(NCMe)_4$.



Scheme 3.3. Reaction of $CoH(dppe)(CO)_2$ with TFE.

In this chapter we investigate reactions of fluoroalkenes with cobalt hydrides containing phosphine and phosphite ligands in order to see if the competing reaction can be controlled by the ligands' steric and electronic properties.

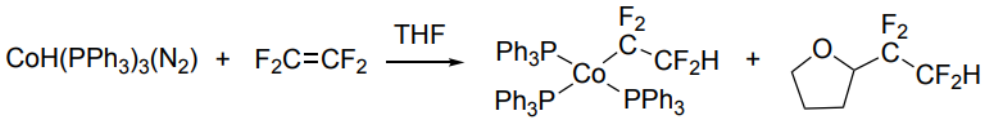
3.2 Results and Discussion

3.2.1 Cobalt hydride complexes

As nickel complexes with phosphite ligands react well with fluoroalkenes, we prepared both the known tri-isopropylphosphite[4] and bulkier tri-ortho-tolyl phosphite cobalt hydride complexes, $CoHL_4$ (**3-1** and **3-2**). While the latter contains an easily dissociated phosphite ligand, we also prepared more electron-rich CoH(triphos)(CO)[5] (**3-3**) and $CoH(PPh_3)_3(N_2)$[6] (**3-4**) that could also potentially afford $[CoHL_3]$ metallacycles.

3.2.2 Reactions of cobalt hydride complexes with TFE

In light of previous reports of TFE insertion into Co carbonyl hydrides,[3] we were surprised that neither of our phosphite complexes **3-1** or **3-2** showed any reactivity with this gas. In contrast, HCo(triphos)CO (**3-3**) reacted with TFE to afford two different products each showing two broad resonances that are unchanged on proton decoupling (**Figure 3.1**). The absence of any P-F coupling in the ^{31}P NMR spectrum or Co-H resonance in the ^{1}H NMR spectrum did not allow us to identify the products. Finally, reaction of $CoH(PPh_3)_3(N_2)$ with TFE in THF gave a mixture of the insertion product, $Co(CF_2CF_2H)(PPh_3)_3$ (**3-5**) and the recently characterized THF fluoroalkylation product, $O[(-CH_2)_3CH(CF_2CF_2H)-]$[7] (**3-6**) (**Scheme 3.4** and **Figure 3.2**). The ^{19}F NMR spectrum of **3-5** included a doublet of triplets at -111.0 (d tr d, $^{3}J_{FF}$ = 8 Hz, $^{3}J_{FP}$ = 66.5 Hz, $C\alpha F_2$) and a doublet of doublet of triplets at -130.6 ppm (d d tr, $^{2}J_{FH}$ = 60, $^{3}J_{FP}$ = 7.9 Hz, $^{3}J_{FP}$ = 24 Hz, $C\beta F_2$).



3-4 3-5 3-6

Scheme 3.4. Reaction of **3-4** with TFE in THF

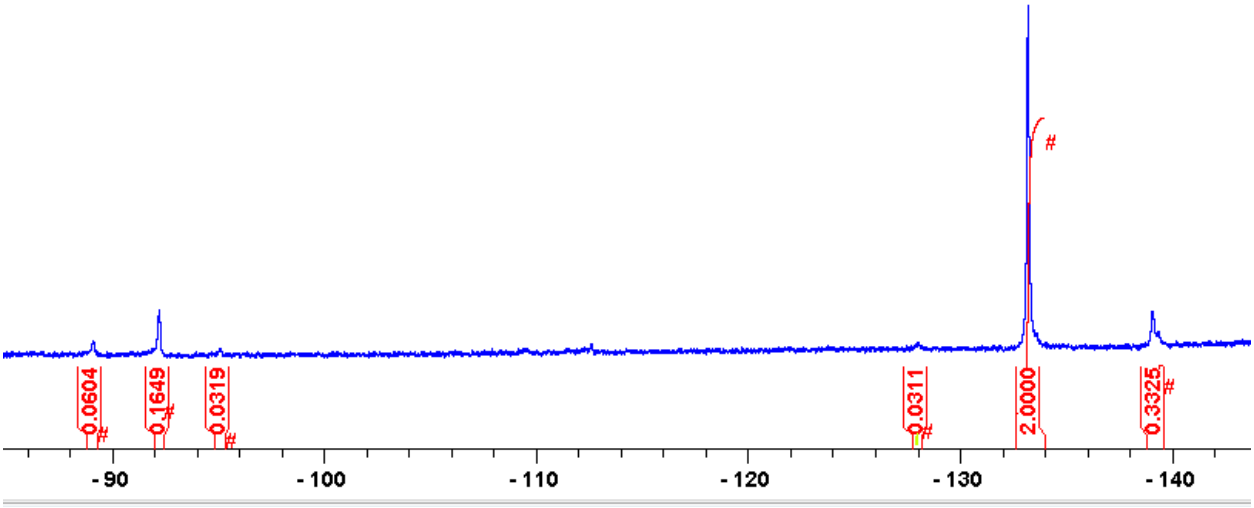


Figure 3.1 ^{19}F NMR spectrum (282 MHz, C_6D_6) of CoH(triphos)CO **3-3** with TFE.

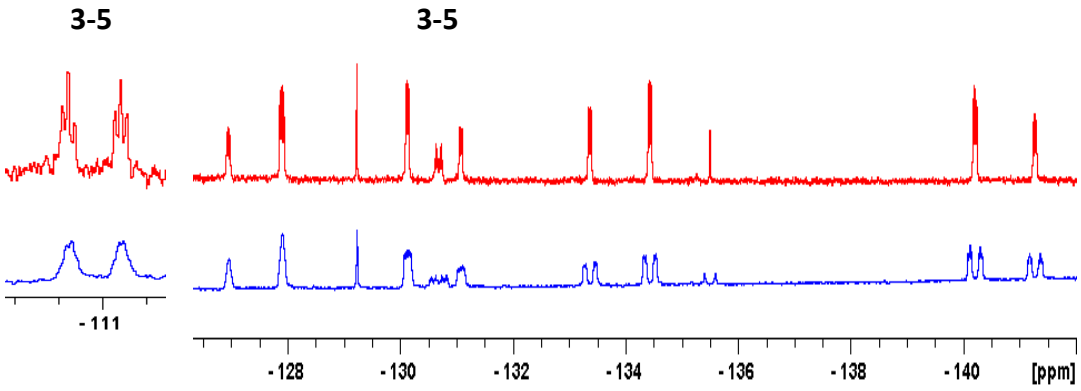


Figure 3.2 ^{19}F (bottom)and $^{19}F\{^1H\}$ (top) NMR spectra (282 MHz, C_6D_6) of $CoH(PPh_3)_3(N_2)$ **3-4** with TFE.

3.2.3 Reactions of cobalt hydride complexes with HFP

After our experiments with TFE we showed that none of our Co-H complexes reacted with $CH_2=CF_2$. In contrast, all our cobalt hydride complexes reacted with HFP (hexafluoropropene, $CF_2=CF(CF_3)$). Treatment of a yellow solution of $CoH[P(O\text{-}i\text{-}Pr)_3]_4$ (**3-1**) with excess HFP in C_6D_6 gave a colour change to light green The ^{19}F NMR spectrum showed formation of one major and two minor products (**3-7, 3-8, 3-9)** as determined by the CF_3 resonances (**Figure 3.3**). The major product showed four different resonances that were unchanged upon proton decoupling, suggesting. formation of an alkene complex (**3-7).** Reaction of HFP with the bulkier phosphite

complex **3-2** also gave alkene complex **(3-10**) as well as larger proportions of the minor products (**3-11, 3-12**) , allowing us to identify the products from **3-1** as two stereoisomers of the alkenyl complex, *E*- and *Z*-Co[CF=CF(CF_3)][P(O-*i*-Pr)$_3$]$_4$ (**3-8** and **3-9**) that each give rise to three different ^{19}F NMR resonances (**Figure 3.3**). Complexes **3-8** and **3-9** can be differentiated from their $^3J_{FF}$ coupling constants of 148 (trans Fs) and 120 Hz (cis Fs). This evidence for C-F bond activation prompts us to assign the structure of the alkene complexes as Co-F complexes, CoF(h^2-CF_2=CF(CF_3)][P(OR)$_3$]$_3$.(**Figure 3.4**). A similar product distribution of **3-13** to **3-15** was observed from reaction of CoH(triphos)(CO) with HFP **(Figure 3.5**).

