Synthesis of Boron, Silicon, and Phosphorus Lewis Acids and Frustrated Lewis Pair Complexes for C=O and C-F Bond Activations

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Department of Chemistry
University of Toronto

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Abstract

The recent proliferation of main group catalysts and stoichiometric reagents useful in effecting transformations of organic molecules has been augmented by development of the chemistry of frustrated Lewis pairs (FLPs). In seeking to both complement and emulate the reactivity of transition metal catalysts, both the synthesis of new Lewis acids and FLPs and the discovery of new reactivity with organic substrates has been explored.

Boron Lewis acids such as $\text{B(C}_6\text{F}_5)_3$ and electrophilic borenium cations are among the most commonly employed main group catalysts, particularly for the hydrogenation of unsaturated bonds. The first chapter of this thesis details explorations in modulating the Lewis acidity of neutral and cationic boron electrophiles by tuning phosphinimine and phosphine-amine ligands. A family of compounds featuring a P-N-B motif are presented.

In seeking to broaden the range of main group catalysts, phosphorus Lewis acids have been explored. The third and fourth chapters presented herein detail the synthesis and catalytic activity of electrophilic phosphonium cations (EPCs). Synthesis of a chloride-substituted dication, and ferrocenyl-based mono- and dications are described, with a particular emphasis on their catalytic
activity in the deoxygenation of ketones. The fifth chapter details the synthesis of phosphorus cations which attempt to model intermediates in EPC-mediated catalysis.

Silylium cations are strongly fluorophilic and have previously been shown to cleave aliphatic C-F bonds. The final chapter presents examples of silylium cations in combination with weak phosphine Lewis bases for the selective cleavage of one C-F bond of an aryl-CF₃ functionality. The FLP-captured PhCF₂ is then converted to PhCF₂H, completing a formal hydrodefluorination process of PhCF₃ to PhCF₂H. Analogous reactivity is observed with aryl-CF₂ compounds.
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List of Symbols and Abbreviations

Å
angstrom, $10^{-10}$ m

°
Degrees

°C
degrees Celsius

δ
chemical shift

Δ
heat

ΔG
Gibbs free energy

ΔH
enthalpy

π
pi

σ
sigma

λ
lambda, wavelength

μL
microliters, $10^{-6}$ L

μmol
micromol, $10^{-6}$ mol

6-31G(d)
type of basis set

AIM
Quantum Theory of Atoms in Molecules

Anal
analytical

atm
atmospheres

B3LYP
a type of DFT exchange-correlational functional

br
broad

C₆D₅Br
deuterated bromobenzene

Calcd.
calculated

CD₂Cl₂
deuterated dichloromethane

CDCl₃
deuterated chloroform

C₇D₈
deuterated toluene

CF₃
trifluoromethyl

CHN
carbon, hydrogen, nitrogen

CO
carbonyl

Cp
cyclopentadienyl anion, $\eta^5$-C₅H₅

Cy
cyclohexyl, C₆H₁₀

d
doublet
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Mes  mesityl
MHz  megahertz, $10^6$ Hz
mg  milligram, $10^{-3}$ g
mL  millilitre, $10^{-3}$ L
mmol  millimol, $10^{-3}$ mol
m/z  mass-to-charge ratio
NBO  Natural Bond Order
NHC  $N$-heterocyclic carbene
NHP  $N$-heterocyclic phosphonium cation
NMR  Nuclear Magnetic Resonance
o  ortho
OTf  trifluoromethanesulfonate
p  para
Ph  phenyl
pH  measure of acidity and basicity (potential hydrogen)
POV-Ray  Persistence of Vision Raytracer
PR$_3$  tertiary phosphine
q  quartet
quint  quintet
Rw  weighted residual
r.t.  room temperature, 25 °C
s  singlet
SIMes  1,3-dimesitylimidazolidin-2-ylidene
T  temperature
t  triplet
td  triplet of doublets
THF  tetrahydrofuran
tm  triplet of multiplets
TMS  trimethylsilyl, Me$_3$Si
tol  toluene
rBu  $tert$-butyl
q quartet
QTAIM Quantum Theory of Atoms in Molecules
V volume
1.1 Acids and Bases

The word “acid” is derived from the Latin *acidus*, which comes from *acēre*, meaning “to be sour.”\(^1\) Similar in etymology to many scientific words, acid originates from a property immediately detectable by human sensory perception.\(^1\) With the advent of the scientific method and experimentalism in the 17th-century, the design of devices to enhance humans’ powers of perception allowed empirical science to extend its reach far beyond the limits imposed by sight, smell, taste, touch and hearing. Galileo’s telescopes are a famous early example. The dual developments of empirical measurement and observation, and the design of devices to enhance the scope of what could be measured and observed allowed the progress of modern science to accelerate rapidly over the past four centuries. In chemistry, this began the unsteady march towards the categorization of matter at the molecular and atomic thresholds, the concept of distinct particles replacing the apocryphal earth, water, wind and fire.\(^2\) It allowed the rationalization in molecular and atomic terms of properties long perceived by the senses.

The word “base” was defined in contrast to acids, by French chemist Guillaume Francois Rouelle in 1754. He noted that only certain substances formed solids in combination with acids, and wrote that such substances form a “base” for the resulting salt, giving the salt a solid form.\(^3\)

In 1884 Svante Arrhenius submitted a doctoral dissertation to the University of Uppsala in which he laid out his theory that salts dissociated into charged particles in solution; as an extension, he postulated that acids were substances that produced hydrogen ions in solution, and bases produced hydroxide ions.\(^4,5\) He received a fourth-class degree, later upgraded to third-class, but his dissertation aroused the interests of Ostwald, Clausius, and van’t Hoff, with whom Arrhenius exchanged ideas and who helped propagate his theories, culminating in his 1903 Nobel Prize.\(^4\) The two major subsequent iterations of acid-base theory, Brønsted and Lowry’s definition of acids as proton donors and bases as proton acceptors, and Lewis’s definition of acids as electron acceptors and bases as electron donors, were both formulated in 1923, though Lewis did not elaborate on his theory until 1938.\(^6\)
Because the properties of acids and bases such as taste, corrosiveness, and the exothermicity of neutralization reactions are so readily perceived, acid-base theory is one of remarkably few fundamental underpinnings of chemistry to have entered the popular lexicon. Lewis’ definition implied that fundamentally any two-electron chemical reaction resulting in the making and breaking of covalent bonds could fit within the acid-base paradigm. Within each acidic or basic molecule or ion, bonds were formed between a single basic electron donor atom and a single acidic electron acceptor atom. Unanswered was a corollary: in cases that acidic and basic sites were prevented from reacting with each other, might they react with something else?