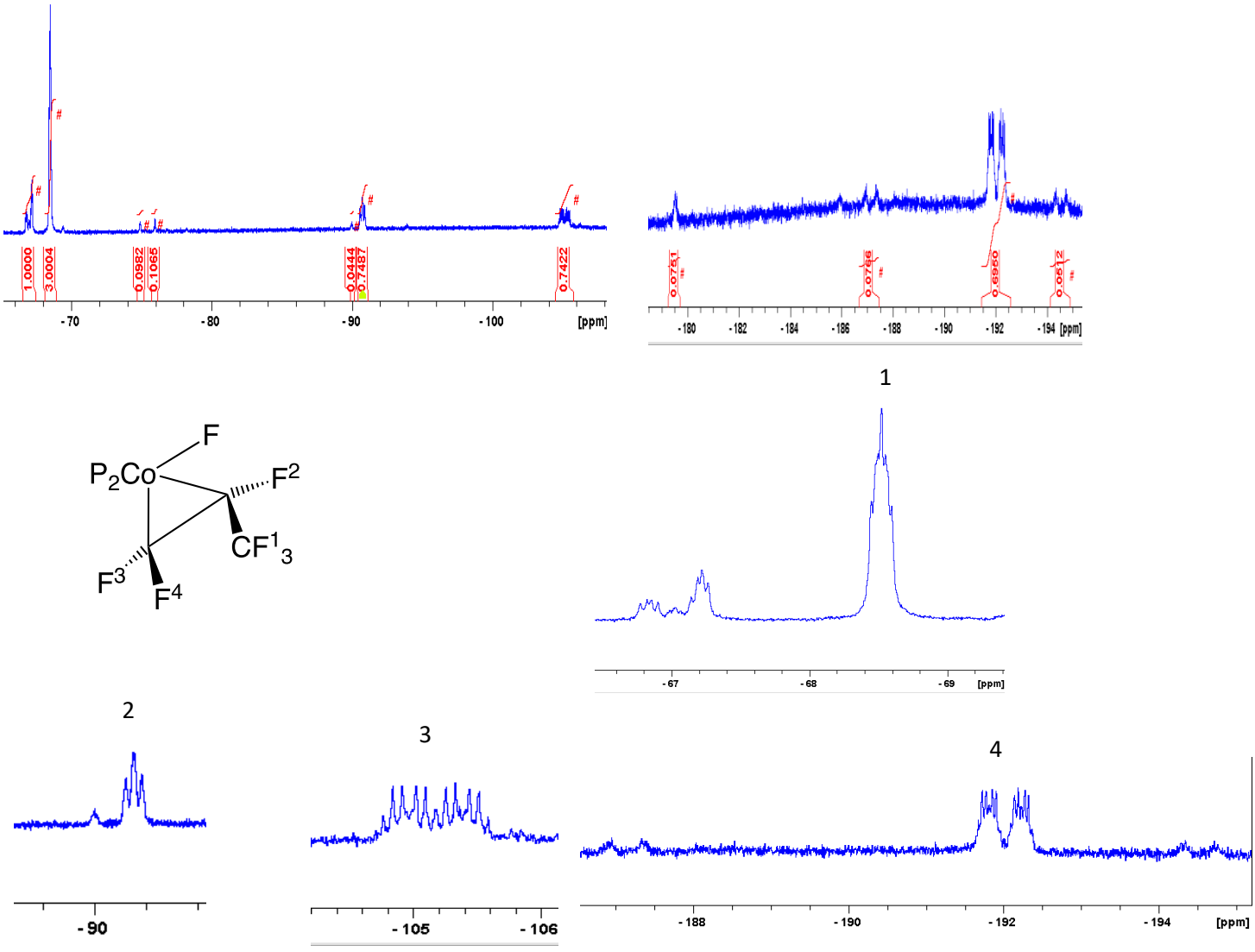


Figure 3.3 ^{19}F NMR spectrum (282 MHz, C_6D_6) of the reaction of HCo[P(O^{i}Pr)$_3$]$_4$ (**3-1**) with HFP.

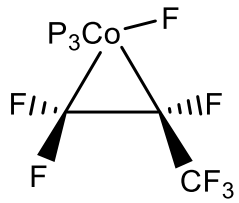
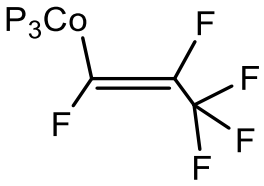
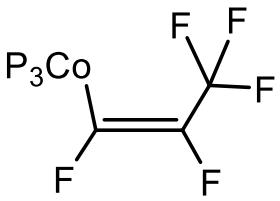
 P= P(OiPr)$_3$ **3-7** P= P(O-o-tol)$_3$ **3-10** P$_3$ = triphos **3-13**	 P= P(OiPr)$_3$ **3-8** P= P(O-o-tol)$_3$ **3-11** P$_3$ = triphos **3-14**	 P= P(OiPr)$_3$ **3-9** P= P(O-o-tol)$_3$ **3-12** P$_3$ = triphos **3-15**

Figure 3.4. Proposed products from reactions of $CoHL_n$ with HFP.

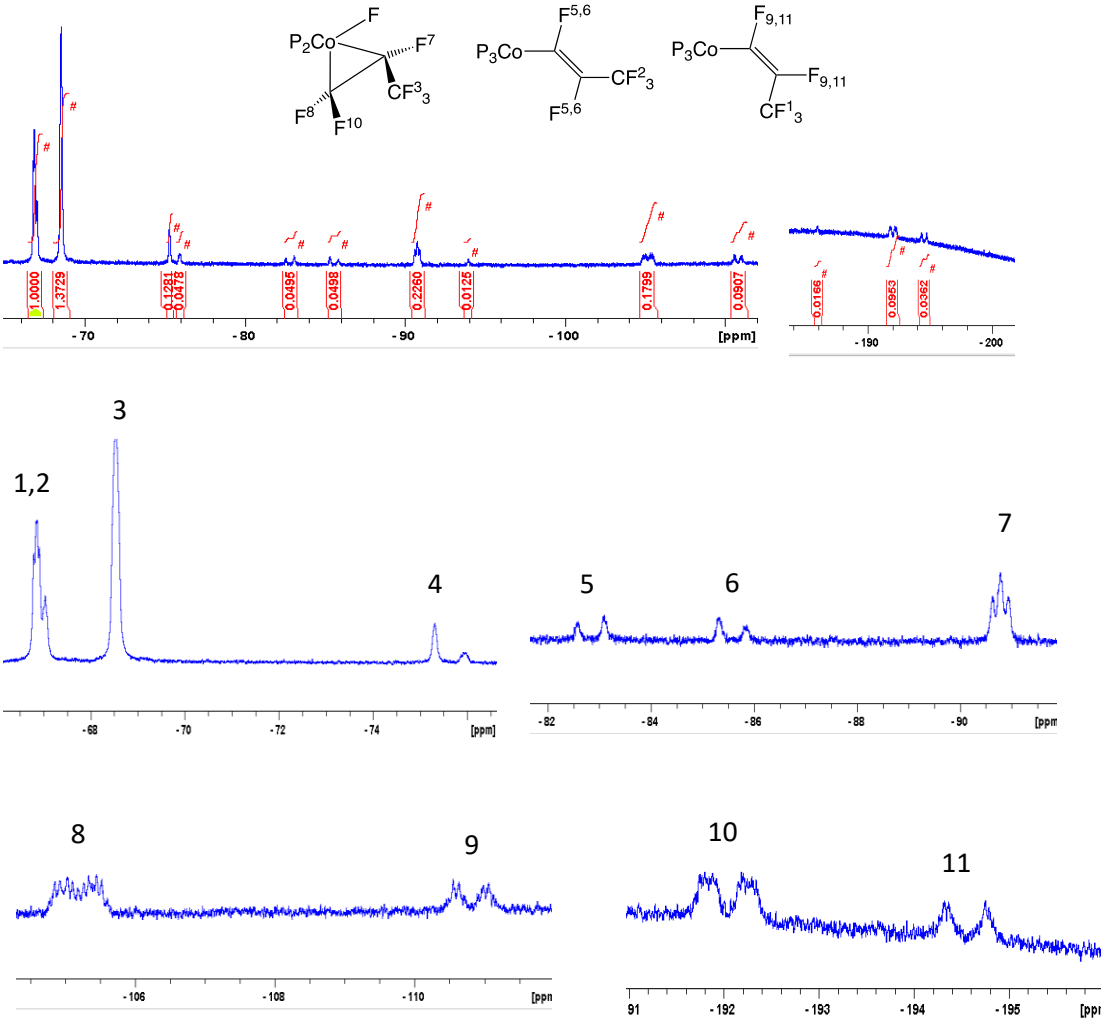


Figure 3.5. ^{19}F NMR spectrum (282 MHz, C_6D_6) of $HCo[P(O\text{-}o\text{-}tolyl)_3]_n$ **(3-2)** with HFP.

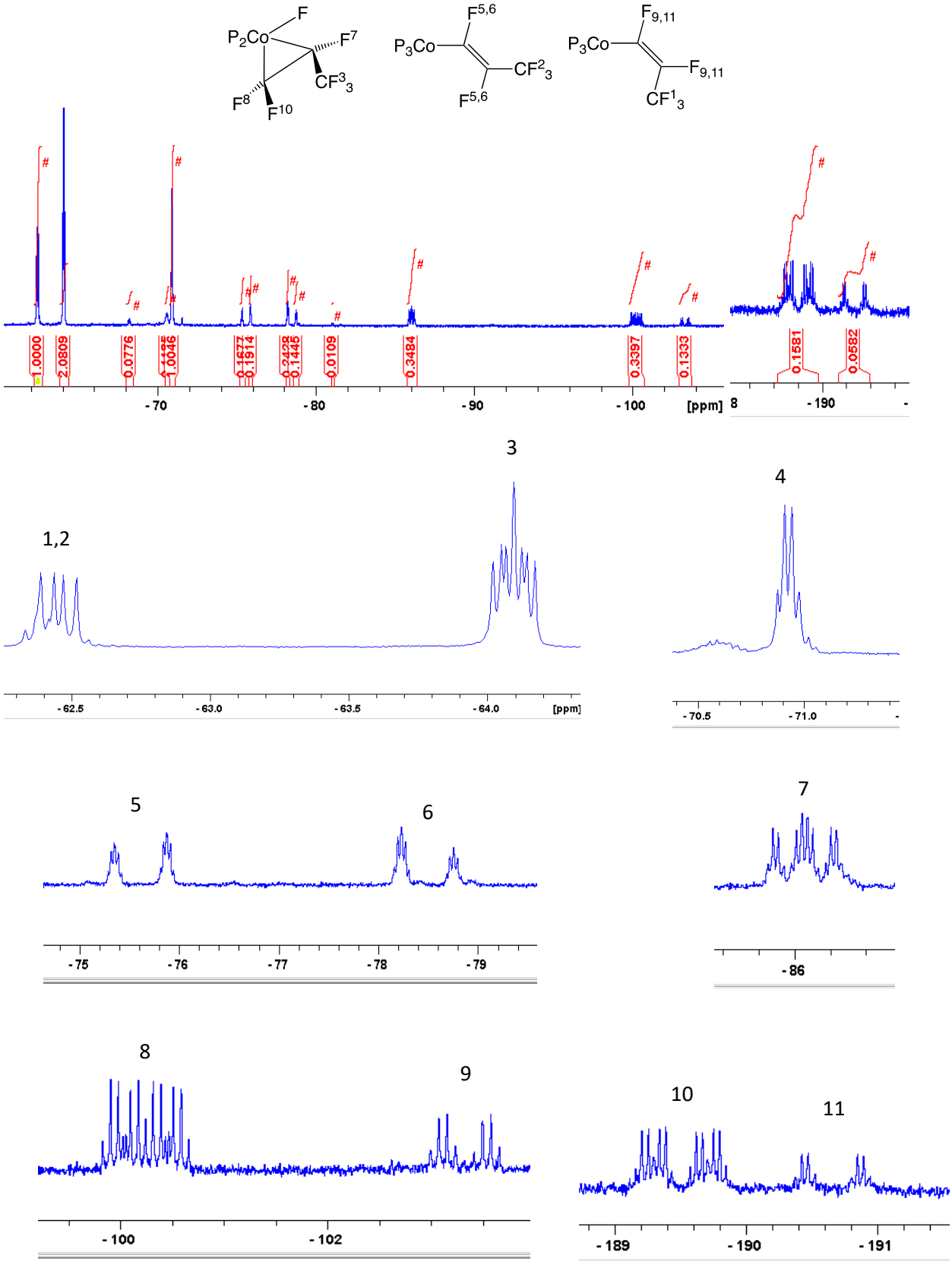
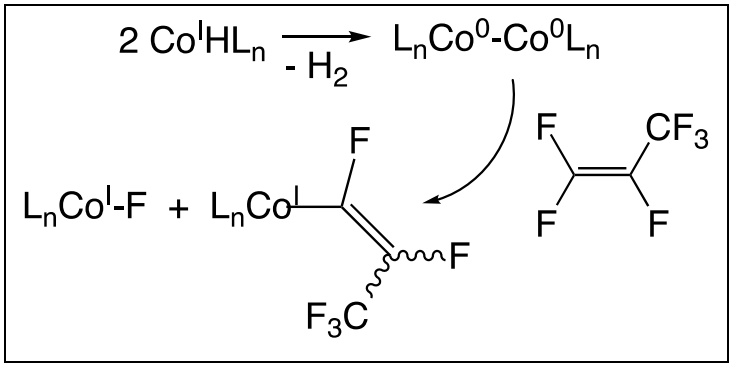


Figure 3.6. ^{19}F NMR spectrum (282 MHz, C_6D_6) of HCo(triphos)CO with HFP.

3.3. Conclusions

In previous work, Ghostine showed that reaction of $CoH(dppe)(CO)_2$ with TFE gave the 18 e- insertion product $Co^{I}(CF_2CF_2H)(dppe)(CO)_2$ and purported 18 e- d^6 metallacycle, $Co^{III}H(1,4\text{-}C_4F_8)(dppe)(CO)$.[3] This reaction was accompanied by a second reaction, however, in which the insertion product reacts with the original hydride to form hydrogenated TFE and the zerovalent dimer $[Co(dppe)(CO)_2]_2$. A similar mechanism leads to the instability of many monovalent cobalt hydrides that produce hydrogen gas and a zerovalent dimer in a bimolecular reaction.[8] When we combine this observation with the reported reaction of $Co_2(CO)_8$ with TFE,[9] we can imagine reaction of the cobalt hydride complex with HFP to give a mixture of alkenyl and Co-F complexes in which the latter undergoes ligand substitution to give the observed olefin complex (**Scheme 3.5**). Additional evidence for zerovalent Co intermediates is provided by the reaction of $CoH(PPh_3)_3(N_2)$ with TFE which is accompanied by radical-initiated Cα-H abstraction from the THF solvent to give **3-6**.



Scheme 3.5. Possible reaction scheme for reactions of cobalt hydrides with HFP.