1.2 The Frustrated Lewis Acid/Base Pair

Prevention of an electron donor atom from accessing an electron acceptor atom can be most easily accomplished by simple steric interference. Reactive atoms located in sites of molecules shielded by large functionalities of the molecule can be prevented from reacting, leading to a sterically frustrated Lewis pair (FLP). An early example of steric frustration of Lewis acid-base pairs was made by H.C. Brown, who, in a report remarkably portentous of developments six-to-seven decades later, reported in 1942 that the Lewis acid triphenylborane did not form an adduct with the Lewis base 2,6-lutidine (Scheme 1.1).7 In the same paper, he reported the adduct of boron trifluoride with 2,6-lutidine. Although not a FLP, Wittig reported a phosphonium borate zwitterion, featuring a phenyl moiety substituted at the 1-position by triphenylborate and at the 2-position by triphenylphosphonium (Figure 1.1).8 This structural motif was prescient of the motifs of intramolecular FLPs designed in the 2010’s, including one reported in Chapter 6 of this thesis. In addition, the proximity of two Lewis acidic centres is a strategy employed recently by researchers including the Stephan group,9-12 the Gabbai group,13-15 and the Jäkle group.16

\[
\begin{align*}
\text{A} & \xrightarrow{\text{BF}_3} \text{BF}_3 \\
\text{N} & \xrightarrow{\text{BPh}_3} \text{no reaction}
\end{align*}
\]

Scheme 1.1 Contrast in reactivity between BF3 and BPh3 with 2,6-lutidine.
Figure 1.1 Zwitterion reported by Wittig featuring phosphonium and borate functionalities.

Nonetheless, it required the activation of the inert H-H bond in 2006\(^1\) with a phosphine-borane intramolecular compound (Scheme 1.2) before the notion of deliberately utilizing unquenched Lewis acid/base pairs to effect other transformations took hold. Prior to this report and dating to the century-old Sabatier process of nickel-catalyzed transformation of CO\(_2\) and H\(_2\) to CH\(_4\) and H\(_2\)O, the history of activation of hydrogen gas was the exclusive purview of transition metals. Catalytic hydrogenation of unsaturated substrates has been central to the development of FLP chemistry since.\(^{18,19}\) A decade into this story, it remains to be seen whether specifically FLP-designed processes or the analysis of a wide range of reactivity within the FLP paradigm is most impactful.

Scheme 1.2 The first reported FLP H\(_2\) activation

1.3 Applications of Frustrated Lewis Pair Chemistry

While the notion of FLPs is one of fundamental acid-base theory, the direct application of this notion to enhance useful chemical technologies is also a sound objective. The great challenges of the twenty-first century including climate change, overpopulation, food and energy production and efficiency, waste processing, and continued progress in medicine are calls to service to which applied science must answer. Because each of these challenges is a material challenge, a challenge of matter, chemical science will be central to solutions. What role can FLPs play? The origin and trajectory of FLP chemistry has dictated that, at least in the first decade of the concept, FLPs have been tied closely to the renewed interest in chemistry of the main group elements, and inorganic chemistry generally.\(^ {18}\) Transition metal FLPs, while a growing subfield,\(^ {20}\) have not yet been as extensively explored as main group FLPs. This is partly due to the fact that initial FLP systems featured main group Lewis acids and bases, and thus much of the focus of FLP development has been on exploring the reactivity of
closely analogous systems. In addition, the fact that models of transition metal bond-forming and bond-breaking processes more rarely use lone pairs of electrons and arrow-pushing mechanisms to describe reactions may be a factor which thus far has limited the use of the FLP paradigm in describing their reactivity. Similarly, invocation of FLP mechanisms for heterogeneous catalytic processes is in its infancy.\textsuperscript{21,22} Wider applications of the FLP concept, such as in catalytic microfluidic processes using FLP catalysts,\textsuperscript{23,24} are beginning to be explored.

It remains to be seen how hydrogenation reactions applied in energy storage applications will be part of the solution to the clean energy challenges. Hydrogenation of unsaturates is broadly relevant to nutrition, materials, fine chemical and pharmaceutical applications, though whether main group FLP catalysts can ultimately compete with transition metal hydrogenation catalysts, with continued developments in efficiency and use of abundant metals,\textsuperscript{25,26} is an open question. Nonetheless, significant progress has been made on the use of FLP catalysts for asymmetric hydrogenations\textsuperscript{27} and FLPs have also been applied to specific hydrogenation reactions that are difficult to achieve with other catalysts, such as the hydrogenation of anilines.\textsuperscript{28}

1.4 Group 13 Lewis Acidic Boron Compounds

Lewis acids have been used as catalysts and co-catalysts long predating the FLP concept.\textsuperscript{29} In most examples, their fundamental role has been simply to withdraw electron density from a substrate, rendering the desired reactive site on the substrate electrophilic. This permits attack of the electrophilic site by an electron donor. Friedel and Crafts’ report of the alkylation of aromatic compounds via FeCl$_3$-mediated activation of alkyl halides in 1877 is the prototypical example.\textsuperscript{30} Since reports in the 1960’s, many modern industrial reactions employing Friedel-Crafts alkylation or acylations use AlCl$_3$ as the Lewis acid catalyst.\textsuperscript{31,32} Simple aluminum catalysts such as AlCl$_3$ and AlMe$_3$, and more complex aluminum catalysts for chiral transformations are widely employed in organic chemistry.\textsuperscript{33}

The trihalide compounds of boron, the lighter congener of aluminum, were investigated as Lewis acidic reagents beginning in the first half of the twentieth century.\textsuperscript{34} In the 1950s and 1960s alkyl- and aryl-substituted boron Lewis acids began to attract attention, resulting in the syntheses of C$_6$F$_5$-substituted boranes, including B(C$_6$F$_5$)$_3$.\textsuperscript{34-36} While sporadic applications of this Lewis acid were
reported over the next three decades, it was only in the 1990s that wider use of B(C₆F₅)₃ as a reagent was applied.³⁴ B(C₆F₅)₃ began to be used as an initiator for olefin polymerization catalysis. It initiated catalysis by abstracting an anionic ligand from group 4 metallocene pre-catalysts.³⁷ In addition, perfluoroaryl-substituted boron species such as HB(C₆F₅)₂ and the anion B(C₆F₅)₄ were increasingly used for hydroboration³⁸ and as a weakly-coordinating anion, respectively.³⁴,³⁷-³⁹ The expanded scope of reactivity of these perfluoroarylboron reagents inevitably led to an exploration of other variants of boron Lewis acids⁴⁰,⁴¹ and additional reactivity.⁴²,⁴³ The activation of non-polar H-H and Si-H bonds resulted in a proliferation of applications in synthesis, both in the context of FLP chemistry¹⁹,⁴⁴ and simply as Lewis acid catalysts.⁴¹

1.5 Group 14 Lewis Acidic Silicon Compounds

Group 14 compounds have also had a significant role in main group Lewis acid catalysis, particularly compounds of silicon.⁴⁵ Silyl ethers are extremely common protecting groups for alcohols in organic synthesis. While silicon is very oxophilic, it also has a high affinity for fluoride ion, permitting Si-O bond cleavage in the presence of fluoride ion in most cases. The fluorophilicity and chlorophilicity of silicon is also exploited in the use of reagents such as trimethylsilyltriflate as “masked Lewis acids,” capable of abstracting a chloride or fluoride ion from various functionalities.

Several recent examples of neutral silicon Lewis acids are worthy of note. The Gabbai group designed a “bidentate” Lewis acid featuring a sulfoxonium cation proximal to a neutral silane to capture fluoride ion,¹⁵ while Mitzel and co-workers sequestered CO₂ with the an intramolecular FLP featuring a neutral C₆F₅-substituted silicon centre as the Lewis acid.⁴⁶ Tilley and Bergman recently reported the hydrosilylation of aldehydes catalyzed by a bis(perfluorocatecholato)silane.⁴⁷

The instability of cationic silicon Lewis acids essentially precluded their practical use until the 1990s. In the 1990s, significant strides in the generation and isolation of silylium cations allowed for their exploitation in synthesis and catalysis. Generally, silylium cations are stabilized by π-donation from aromatic solvents,⁴⁸ although free [Mes₃Si]⁺ was reported with a carborane anion,⁴⁹ stabilized only by the steric protection afforded by bulky substituents. Very weakly coordinating anions are also
generally necessary. In a convergence of developments in electron-deficient group 13 and group 14 chemistry, \([\text{Et}_3\text{Si(tol)}][\text{B(C}_6\text{F}_5)_4]\) was reported in 1993.\(^{50}\)

Syntheses of silylium cations from silanes generally follow a few common synthetic methodologies. Abstraction of an equivalent of hydride ion with a more hydridophilic Lewis acid such as \([\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]\) (Scheme 1.2 A),\(^{50}\) or use of an allyl (Scheme 1.2B)\(^{51}\) or diene (Scheme 1.2C)\(^{52}\) leaving group is often employed.

![Scheme 1.3](image)

**Scheme 1.3** Three common methods for generation of silylium cations.

Silylium cations have been used recently in catalysis,\(^{53}\) to mediate Diels-Alder reactions of inert dienes,\(^{54,55}\) C–F bond activations including hydrodefluorination of fluoroalkanes,\(^{56}\) Friedel-Crafts hydrosilylation,\(^{57}\) reduction of imines,\(^{58}\) and dehydrogenative ring annulations.\(^{59}\) Due to their generally strongly Lewis acid nature and reduced stability, silylium cations are just beginning to be explored in FLP reactivity, with recent reported examples of CO\(_2\) sequestration by a silylium cation/nitrogen FLP\(^{60}\) and H\(_2\) activation by a silylium cation/silylene FLP.\(^{61}\)

### 1.6 Group 15 Lewis Acidic Phosphorus Compounds

The pnictogen elements also present opportunities for the synthesis of new Lewis acids, and are relatively less explored compared to group 13 and group 14 Lewis acids. Among the attractive properties of main group Lewis acid catalysts is their relative abundance and low cost compared to
many transition metal catalysts. Among the pnictogen elements, phosphorus accounts for the greatest proportion in the earth’s crust, with an abundance of 0.099%. Although there is some controversy over whether or not it will be necessary to reduce phosphorus consumption, the problem is not the absolute abundance of the element but the fact that phosphorus is widely distributed rather than concentrated in the crust, and thus can still be energy- and money-intensive to accumulate. Phosphorus is mainly sourced from phosphate rock, containing apatite, a group of various calcium phosphate minerals. This is currently relatively inexpensive, and is the feedstock for most commercial phosphorus compounds. Many P(III) compounds are derived from P₄, a product of phosphate reduction.

While phosphines are classically and ubiquitously used as basic L-type ligands in transition metal chemistry, the accessibility of the P(V) oxidation state also permits phosphines to act as Lewis acids. Phosphonium P(III) cations, phosphonium P(V) cations, and neutral P(V) phosphoranes have all shown the ability to be electron acceptors. Simple examples of the latter two categories include neutral PX₅ (X = F, Cl) compounds and [PX₆]⁻ anions. Perhaps the most famous examples of phosphorus Lewis acids in synthesis are the phosphonium ylide intermediates in the Wittig reaction. In the prototypical Wittig reaction mechanism, the Lewis acidity of a cationic phosphonium intermediate is key to initiating deoxygenation of the carbonyl substrate.

The first formal phosphenium cations were reported by Dimroth and Hoffmann in 1964 (Scheme 1.4). Charge delocalization, evident in these benzothiazolium salts, has been a recurring motif in stable phosphenium cations since. In a 1985 review, Cowley and Kempe emphasized the Lewis acidic nature of some of the early phosphenium cations. Methods of generating phosphenium cations have often involved chloride ion abstraction from chlorophosphine precursors and stabilization of the resulting phosphenium species by carbenes or weakly-coordinating anions. Some of the early examples included electrophilic reactions of phosphenium cations resulting in insertions into C-H bonds in Cp₂Sn, as well as reactions with 1,3- and 1,4-dienes to give cyclopentene-phosphonium derivatives.
In 2000, Nieger reported N-heterocyclic phosphenium cations isovalent to Arduengo-type N-heterocyclic carbenes. Computational and reactivity studies demonstrated that these cations possessed considerable Lewis acidity. Burford, Ragogna, and Power have all investigated the Lewis acid reactivity of phosphenium cations. In 2012, Slattery and Hussein computed fluoride ion affinity (FIA) values for a range of phosphenium cations, finding that some possessed greater fluorophilicities than the more common main group Lewis acids BF$_3$, BCl$_3$, AlCl$_3$, and SbF$_5$. FLPL H$_2$ activation with a 1,3,5-triphosphabenzene featured phosphorus as both Lewis base and Lewis acid, with experimental and computational evidence supporting a cationic phosphenium resonance contributor as the Lewis acid. An elegant report by Radosevich in 2014 featured a catalytic P(III)-P(V) redox cycle in the transfer hydrogenation of azobenzenes. Key was the ambiphilic nature of the geometrically-strained P(III) centre in the starting material, permitting oxidation to P(V) by formal oxidative addition of H$_2$ from amine-boranes. Gabbai has demonstrated that compounds featuring Lewis acidic borane functionalities have enhanced fluorophilicity when a proximal phosphonium centre is incorporated, resulting in a bridged fluoride ion binding mode.

Research in the Stephan laboratory focused on the synthesis of more strongly Lewis acidic phosphonium compounds. Design of these electrophilic phosphonium cations (EPCs) took inspiration from highly electrophilic boron Lewis acids, incorporating strongly electron-withdrawing substituents such as fluorinated aryl rings. While cation [P(C$_6$F$_5$)$_4$] has not been reported, EPC [(C$_6$F$_5$)$_3$PF] was readily accessed by oxidative fluorination of P(C$_6$F$_5$)$_3$ by XeF$_2$ followed by abstraction of fluoride ion with silicon Lewis acids. This proved strongly Lewis acidic, capable of effecting the catalytic defluorination of aliphatic fluorides (Scheme 1.5). The demonstration of this initial reactivity encouraged pursuit of both other phosphorus Lewis acids and other catalytic and stoichiometric reactivity.
Scheme 1.5 Catalytic hydrodefluorination of fluoroalkanes with an electron-deficient phosphonium cation catalyst.

A significant portion of this thesis details studies in the pursuit of these two goals. In analogy with the development of Lewis acidic borenium catalysts, EPCs were developed featuring multiple cationic charges as an alternative method of achieving high Lewis acidities, and hence catalytic activities.

Of both fundamental and practical interest is the investigation of the mechanisms by which these EPC catalysts operate. Pursuant to this, both computational studies and synthesis of analogues of proposed intermediates in catalytic C-F and C=O bond activations are detailed. Structurally-characterized adducts of borane and alane Lewis acids with silanes have been reported in recent years, yielding additional information on the mechanisms of Si-H activations by these catalysts.