3.4 Experimental Section

3.4.1 General

An MBraun glove box and Schlenk techniques were used to carry out the experiments under nitrogen. A J. C. Meyer solvent purification system was used to dry the benzene, tetrahydrofuran (THF) and hexanes using activated alumina columns. Stirring over activated alumina (ca. 10 wt.%) was used to dry the benzene-d_6 (C_6D_6) overnight, followed by filtration. Activated 4 Å molecular sieves (heated at ca. 250 ^oC for >10 h under vacuum) were added to all solvents stored in the glovebox. All glassware was heated in an oven for >2 h at 150 ^oC. Commercial chemicals anhydrous cobalt(II) chloride ($CoCl_2$, 98%, Alfa Aesar), triphenylphosphine (PPh_3, 99%, Aldrich), triisopropylphosphite [$P(O^iPr)_3$, 95%, Strem], tri(o-tolyl)phosphite [$P(O\text{-}o\text{-}tol)_3$, 95%, Strem], bis(diphenylphosphinoethyl)-phenylphosphine (triphos, 97%, Aldrich), and hexafluoropropene (Synquest) were used as obtained. Co complexes $CoH[P(O\text{-}i\text{-}Pr)_3]_4$, CoH(triphos)(CO) and $CoH(PPh_3)_3(N_2)$ were prepared by literature procedures.[4-6] Pyrolysis was used to prepare tetrafluoroethylene from polytetrafluoroethylene (powdered, Scientific Polymer Products) under vacuum using a modified literature procedure [10-20 mTorr, 25 g scale, 650 ^oC, R(+)-limonene (97%, Aldrich) for product stabilization producing 97-98% pure TFE.[10] A 300 MHz Bruker Avance instrument was used to record the ^{19}F and $^{31}P[^1H]$ NMR spectra at room temperature (21-23 ^oC) and ^{19}F and ^{31}P NMR shifts are reported relative to 1,3- bis(trifluoromethyl)benzene (BTB) at -63.5 ppm and phosphoric acid (85 % aqueous solution) at 0 ppm.

3.4.2 Synthesis of $CoH[P(O\text{-}o\text{-}tol)_3]_4$ (3-2)

Solid cobalt dichloride (0.25 g, 1 mmol) was dissolved in a mixture of methanol (30 ml) and 0.305 g of tri(o-tolyl)phosphite (1 mmol) and the reaction cooled to -78°C after which time $NaBH_4$ (0.38 mg) was added. After warming to RT and stirring for 3 h, the solvent was removed and the solid washed with cold hexane and dried to give 0.158 mg of a yellow solid (43% yield).

3.4.3 Reactions of cobalt hydrides with fluoroalkenes

The solid Co hydride (ca. 20 mg) was dissolved in 0.6 mL of C_6D_6 (or THF for **3-4**), charged to an NMR tube and an excess of the fluoroalkene was injected into the tube after which time the reaction products were characterized by ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy.

3.4.3.1 Reaction of 3-4 with TFE in THF/C_6D_6

NMR spectra of **3-6** matched that in the previous report.[8] For **3-5**: ^{19}F NMR (THF/C_6D_6, 282 MHz) -111.0 (dtrd, $^3J_{FP}$ = 66.5, $^3J_{FF}$ = 8, $^3J_{FH}$=2.5 Hz, $C_\alpha F_2$), -130.6 ppm (ddtr, $^2J_{FH}$ = 60, $^4J_{FP}$ = 24, $^3J_{FF}$ = 8 Hz, $C_\beta F_2$).

3.4.3.2 Reaction of 3-1 with HFP

3-7 ^{19}F NMR (C_6D_6, 282 MHz) -68.5 (mult, CF_3), -91 (ddq, 56, 37, 8.5, CF), -106 (ddq, 75, 44, 22 Hz, CF_3), -192.3 ppm (dq, 120, 14Hz, CF), $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) 128 ppm (mult).

3-8 ^{19}F NMR (C_6D_6, 282 MHz) -67.2 (dd, 22, 13 Hz, CF_3), -105.3 (dq, 139, 18 Hz, CF), -110.1 (dq, 139, 16 Hz, CF).

3-9 ^{19}F NMR (C_6D_6, 282 MHz) -75.9 (dd, 25, 10 Hz, CF_3), -187 (dq, 121, 13 Hz, CF), -192.3 (dq, 120, 14 Hz, CF),

3.4.3.3 Reaction of 3-2 with HFP

3-10 ^{19}F NMR (THF/C_6D_6, 282 MHz) -68.5 (br,s, CF_3), -90.8 ('tr', 42Hz, CF), -110.8 (d mult, 116, 54.5, 20.5), -192.0 ppm (dd mult, 115, 22 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz), 168 ppm (mult).

3-11 ^{19}F NMR (THF/C_6D_6, 282 MHz) -67.0 (br,s, CF_3), -82.9, -85.6 (d mult, 148 Hz, CF), 76.1 ppm (ddd, 9 Hz, CF_3),

3-12 ^{19}F NMR (THF/C_6D_6, 282 MHz) -66.9 (br,s, CF_3), -105.2 (d mult, 120 Hz, CF), -194.6 ppm (d mult, 120 Hz, CF).

3.4.3.4 Reaction of 3-3 with HFP

3-13 ^{19}F NMR (THF/C_6D_6, 282 MHz) -64.1 (ddd, 21, 13.5, 8.5 Hz, CF_3), -86.0 (ddq, 55, 37, 8.5 Hz, CF), -100.2 (ddq, 116, 55, 21 Hz, CF), -189.5 (ddq, 116, 37, 13 Hz, CF).

3-14 ^{19}F NMR (THF/C_6D_6, 282 MHz) -62.3 (dd, 13, 10 Hz, CF_3), -75.7 (dqd, 148, 10, 8.5 Hz), -78.5 (dqd, 148, 10, 8.5 Hz, CF).

3-15 ^{19}F NMR (THF/C_6D_6, 282 MHz) -62.4 (dd, 22, 13.5 Hz), -103.1 (dq, 119.5, 22 Hz, CF), -190.6 (dq, 119.5, 13.5 Hz, CF).

3.5 References

1. Coyle, T. D.; Kings, R. B.; Pitcher, E.; Stafford, S. L.; Teichel, P.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* 1961, *20*, 172.
2. Teng, X.; Vicic, D. A. *Organometallics* **2020**, *39*, 3715.
3. Ghostine, K. University of Ottawa MSc thesis, **2018**.
4. Baker, R. W.; Pauling, P. *Chem. Commun.* **1971**, 322.
5. Yamamoto, A.; Kitazume, S.; Pu, L. S.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93,* 371.
6. Meek, D. W.; Dubois, D. L.; Tiethof, J. *ACS Symp. Ser.* **1976**, *28*, 335.
7. Barnawi, B. University of Ottawa MSc thesis, **2021**.
8. Beveridge, A. D.; Clark, H. C. *J. Organomet. Chem.* **1967**, *11*, 601.l
9. Hunadi, R. J.; Baum, K. *Synthesis* **1982**, 39, 454.
10. Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

Chapter 4: Contributions to Knowledge and Future Outlook

4.1 Contributions to Knowledge

Over the last 13 years the Baker group has significantly expanded our knowledge of the synthesis and reactivity of first row transition metal organofluorine complexes.[1-21] In particular, for d^8 fluoronickelacyclopentanes, they showed that, in some cases, Cα-F abstraction with a Lewis acid results in ring contraction,[5,12] as opposed to the previously reported migration of an ancillary ligand.[22] In Chapter 2 we prepared an electron-rich perfluoronickelacyclopentene and investigated its reaction with the Lewis acid TMSOTf. Although more complete characterization will be required before publication, we proposed that the above reaction also results in ring contraction, followed by retrocyclization of the presumed cyclobutenyl intermediate to afford a novel perfluorodienyl complex. If this complex can be isolated and characterized by X-ray diffraction and mass spectrometry, this would be the first example of this type of complex.

Although both of the first perfluorometallacyclopentane complexes were d^6 Fe and Co complexes prepared by the Stone group,[23,24] their reactivity remains underdeveloped.[21] Moreover, in spite of numerous attempts by Karine Ghostine[25] and later by me to prepare new examples of Co metallacycles from TFE have met with limited success. One promising result obtained by Ghostine, however, was derived from reaction of $CoH(dppe)(CO)_2$ with TFE that formed both the Co-CF_2CF_2H insertion product and an additional product proposed to be a Co hydride perfluorocobaltacyclopentane.[25] As this reaction was accompanied by formation of HCF_2CF_2H and the zerovalent $[Co(CO)_2(dppe)]_2$ dimer, we investigated reactions of other phosphite and phosphine cobalt hydrides in an attempt to avoid this competing side reaction. Surprisingly, no evidence of TFE insertion was seen for the phosphite or bis(phosphine) complexes whereas observation of the Co-CF_2CF_2H insertion product using $CoH(N_2)(PPh_3)_3$ was accompanied by radical formation as evidenced by formation of perfluoroethylated THF solvent. While reactions of our cobalt hydrides with HFP were more fruitful, they did not involve insertion of the fluoroalkene into the Co-H bond. Instead, the reaction pathways appeared to involve initial electron transfer and C-F bond activation as seen previously using carbonylmetallates.[26.]