Finally, the Lewis acidity of phosphonium cations has a long history of stoichiometric reactivity dating from reports of the Wittig reaction in the 1950’s. Carbon centres most commonly undergo substitution reactions by classic S_N1 or S_N2 mechanisms. Substitution of substituents at transition metal centres is commonly viewed within the association/dissociation or oxidative addition/reductive elimination paradigms. The nature of phosphorus hypervalency permits substitution by mechanisms best examined by association/dissociation models. Tetracoordinate phosphonium cations derive their Lewis acidity from the lowest-energy \( \sigma^* \) orbital, generally oriented opposite the bond to the most electronegative electronegative substituent. Electronic donation into this orbital results in a geometric change from tetrahedral to trigonal bipyramidal, with the donor substituent and the most electronegative substituent residing at the axial, or apical positions, and other substituents at the equatorial positions. The axial and equatorial substituents are then chemically inequivalent, with the axial substituents engaged in three-centre-four-electron bonding that can render them significantly more labile than the substituents in the equatorial positions. This promotes the loss of the apical substituents, and phosphonium compounds have been designed to favourably dispose certain functionalities to the apical position, favouring elimination and thus controlling reactivity. This type of mechanism has recently been harnessed to permit the cleavage of P-C bonds, generally quite
robust in tricoordinate phosphine or tetracoordinate phosphonium compounds. The final chapter of this thesis is devoted to harnessing this effect in conjunction with an FLP bond activation mode, in which a phosphine initially acts as a Lewis base to form a P-C bond resulting in a phosphonium cation, then subsequently this P-C bond is cleaved to liberate the apicophilic organic substituent as an anion which is protonated by water.

1.7 Scope of Thesis

The objective of the graduate research presented herein was to discover new main group Lewis acids that could mediate interesting and useful stoichiometric and catalytic reactivity. Both FLP chemistry and Lewis acid chemistry are explored. The initial work in Chapter 2 outlines the synthesis and design of new borane and borenium cationic Lewis acids. This work was undertaken in collaboration with post-doctoral fellows Dr. Michael Holthausen and Dr. Rebecca Melen. These compounds feature a P-N-B motif, with the boron centre either ligated by phosphinimine or phosphine-amine functionalities, either neutral or bearing a formal positive charge. The objective was not to synthesize the most powerful Lewis acidic boranes but to synthesize boranes and borenium cations where the Lewis acidity could be rationally modulated based on tuning of the substituents of the P-N ligands. Though these P-N-B complexes proved ineffective for several FLP-type transformations, they did demonstrate Lewis acidity at the boron centre resulting in thermally-induced intramolecular aromatic C-F activation, resulting in the formation of cationic phosphonium centres, reactivity that presaged later themes of this graduate work.

The design and reactivity of electrophilic phosphonium cations (EPCs) is presented in Chapters 3 and 4, with the synthesis and reactivity of cationic and dicationic EPCs detailed. The use of these EPCs in catalysis is explored, with a focus on the catalytic deoxygenation of ketones in the presence of silanes. The initial deoxygenation reactivity of EPCs was investigated by post-doctoral fellow Dr. Michael Holthausen and Ph.D. student Meera Mehta. Where relevant, examples of their work are presented in Chapter 3. The synthesis and catalysis of the catalyst presented was solely the work of this author, as was all of the synthesis, catalysis and electrochemistry presented in Chapter 4. Variations in the deoxygenation of different ketone substrates are analyzed and a mechanism calculated by Professor Stefan Grimme and Dr. Zheng-Wang Qu at the Mulliken Center for Theoretical Chemistry at the University of Bonn is presented.
Chapter 5 explores the synthesis of bifunctional naphthyl compounds with the goal of examining interactions between phosphonium cations and functionalities relevant to EPC catalysis. Synthesis of naphthyl-based silylphosphines and a trifluoromethylphosphonium cation is detailed. Analysis of the solid-state structure and variable-temperature NMR spectra presented evidence of an interaction between a phosphonium centre and a proximal CF$_3$ functionality. To corroborate this, Natural Bond Order (NBO) calculations were undertaken, complemented by analysis using the Quantum Theory of Atoms in Molecules (QTAIM or AIM) with the assistance of post-doctoral fellow Dr. Timothy Johnstone and Ph.D. student Levy Cao. Details of this analysis are presented. The final section of this chapter details a palladium-phosphonium cation naphthyl complex, synthesized with the goal of inducing a Z-type interaction between Pd and P. This work was undertaken in collaboration with Ruben Mirzoyan, an undergraduate student whose project this author supervised.

Chapter 6 explores silylium cation-phosphine FLPs in aliphatic C–F bond activations. The research presented in this chapter represents an unexpected confluence of themes of the preceding chapters, exploring a naphthyl compound in FLP-type C–F bond activation resulting in the formation of phosphonium cations. Although this work was initially targeted toward developing a fluoroalkyl-substituted phosphonium cation, the C–F bond activation aspect presented a more interesting topic of exploration. Proximity of a phosphine Lewis base to the silylium cation permitted activation of a single C–F bond from aryl-CF$_3$ functionalities. The intramolecular FLP system presented was initially synthesized by post-doctoral fellow Dr. Adam Ruddy, and investigated for different reactivity by Dr. Ruddy and Ph.D. student Alex Waked. A formal single-fluoride ion hydrodefluorination process is presented. In addition, calculations undertaken by Professor Stefan Grimme and Dr. Hui Zhu at the Mulliken Center for Theoretical Chemistry at the University of Bonn explore the mechanism of the initial C–F activation of the naphthyl compound. Work in this area is ongoing.
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Chapter 2: Synthesis and Reactivity of Phosphinimine-Substituted Boranes and Borenium Cations

2.1 Introduction

2.1.1 Phosphinimine Complexes of Transition Metals and Boranes

Phosphinimine-based ligands are valued in transition metal chemistry for their structural diversity and electronic tunability.\(^1\) They can act as \(\sigma\)-donors and \(\pi\)-donors. Phosphinimine complexes of early transition metals are particularly useful as effective catalysts for olefin polymerization.\(^2\)\(^-\)\(^6\) However, related boron-based compounds featuring phosphinimine substituents have been much less investigated.\(^7\) Dehnicke and co-workers have reacted mixtures of \(\text{BX}_3\) (\(X = \text{F, Cl, Br}\)) and silylated phosphinimines of type \(\text{R}_3\text{P}=\text{NSiMe}_3\) (\(R = \text{alkyl, aryl}\)) in various stoichiometries. They reported the formation of four-membered heterocycles of type \((\text{R}_3\text{P}=\text{NBX}_2)_2\) and derivatives thereof.\(^8\)\(^-\)\(^10\) The Dehnicke group also reported the \(\text{tris}\)-phosphinimine-substituted species \((\text{Ph}_3\text{P}=\text{N})_3\text{B}\) obtained by reaction of \(\text{BCl}_3\) with three equivalents \(\text{Ph}_3\text{PNLi}\).\(^11\)

Our group prepared the dichloroborane \(t\text{Bu}_3\text{P}=\text{NBCl}_2\) by reaction with the sterically-demanding \(t\text{Bu}_3\text{PNLi}\) with \(\text{BCl}_3\).\(^12\) Reaction of \(\text{BH}_3(\text{SMe}_2)\) with two equivalents of \(t\text{Bu}_3\text{P}=\text{NH}\) resulted in the \(\text{bis}\)-phosphinimine borane \((t\text{-Bu}_3\text{P}=\text{N})_2\text{BH}\); subsequent abstraction of hydride yielded the linear borinium ion salt \([(t\text{-Bu}_3\text{P}=\text{N})_2\text{B}]\text{[B(C}_6\text{F}_5]_4}\), stabilized by both the bulk and \(\pi\)-donation of the ligand.\(^13\) In addition, we investigated steric effects that influence reactions between phosphinimines and catechol or pinacol boranes.\(^14\),\(^15\) In these cases either monomeric boranes such as \(\text{R}_3\text{P}=\text{NB}(\text{O}_2\text{C}_2\text{Me}_4)\) or dimeric heterocycles of type \((\text{R}_3\text{P}=\text{NB}(\text{O}_2\text{C}_6\text{H}_4)_2)\) are observed.