Although further characterization is likely to confirm the structures of the resulting alkenyl complexes, more work is necessary to confirm the identity of our proposed Co-F HFP alkene complexes. Nonetheless, these findings confirm that reactions of fluoroalkenes with low-valent metal complexes are not limited to formation of alkene complexes, metallacycles, or even insertion complexes.

4.2 Future Outlook

The work described in this thesis has opened several new doors into our understanding of metal organofluorine complexes. For our fluoronickelacyclobutene work, purification of the Ni dppe complex should remove any impurities associated with the phosphite ligands, possibly leading to a cleaner reaction with TMSOTf. The slow pace of the latter reaction may also require some gentle heating to go to completion so that the new Ni dienyl complex can be fully characterized including mass spectrometry and X-ray diffraction of single crystals.

Further characterization and reactivity of the $Co(CF_2CF_2H)(PPh_3)_3$ complex will determine whether a second equivalent of TFE can react to form a new Co(III) perfluorometallacycle hydride complex which should contain a labile PPh_3 ligand, providing access to the $Co[(CF_2)_3CF_2H](PPh_3)_3$ product. Another point to be studied in the future is the selective Cα–F bond activation of these Co complexes by reacting them with H_2 and different kinds of Lewis acids. This area remains largely unexplored and has the potential to generate attractive additions to current catalytic fluoroalkene transformations utilizing nickel[26] and copper[27].

To sum up, this research paves the way for the next group of chemists to discover effective catalysts for the formation of new fluoroalkenes, cyclic structures and polymers.

4.3 References

1. Harrison, D. J.; Gorelsky, S. I., Lee, G. M.; Korobkov, I.; Baker, R. T. *Organometallics*, **2013**, *32*, 12-15.

2. Giffin, K. A.; Harrison, D. J.; Korobkov, I.; Baker, R. T. *Organometallics* **2013**, *32*, 7424-7430.

3. Harrison, D. J.; Lee, G. M.; Leclerc, M. C.; Korobkov, I.; Baker, R. T. *J. Am. Chem. Soc.* **2013**, 135, 18296-18299.

4. Lee, G. M.; Harrison, D. J.; Korobkov, I.; Baker, R. T. *Chem. Commun.* **2014**, 50, 1128- 1130.

5. Andrella, N. O.; Sicard, A. J.; Korobkov, I.; Baker, R. T., *Chem. Sci.,* **2015**, *6*, 6392-6397.

6. Giffin, K. A.; Korobkov, I.; Baker, R. T. *Dalton Trans.,* **2015**, *44*, 19587-19596.

7. Fuller, J. T.; Harrison, D. J.; Leclerc, M. C.; Baker, R. T.; Ess, D. H.; Hughes, R. P. *Organometallics* **2015**, 34, 5210-5213.

8. Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics* **2015**, 34, 4598-4604.

9. 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.

10. Harrison, D. J.; Daniels, A. L.; Korobkov, I.; Baker, R. T. *Organometallics,* **2015**, *34*, 5683-5686.

11. Lee, G. M.; Leung, A. S. C.; Harrison, D. J.; Korobkov, I.; Hughes, R. P.; Baker, R. T. *Organometallics* **2017**, 36, 5683-5686.

12. 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.

13. Lee, G. M.; Clément, R.; Baker, R. T. *Catal. Sci. Technol.* **2017**, *7*, 4996-5003.

14. Lee, G. M.; Korobkov, I.; Baker, R. T. *J. Organomet. Chem.* **2017**, *847*, 220-227.

15. Andrella, N. O.; Liu, K.; Gabidullin, B. M.; Vasiliu, M.; Dixon, D. A.; Baker, R. T. *Organometallics* **2018**, *37*, 422-432.

16. Harrison, D. J.; Guan, J.; Daniels, A. L.; Gabidullin, B. M.; Hall, M. A.; Baker, R. T. *Angew. Chem. Int. Ed.* **2018**, *57,* 5772-5776.

17. Giffin, K. A.; Pua, L. A.; Korobkov, I. Baker, R. T. *Polyhedron* **2019**, *127,* 458-466.

18. Daniels, A. L.; Da Gama, J. G.; Edjoc, R.; Gabidullin, B. M.; Baker, R. T. *Inorganics*, 2019, *7*, 3.

19. Andrella, N. O.; Xu, N.; Gabidullin, B. M.; Ehm, C.; Baker, R. T. *J. Am. Chem. Soc.* **2019***, 141*, 11506-11521.

20. Ghostine, K.; Gabidullin, B. M.; Baker, R. T. *Polyhedron* **2020**, *185*, 114587-114592

21. Rochon, A.; Elsby, M. R.; Baker, R. T. *Can. J. Chem*. **2020**. https://doi.org/10.1139/cjc2020-0372.

22. Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7* (7), 1642–1648.

23. Manuel, T. A.; Stafford, S. L.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 249.

24. Coyle, T. D.; Kings, R. B.; Pitcher, E.; Stafford, S. L.; Treichel, P.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* **1961**, *20*, 172.

25. Ghostine, K. University of Ottawa MSc thesis, 2018.

26. Baker, R. T.; Sicard, A. J., US patent 10,703,695, 2020; US patent 10,882,802, 2021.

27. Baker, R. T.; Andrella, N. O., US patent 10,774,021, 2020.

Appendices

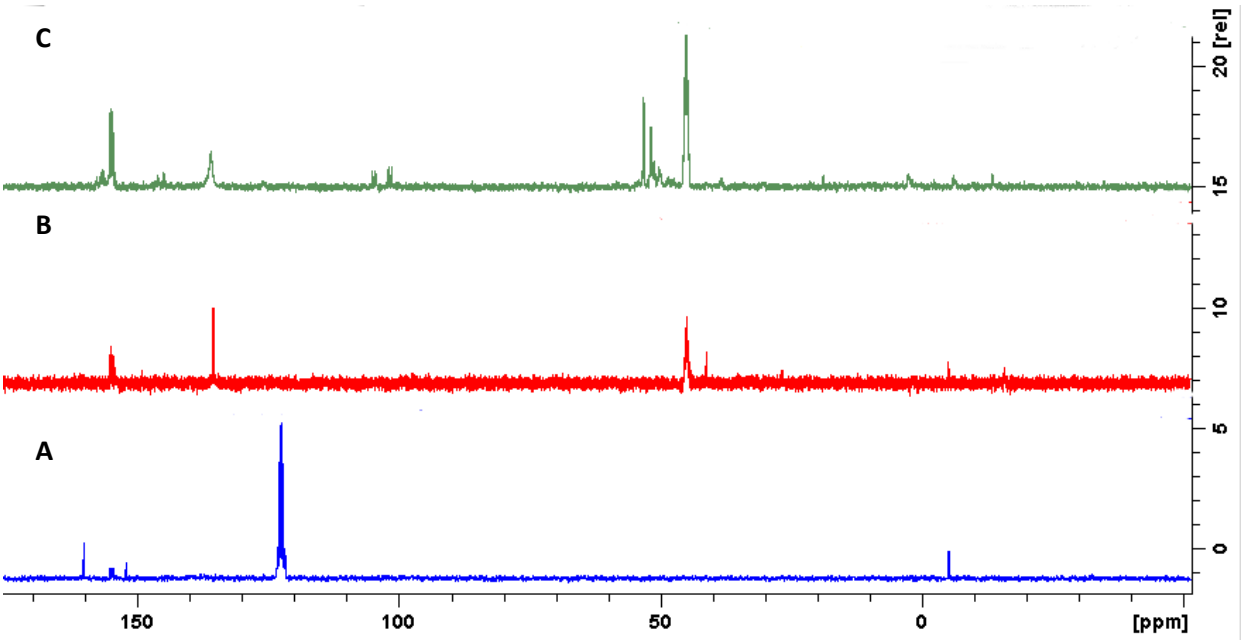


Figure A.1. Comparing $^{31}P\{^{1}H\}$ NMR spectra (121 MHz, C_6D_6) of **2.1** (**A**), **2.2** (**B**), and **2.2** with TMSOTf (**C**).