A few phosphinimine-borane adducts of type \(\text{R'}_3\text{PN}^-\text{BR}_2\) have been reported\(^12\),\(^16\)\(^-\)\(^18\) with some combinations showing FLP-type chemistry.\(^19\) However, to the best of our knowledge, related borenium ions of type \([\text{R'}_3\text{PNR}^-\text{BR}_2]^+\) have not been reported in the literature. It has been demonstrated that incorporation of a positive charge enhances the electrophilicity of boron centres, allowing borenium cations to act as effective catalysts in a variety of transformations including hydrogenations of unsaturated compounds,\(^20\)\(^-\)\(^27\) hydroboration of alkenes,\(^28\) \(\text{trans}\)-hydroboration of alkynes,\(^29\) borylation of aromatic\(^30\) and aliphatic\(^31\) compounds, hydrosilylation of ketones,\(^32\),\(^33\) enantioselective Diels-Alder
reactions\textsuperscript{34} and even oxidation of dihydrogen in combination with electrochemical methods.\textsuperscript{35} It was envisioned that accessing a family of borenium ion salts [R’\text{3}P=NR”−BR\text{2}]\textsuperscript{+} by alkylation of the imine-N atom of phosphinimine-substituted boranes would be interesting. With significant steric and electronic variation possible by choosing different organic substituents on the phosphorus, nitrogen or boron atoms, it would be possible to tune the Lewis acidity and reactivity of these cations.

### 2.2.1 Synthesis of Phosphinimine-Substituted Boranes

Several approaches to synthesizing phosphinimine-substituted boranes R’\text{3}P=N−BR\text{2} could be envisioned. Reaction of phosphinimines R’\text{3}P=NH with boranes R\text{2}BH (Scheme 2.1A), or reaction of trimethylsilyl-substituted phosphinimines with haloboranes R\text{2}BX (Scheme 2.1B) would result in the desired products via elimination of H\text{2} or TMSX, respectively. A new approach to phosphinimine-substituted boranes was also recently developed in our group based on Staudinger oxidation of phosphines R\text{3}P with boron azides R\text{2}BN\text{3} (Scheme 2.1C) resulting in the desired phosphinimine-substituted boranes via N\text{2} elimination.\textsuperscript{36} This was complemented by a report from Bertrand and co-workers, who used azidophosphines R\text{2}PN\text{3} in reactions with Mes\text{2}BF to prepare phosphinimine-substituted boranes R\text{2}FP=NBMes\text{2}.\textsuperscript{37} This was mediated by photolytic release of N\text{2} and resulted in migration of the fluoride ion from boron to phosphorus. It was decided to focus synthetic approaches on the strategies of Scheme 2.1B and C.

![Scheme 2.1: Approaches to synthesizing phosphinimine-boranes R’\text{3}PN−BR\text{2}](image)

\textbf{Scheme 2.1:} Approaches to synthesizing phosphinimine-boranes R’\text{3}PN−BR\text{2}
In collaboration with post-doctoral fellow Dr. Michael Holthausen, a range of tertiary phosphinimine-substituted boranes of varying steric and electronic character were prepared in good yields.\(^{38}\) Previously, post-doctoral fellow Dr. Rebecca Melen had reported compounds of the type Cy\(_2\)BN=PR’\(_3\) in a separate report (Scheme 2.2).\(^{36}\) Although the preparations of compounds 2-1, 2-2, 2-3, 2-8 and 2-9 are depicted by reaction of TMS-substituted phosphinimines with R\(_2\)BX, these compounds could also be prepared by Staudinger oxidation of their respective tertiary phosphine starting materials with boron azides R\(_2\)BN\(_3\). Compounds 2-10, 2-11, 2-12, and 2-13 were prepared exclusively by the latter route, while 2-4, 2-5, 2-6, and 2-7 were prepared exclusively by the former route.

**Scheme 2.2: Synthesis of phosphinimine-boranes 2-1 to 2-13**

These compounds were characterized by multinuclear NMR spectroscopy and solid-state structures were obtained for 2-1, 2-3 and 2-6, (Figure 2.1) while structures for 2-10, 2-11 and 2-12 were previously reported by Dr. Melen.\(^{36}\) The \(^{11}\)B and \(^{31}\)P NMR resonances for these compounds are tabulated in Table 2.1. While the chemical shift range of the \(^{11}\)B resonances are characteristic of the R groups on these R’\(_3\)P=N-BR\(_2\) compounds (R = Mes: \(\delta = 44-48\) ppm; R = 9-BBN: \(\delta = 51-56\) ppm; R = C\(_6\)F\(_5\): \(\delta = 33-37\) ppm; R = Cy: \(\delta = 48-52\) ppm), those species with more strongly donating substituents on the phosphorus
atom exhibit $^{11}$B NMR chemical shifts which are slightly upfield in the order $t$Bu $\approx$ Cy $<$ Et $<$ Ph, representative of more $\pi$-character in the N-B bond and hence more electron density at the boron atom.

**Figure 2.1** POV-ray depiction of **2-1** (top left), **2-3** (top right) and **2-6** (bottom) with H atoms omitted for clarity. C: black; P: orange; B: green-copper; N: blue.

**Table 2.1** $^{31}$P{$^{1}$H} and $^{11}$B{$^{1}$H} NMR parameters for compounds **2-1** to **2-13**

<table>
<thead>
<tr>
<th></th>
<th>$^{31}$P{$^{1}$H}</th>
<th>$^{11}$B{$^{1}$H}</th>
<th>$^{31}$P{$^{1}$H}</th>
<th>$^{11}$B{$^{1}$H}</th>
<th>$^{31}$P{$^{1}$H}</th>
<th>$^{11}$B{$^{1}$H}</th>
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<tbody>
<tr>
<td><strong>2-1</strong></td>
<td>22.1</td>
<td>45.3</td>
<td>22.8</td>
<td>53.1</td>
<td>16.0</td>
<td>37.0</td>
</tr>
<tr>
<td><strong>2-2</strong></td>
<td>18.8</td>
<td>44.5</td>
<td>6.5</td>
<td>56.1</td>
<td>14.7</td>
<td>50.0</td>
</tr>
<tr>
<td><strong>2-3</strong></td>
<td>4.8</td>
<td>48.0</td>
<td>33.3</td>
<td>51.8</td>
<td>17.6</td>
<td>48.5</td>
</tr>
<tr>
<td><strong>2-4</strong></td>
<td>34.8</td>
<td>53.4</td>
<td>31.5</td>
<td>33.8</td>
<td>0.8</td>
<td>52.0</td>
</tr>
<tr>
<td><strong>2-13</strong></td>
<td>33.3</td>
<td>49.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.2 Solid-state P-N=B bond angles of compounds 2-1, 2-3, 2-6, 2-10, 2-11, 2-12

<table>
<thead>
<tr>
<th>Bond Angle(°)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>140.5(1)</td>
</tr>
<tr>
<td>2-3</td>
<td>137.3(1)</td>
</tr>
<tr>
<td>2-6</td>
<td>130.9(1)</td>
</tr>
<tr>
<td>2-11</td>
<td>145.0(2) av</td>
</tr>
<tr>
<td>2-12</td>
<td>141.51(8)</td>
</tr>
<tr>
<td>2-13</td>
<td>162.8(1)</td>
</tr>
</tbody>
</table>

In the solid state, very similar N-B bond lengths of 1.394(4) Å (av.) for 2-1, 1.402(2) Å for 2-3 and 1.409(2) Å for 2-6 are exhibited. Solid-state bond lengths reported for 2-11, 2-12, and 2-13 were 1.398(4), 1.408(2) (av.), and 1.388(2), respectively. As expected, these are between the range typical for N-B single and double bond lengths and similar to that reported for the bis-phosphinimine-borane (t-Bu₃PN)₂BH (1.41(5) Å)\(^{13}\). The variance in the observed N-B bond lengths is consistent with the trend observed for the \(^{11}\)B NMR chemical shifts with Ph₃P derivatives 2-3, 2-6 and 2-12 exhibiting slightly longer bond lengths than Et₃P derivative 2-1, Cy₃P derivative 2-11 or tBu₃P derivative 2-13. However, the differences are relatively small, with the longest and shortest N-B bond lengths in these structures varying by only 0.02 Å. These NMR and structural trends indicate that tuning the substitution on the phosphorus atom gives rise to small but predictable differences in the electronic environment about the boron atom, confirming our hypothesis that using phosphinimine ligands would permit fine-tuning of electron density at boron atoms of P=N-B-type complexes.

The P=N-B bond angles for these structurally-characterized compounds are given in Table 2.2. Consistent with the N-B bond lengths observed, which indicate considerable \(\pi\)-donation from the nitrogen atom to the boron atom, all of these angles fall between 120° and 180°, the angles expected for \(sp^2\) or \(sp\) hybridization extremes at nitrogen. Derivative 2-13, featuring tert-butyl substituents at the phosphorus atom, exhibited by far the largest bond angle at 162.8(1)°, while 2-11, featuring cyclohexyl
substituents at the phosphorus atom, exhibits the second-largest angle at 145.0(2)°. While these can be rationalized by electronic arguments, as tert-butyl and cyclohexyl substituents are the most electron-donating and hence would impart the most electron density into the N-B bond, these substituents are also by far the largest sterically with Tolman cone angles of 182° and 170° for tBu3P and Cy3P, respectively.39 Furthermore, derivatives 2-1, 2-3, 2-6, and 2-12 all exhibit bond angles in the range of 137-142°, despite the fact that 2-1 has electron-donating ethyl substituents at phosphorus while 2-3, 2-6 and 2-12 have electron-withdrawing phenyl substituents. Tolman cone angles for Et3P and Ph3P are 132° and 145°, respectively.39 Thus, justification of the observed P=N-B angles based on the cone angles of the phosphine functionalities may be of greater importance than variances in electron donation.36

### 2.2.2 Synthesis of Phosphinimine-Substituted Borenium Ions

While the above borane compounds exhibited the expected tunability based on steric and electronic design of the phosphinimine ligands, the N-B π-donation significantly quenches the electrophilicity of the boron atom, and hence, these were not expected to be strong Lewis acids. Methylation of the nitrogen atom to quench the π-basicity would give rise to formal borenium cations. Resonance forms are depicted in Figure 2.2.

![Figure 2.2](image)

**Figure 2.2** Canonical resonance depictions of compounds [R’₃P=N(Me)BR₂]⁺

Synthesis of these types of cations was investigated by reaction of boranes with MeOTf (Scheme 2.3). In most cases, N-methylation of 2-4–2-13 proceeds cleanly giving products 2-14 – 2-20 in good yields with the exceptions of 2-7 and 2-9. In the case of 2-7, it is hypothesized that the tert-butyl groups at phosphorus precluded methylation of the nitrogen atom due to steric interference. In the case of C₆F₅-substituted borane Ph₃P=NB(C₆F₅)₂ 2-9, the lack of reactivity with MeOTf is attributed to electronic factors. Methylation of Et₃P=NB(C₆F₅)₂ 2-8, featuring more electron-donating ethyl groups at the
phosphorus atom, was successful to yield 2-17, indicating that the electronic threshold for methylation of the imine nitrogen atom lies between 2-8 and 2-9. This affirmed the hypothesis that subtle electronic variation in these complexes could result in differing reactivity. The $^{11}$B and $^{31}$P NMR shifts of these phosphinimine-borenium ion compounds are tabulated in Table 2.3.

![Scheme 2.3 Synthesis of salts 2-14 – 2-20](image)

**Table 2.3** $^{31}$P{$^1$H} and $^{11}$B{$^1$H} NMR Parameters for Compounds 2-14 to 2-20

<table>
<thead>
<tr>
<th></th>
<th>$^{31}$P{$^1$H}</th>
<th>$^{11}$B{$^1$H}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-14</td>
<td>73.3</td>
<td>61.7</td>
</tr>
<tr>
<td>2-15</td>
<td>43.9</td>
<td>62.9</td>
</tr>
<tr>
<td>2-16</td>
<td>66.2</td>
<td>64.3</td>
</tr>
<tr>
<td>2-17</td>
<td>80.9</td>
<td>39.0</td>
</tr>
<tr>
<td>2-18</td>
<td>74.8</td>
<td>56.7</td>
</tr>
<tr>
<td>2-19</td>
<td>72.7</td>
<td>57.5</td>
</tr>
<tr>
<td>2-20</td>
<td>47.7</td>
<td>58.8</td>
</tr>
</tbody>
</table>

Compounds 2-18, 2-19, and 2-20 exhibited downfield shifts of 10-13 ppm in the $^{11}$B NMR spectra compared to precursors 2-1, 2-2, and 2-3, while 2-14, 2-15, 2-16 and 2-17 exhibited slightly smaller downfield shifts of 7-9 ppm. These modest shifts in the $^{11}$B NMR resonances compared to their borane precursors were consistent with modestly reduced electron density at the boron atom.

Solid-state structures were obtained for 2-16, 2-17 and 2-20 (Figure 2.3). For each of these compounds, the P=N-B angle is much closer to 120° than in the solid-state structures of the precursor boranes, indicating more sp$^2$ character about the nitrogen atom. The N-B bonds are slightly elongated from the precursors but are still shorter than typical N-B single bond lengths of c.a. 1.51 Å.$^{12,16-18,36}$ This is indicative of the contribution of resonance form B depicted in Figure 2.2, in which the electron
density from the P=N π-bond is localized at the nitrogen atom and thus available for π-donation into the empty p-orbital at the boron atom. This model is also correlated by the observed $^{31}$P NMR chemical shifts of 2-16 and 2-17, which are in the range typical of many R$_3$PX phosphonium cations.

Figure 2.3 POV-ray depiction of cations of 2-16 (top left), 2-17 (top right) and 2-20 (bottom) with H atoms and [OTf] anions omitted for clarity. C: black; P: orange; B: green-copper; N: blue.

Table 2.4 $^{31}$P{$_{^1}$H} and $^{11}$B NMR parameters for compounds 2-16, 2-17, 2-20

<table>
<thead>
<tr>
<th></th>
<th>P-N (Å)</th>
<th>N-B (Å)</th>
<th>P-N-B (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-16</td>
<td>1.670(2)</td>
<td>1.443(3)</td>
<td>122.2(1)</td>
</tr>
<tr>
<td>2-17</td>
<td>1.704(2)</td>
<td>1.404(3)</td>
<td>129.5(1)</td>
</tr>
<tr>
<td>2-20</td>
<td>1.682(2)</td>
<td>1.456(3)</td>
<td>127.2(2)</td>
</tr>
</tbody>
</table>
Both neutral P=N-B compounds 2-1–2-13 and their cationic analogues were examined for FLP-type reactivity with H₂, CO₂, and various alkynes. No activation of either H₂ or CO₂ was observed, and though some possible interaction with the C-C π-electrons was evinced by the formation of coloured solutions upon addition of alkyne PhCCH, no evidence was obtained for 1,2-addition of the FLP complexes.