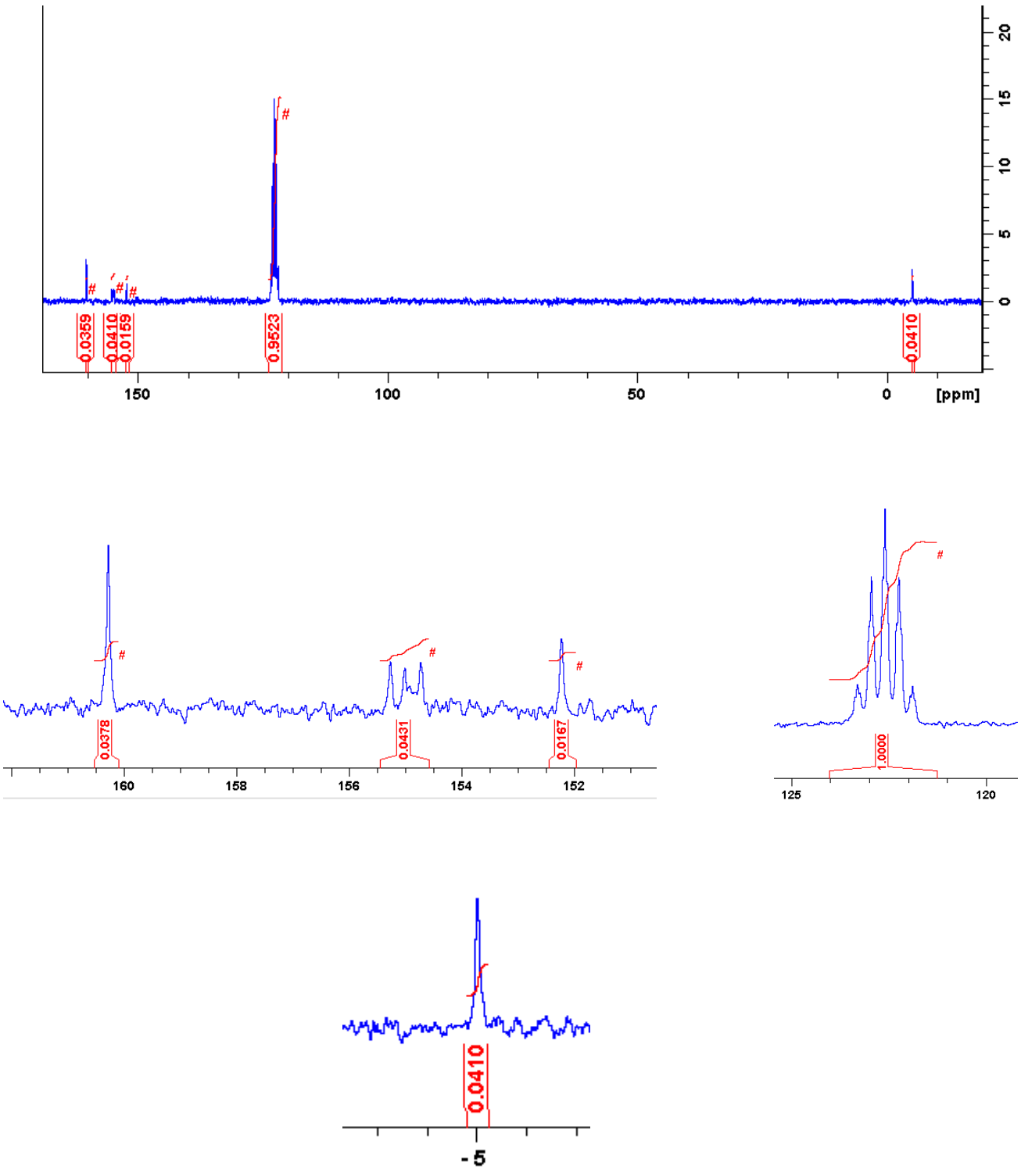


Figure A.2. $^{31}P[^{1}H]$ NMR spectrum of **2-1** (121 MHz, C_6D_6) (**B**).