2.3.1 Synthesis of Phosphine-Amine-Substituted Boranes and Borenium Ions

In contrast to the reactivity of boron azides with tertiary phosphines, reaction of boron azide (C₆F₅)₂BN₃ with secondary phosphines tBu₂PH and (C₅H₉)₂PH (Scheme 2.4) yielded the P(III) P-N-B linked compounds resulting from the prototropic tautomerization depicted in Figure 2.4. The P(V) tautomers, which would have been easily distinguished by one-bond P-H coupling in the ³¹P and ¹H NMR spectra, were not observed. 2-21 exhibited a singlet in the ³¹P{¹H} NMR spectrum at 74.4 ppm and a singlet in the ¹¹B NMR spectrum at 39.3 ppm. 2-22 exhibited a singlet in the ³¹P NMR spectrum at 54.3 ppm and a singlet in the ¹¹B NMR spectrum at 38.8 ppm.

Scheme 2.4 Synthesis of phosphine amine-boranes 2-21, 2-22 and salt 2-23

Figure 2.4 Tautomerization of P(V)-N-B compounds to P(III)-N-B

25
As significant quantities of tBu$_2$PH were available and 2-21 and 2-22 did not show appreciable electronic differences, it was decided to focus on deriving a cation from 2-21. Addition of MeOTf to 2-21 in toluene resulted in rapid methylation of the phosphorus atom resulting in salt 2-23 (Scheme 2.4). 2-23 exhibited a singlet in the $^{31}$P NMR spectrum at 76.8 ppm and a singlet in the $^{11}$B NMR spectrum at 36.7 ppm. These resonances are shifted by only 2-3 ppm from 2-21, indicating that N-methylation had only a slight effect on the electronic environments of the adjacent phosphorus and boron atoms. The methyl protons appeared as a doublet at 1.14 ppm in the $^1$H NMR spectrum with $^2J_{PH} = 16$ Hz.

Heating 2-23 to 110$^\circ$ C in toluene for forty-eight hours resulted in quantitative formation of a new product. The $^{31}$P NMR spectrum exhibited a singlet at 85.3 ppm while the $^{11}$B NMR spectrum exhibited a doublet at 4.3 ppm. The $^{19}$F NMR spectrum was significantly more complex than 2-21, showing eight resonances, integrating in a 2:2:1:1:1:1:1:1 ratio. The resonance at -155.1 ppm was a broad doublet indicative of 1-bond B-F coupling. Based on the NMR evidence we postulated the formation of zwitterionic compound 2-24. This structural formulation was confirmed by x-ray diffraction analysis (Figure 2.5). Though the data was not of sufficient quality to report accurate values for bond lengths and angles, it demonstrated the atomic connectivity of the structure. 2-24 is the result of attack of the basic phosphine at the ortho carbon atom of one of the C$_6$F$_5$ rings of the borane, resulting in formation of the five-membered C-C-P-N-B heterocycle and migration of fluoride ion to the boron atom. Similar intramolecular reactivity has been observed with other C$_6$F$_5$-substituted boranes featuring proximal basic phosphines.$^{40-42}$

![Figure 2.5 POV-ray depiction of zwitterion 2-24 with H atoms omitted for clarity. C: black; P: orange; B: green-copper; N: blue; F: magenta](image-url)
This reactivity is some evidence that the boron centre in compound 2-21 has considerable Lewis acidity, as it acts as a fluoride ion acceptor to form zwitterion 2-24. It would certainly be conceivable that, were the Lewis acidity at the boron atom quenched, the fluoride ion would act as a non-coordinating counter ion when displaced. It is well-established that \( \text{C}_6\text{F}_5 \) rings are susceptible to nucleophilic aromatic substitution at the ortho and para-positions; indeed this is the mechanism by which the first intramolecular phosphorus-boron FLP capable of hydrogen activation was synthesized.\(^{43}\)

**Scheme 2.5** Formation of zwitterion 2-25 and salt 2-26

Reaction of 2-24 with one equivalent of [Et\(_3\)Si(tol)][B(\(\text{C}_6\text{F}_5\))\(_4\)] resulting in formation of Et\(_3\)SiF in the reaction mixture, presumably resulting from abstraction of fluoride ion from the boron atom. A solid was isolated and analysed by multinuclear NMR spectroscopy. The \(^{31}\text{P} \) NMR spectrum exhibited a clean singlet at 101.0 ppm, consistent with a considerably more electron-deficient phosphonium centre. The only signal observed by \(^{11}\text{B} \) NMR was for the [B(\(\text{C}_6\text{F}_5\))\(_4\)] counterion at \(-16.3\) ppm. It is plausible that the boron atom is NMR silent. The \(^{19}\text{F} \) NMR spectrum exhibited the expected fluorine resonances for the cation and anion with integrated ratios consistent with the formation of salt 2-25. The resonance observed for the B-F fluorine atom in 2-24 notably absent. A structure of salt 2-26, the result of loss of a \( \text{C}_6\text{F}_5 \) moiety and retention of the fluoride ion bound to the boron atom, was obtained from by-products of another reaction mixture (Figure 2.6). It was apparent that this bizarre structure was not a major reaction product and the mechanism by which [\(\text{C}_6\text{F}_5\)]\(^-\) was lost while fluoride was retained is unclear.
2.4.1 Conclusions

Phosphinimine-borane complexes of type $R'_3PN-\text{BR}_2$ could be synthesized readily by reaction of boron azides $R_2BN_3$ with phosphines, or by reaction of TMS-substituted phosphinimines $R_3P=\text{NTMS}$ with haloboranes $R_2BX$. Analysis of multinuclear NMR spectra presented small differences in the electronic environment around the boron centre, though the geometry exhibited by solid-state structures seemed to be more influenced by steric requirements of the substituents on the phosphorus atom. Each of these phosphinimine-boranes could be methylated at the nitrogen atom with MeOTf to give the corresponding OTf salts with the exception of the most electron-deficient $(C_6F_5)_2BNPPh_3$ 2-9. These OTf salts exhibited small but notable differences in their NMR spectroscopic and solid-state parameters from their neutral precursors, consistent with modestly more electron-deficient environments about the phosphorus and boron atoms.

Analogous reaction of secondary phosphines $R_2PH$ with boron azides resulted in the exclusive observation of the P(III) tautomers $R'_2PNHBR_2$. $t$Bu$_2$PNHB$(C_6F_5)_2$ 2-21 underwent analogous reaction with MeOTf to give the salt $[t$Bu$_2$PN(Me)HB$(C_6F_5)_2][\text{OTf}]$ 2-23. When heated, the phosphine functionality of 2-21 exhibited nucleophilic attack of one of the $C_6F_5$ rings at the para-position resulting in heterocyclic zwitterion 2-24. Despite the fact that neither the neutral nor cationic P-N-B compounds underwent FLP-type reactivity with $H_2$, $CO_2$, or alkynes, the formation of 2-24 was evidence of some
Lewis acidity at the boron centre of 2-21. The boron-bound fluorine atom could subsequently be abstracted with the more fluorophilic Lewis acid [Et₃Si(tol)][B(C₆F₅)₄], resulting in salt 2-25.