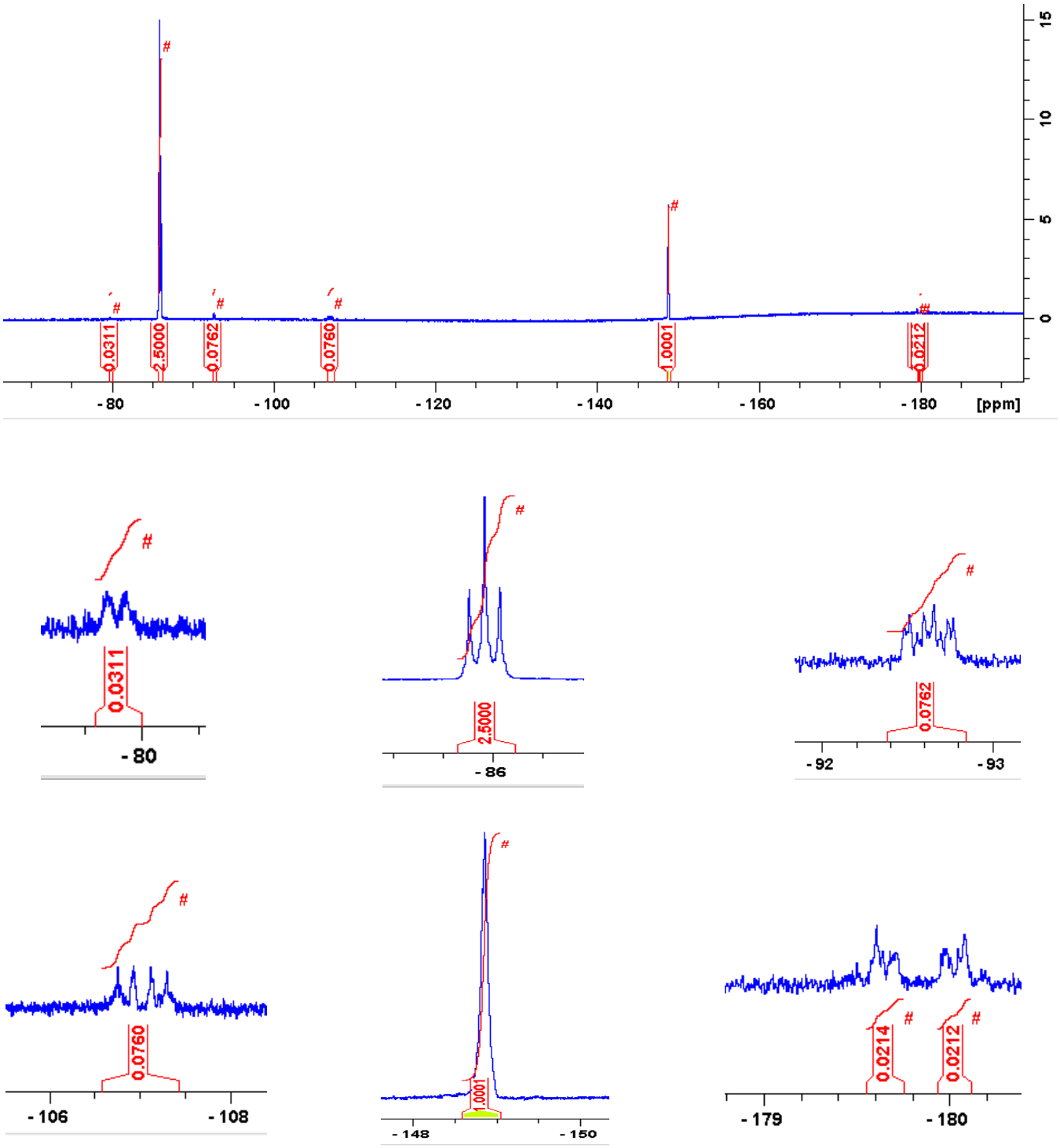


Figure A.3. ^{19}F NMR spectrum (282 MHz, C_6D_6) of **2-1** with insets (**A)**

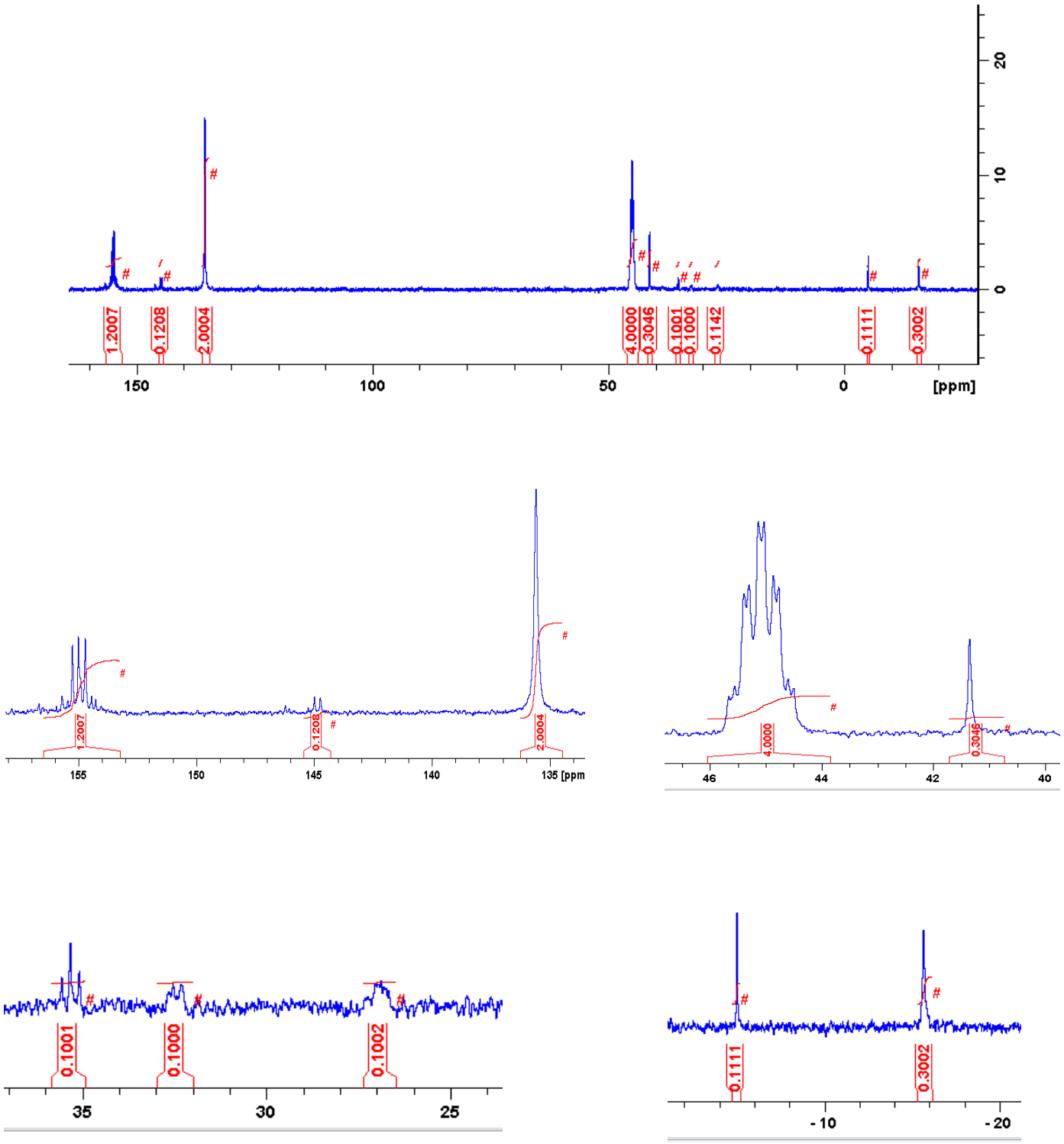


Figure A.4. $^{31}P[^{1}H]$ NMR spectrum of **2-2** (121 MHz, C_6D_6) (**B**).

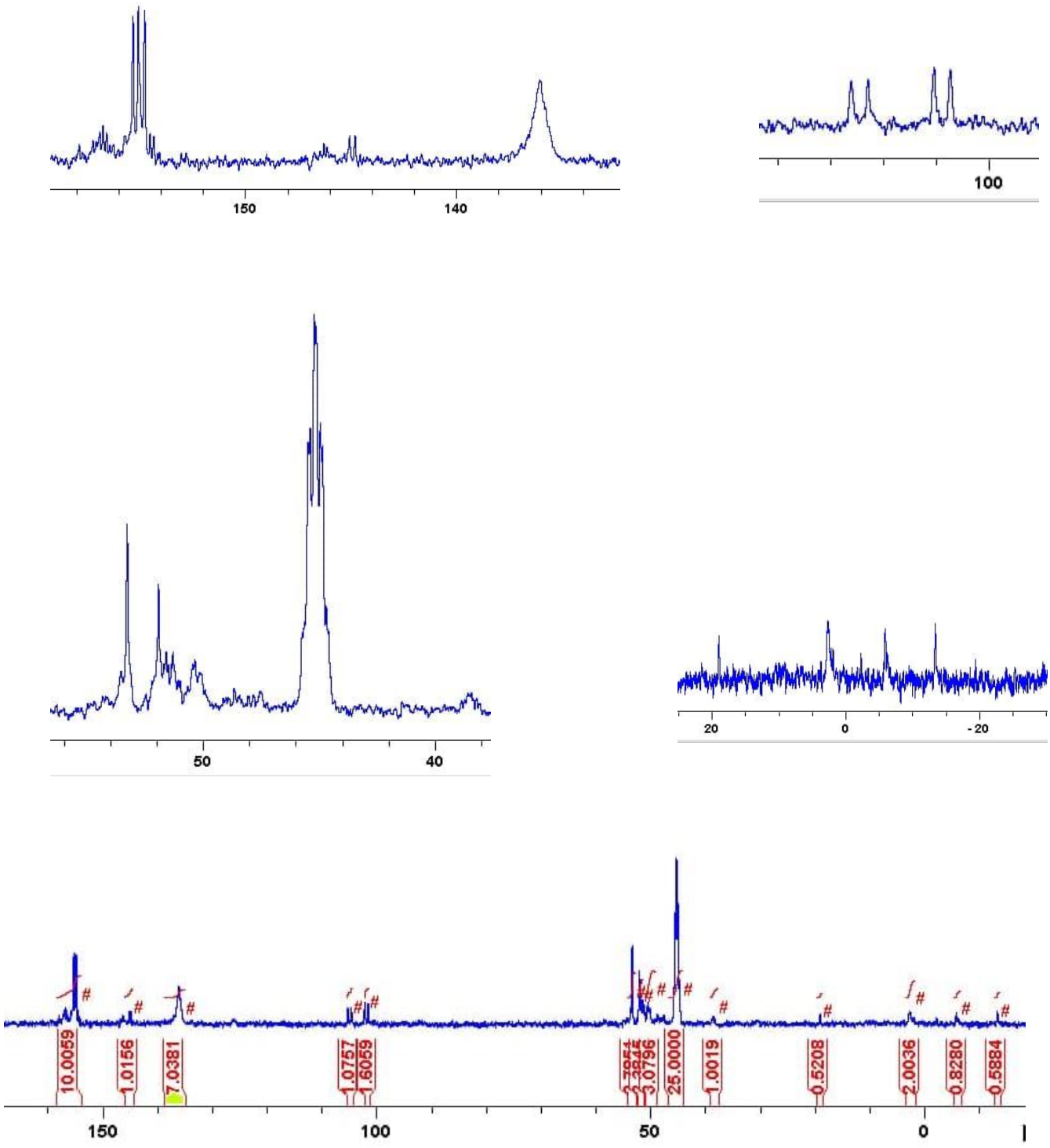


Figure A.5. New ^{31}P NMR resonances arising from reaction of **2-2** with TMSOTf in C_6D_6.

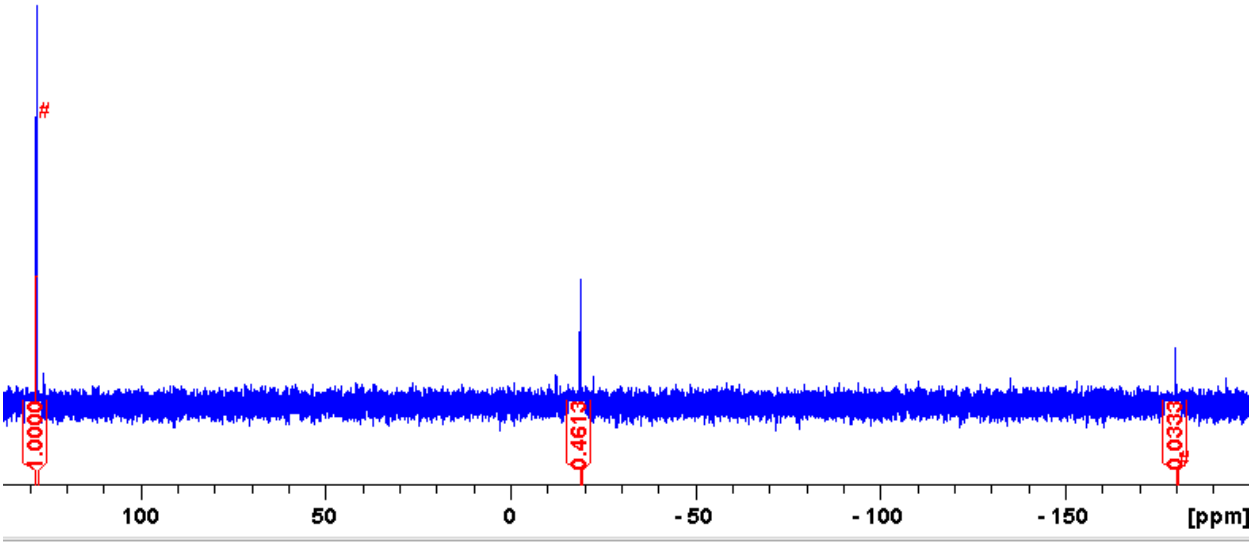


Figure A.6. ^{31}P NMR spectrum (121 MHz, C_6D_6) of $HCo[P(O^iPr)_3]_4$ **(3-1)** with HFP.

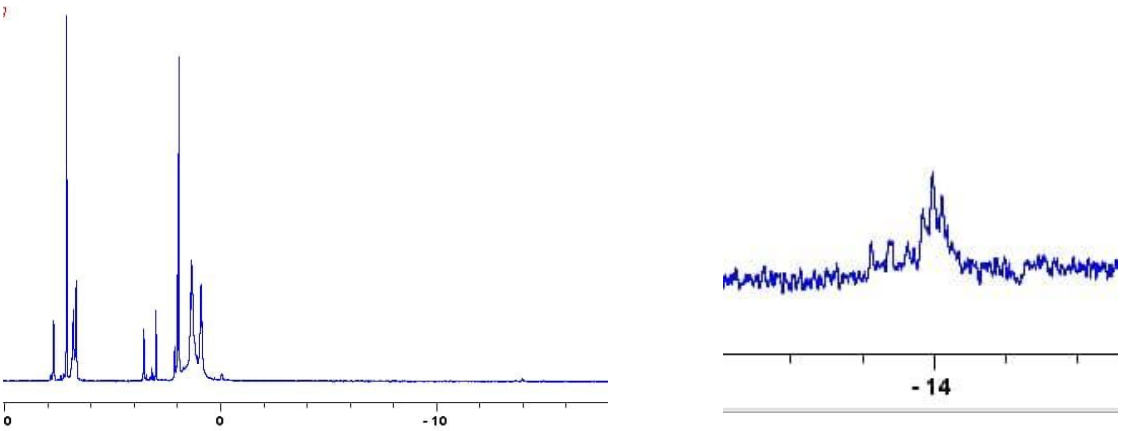


Figure A.7. ^1H NMR spectrum (300 MHz, C_6D_6) of $HCo[P(O\text{-}o\text{-tolyl})_3]_n$ (**3-2)**.

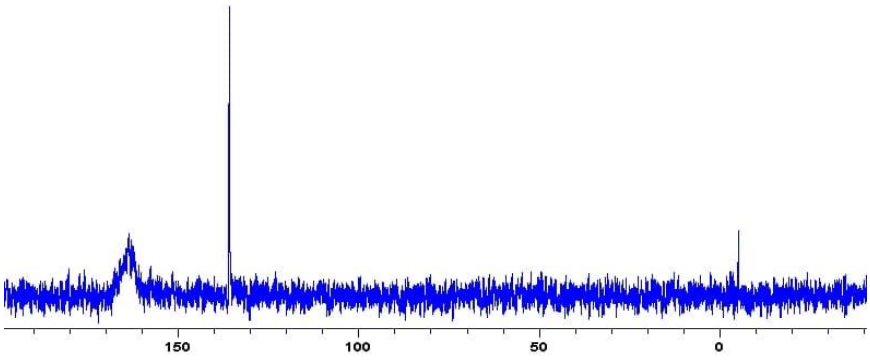


Figure A.8. $^{31}P[^1H]$ NMR spectrum (121 MHz, C_6D_6) of $HCo[P(O\text{-}o\text{-tolyl})_3]_n$ (**3-2)**.

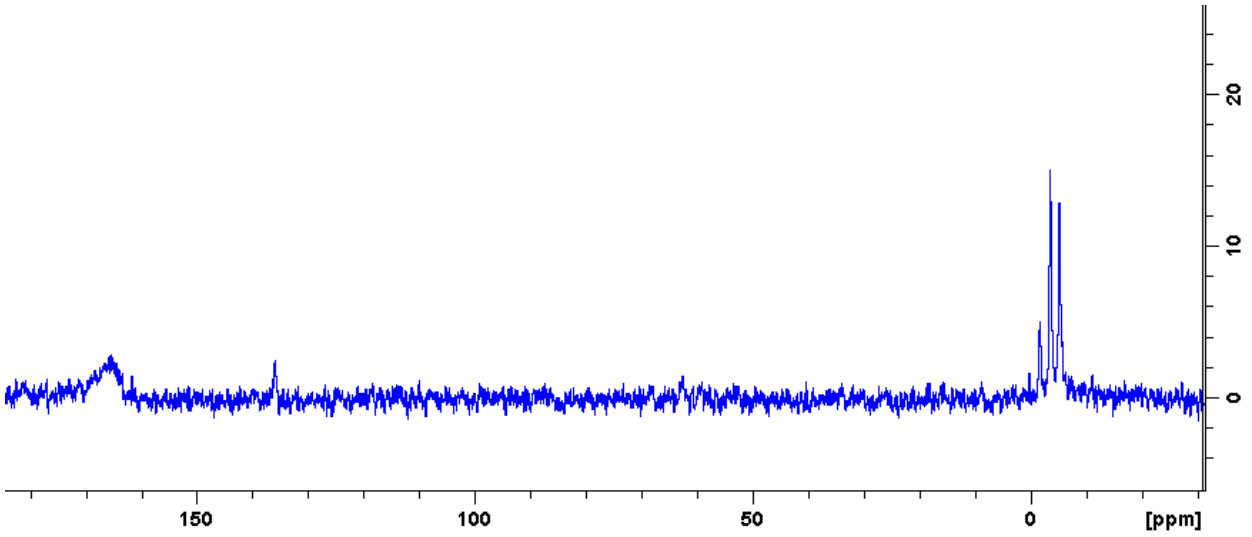


Figure A.9. $^{31}P[^{1}H]$ NMR spectrum (C_6D_6, 121 MHz) of reaction of $CoH[P(O\text{-}o\text{-}tol)_3]_n$ (**3-2**) with HFP.