2.5 Experimental Details

2.5.1 General

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques or a nitrogen-filled glove box (MBRAUN). All solvents (including deuterated solvents) were dried, degassed and stored over molecular sieves. Phosphines, Mes₂BF, Cy₂BCl solutions, and MeOTf were commercially available and used as received. [SiEt₃][B(C₆F₅)₄],⁴⁴ (C₅F₅)₂BCl⁴⁵ and Cl-9-BBN⁴⁶ were prepared according to literature methods. ¹H, ¹³C, ¹¹B, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker Avance III or a Bruker Avance 500 spectrometer. A Perkin-Elmer analyser was used for carbon, hydrogen and nitrogen elemental analyses. ¹H NMR data, referenced to external Me₄Si, are reported as follows: chemical shift (δ/ppm), coupling constant (Hz), normalized integrals. ¹³C{¹H} NMR chemical shifts (δ/ppm) are referenced to external Me₄Si. Assignments of individual resonances were done using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer. Elemental analyses were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyser. Catalytic trial were performed in 5 mm NMR tubes using 0.75 mL of CD₂Cl₂. Spectra were referenced to residual solvent of d₈-toluene (¹H = 2.08 for methyl; ¹³C = 20.40 for CH₃), CD₂Cl₂ (¹H = 5.32, ¹³C = 54.0), or C₆D₅Br (¹H = 7.28 ppm for meta proton; ¹³C = 122.4 ppm for ipso carbon). Chemical shifts are listed in ppm and coupling constants are listed in Hz. NMR assignments are supported by additional 2D experiments. High-resolution mass spectrometry (HRMS) was performed in house.

X-ray Diffraction Studies: Crystals were coated in paratone oil and mounted in a cryo-loop. Data were collected on a Bruker APEX2 X-ray diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å). The temperature was maintained at 150(2) K using an Oxford cryo-stream cooler for both, initial indexing and full data collection. Data were collected using Bruker APEX-2 software and processed using SHELX and Olex2 an absorption correction applied using multi-scan within the APEX-
2 program. All structures were solved by direct methods within the SHELXTL package^47 and refined with Olex2.^48,49

2.5.2 Syntheses & Characterization

Synthesis of R$_3$PNBMes$_2$ 2-1, 2-2, 2-3 (R = Et: 2-1, R = Cy: 2-2, R = Ph: 2-3) These compounds were prepared in a similar manner and, thus, only a general synthetic protocol is given. A solution of Mes$_2$BF (134 mg, 0.5 mmol, 1.0 eq.) in toluene (3 mL) was added to a solution of the respective phosphinimine (0.5 mmol, 1.0 eq.) in toluene (3 mL). The reaction mixture was stirred for two days at 90°C. A small amount of a colourless precipitate was formed and removed by filtration. All volatiles were removed in vacuo giving a white solid which was washed with n-hexane or pentane (2 x 1 mL) and dried in vacuo yielding the respective phosphinimine-substituted boranes as white solids. Single crystals of 2-1 and 2-3, suitable for x-ray single crystal structure determination were obtained by slow diffusion of n-hexane into Et$_2$O solution (2-3) or cooling of a saturated pentane solution to -35°C (2-1).

2-1: Yield: 94% $^1$H NMR (toluene-d$_8$, [ppm]): δ = 0.63 (9H, m, CH$_2$CH$_3$), 1.17 (6H, m, CH$_2$CH$_3$), 2.22 (6H, s, p-CH$_3$), 2.46 (12H, s, o-CH$_3$), 6.77 (4H, s, m-H); $^{11}$B($^1$H) NMR (toluene-d$_8$, [ppm]): δ = 46.0 (s); $^{13}$C($^1$H) NMR (toluene-d$_8$, [ppm]): δ = 6.6 (d, CH$_2$CH$_3$, $^2$J$_{CP}$ = 14.8 Hz), 19.6 (d, CH$_2$CH$_3$, $^2$J$_{CP}$ = 206.6 Hz), 21.8 (s, p-CH$_3$), 24.2 (s, o-CH$_3$), 129.0 (s, Mes), 136.1 (s, Mes), 140.7 (s, Mes); $^{31}$P($^1$H) NMR (toluene-d$_8$, [ppm]): δ = 22.1 (s); elemental analysis for C$_{24}$H$_{37}$BNP: calcd.: C 75.6, H 9.8, N 3.7; found: C 74.7, H 10.1, N 3.6; ESI MS: m/z: 382.3 (calcd. for M+: 382.3)

2-2: Yield: 94% $^1$H NMR (toluene-d$_8$, [ppm]): δ = 0.72 - 1.83 (33H, m, C$_6$H$_{11}$), 2.22 (6H, s, p-CH$_3$), 2.52 (12H, s, o-CH$_3$), 6.79 (4H, s, m-H); $^{11}$B($^1$H) NMR (toluene-d$_8$, [ppm]): δ = 44.4 (s); $^{13}$C($^1$H) NMR (toluene-d$_8$, [ppm]): δ = 21.7 (s, p-CH$_3$), 24.2 (s, o-CH$_3$), 27.1 (d, CH$_2$, $^2$J$_{CP}$ = 6.5 Hz), 27.7 (d, CH$_2$, $^3$J$_{CP}$ = 10.5 Hz), 28.2 (d, CH$_2$, $^3$J$_{CP}$ = 47.6 Hz), 37.7 (d, CH, $^1$J$_{CP}$ = 244.6 Hz), 129.1 (s, Mes), 135.8 (s, Mes). 140.4 (s, Mes); $^{31}$P($^1$H) NMR (toluene-d$_8$, [ppm]): δ = 18.8 ppm (s), elemental analysis for C$_{36}$H$_{55}$BNP: calcd.: C 79.5, H 10.2, N 2.5; found: C 79.50, H 9.92, N 3.16; ESI MS: m/z: 544.4 (calcd. for M+: 544.4)

2-3 Yield: 81% $^1$H NMR (toluene-d$_8$, [ppm]): δ = 2.18 (6H, s, p-CH$_3$), 2.37 (12H, s, o-CH$_3$), 6.62 (4H, s, m-H), 6.88 – 9.95 (6H, m, m-Ph), 6.96 - 7.03 (3H, m, p-Ph), 7.51 - 7.58 (6H, m, o-Ph); $^{11}$B($^1$H) NMR
(toluene-ds, [ppm]): $\delta = 48.0$ (1B, s(br), $\Delta v_{1/2} = 800$ Hz); $^{13}$C{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 21.2$ (s, $p$-CH$_3$), 23.8 (s, $o$-CH$_3$), 128.1 (d, $m$-Ph, $^3J_{CP} = 12.1$ Hz), 128.4 (s, $m$-H), 130.9 (d, $p$-Ph, $^4J_{CP} = 2.9$ Hz), 132.2 (d, $i$-Ph, $^1J_{CP} = 101.6$ Hz), 132.8 (d, $o$-Ph, $^2J_{CP} = 9.5$ Hz), 135.5 (s, $p$-CH$_3$), 140.2 (s, $o$-CH$_3$); $^{31}$P{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 4.8$ (1P, s); an elemental analysis was not performed due to the low melting point; DART MS: m/z: 253.2 (calcd. for [M$^+$]: 253.2), 135.1 (calcd. for [Et$_3$PNH$_3$]$^+$: 135.1), 134.1 (calcd. for [Et$_3$PNH$_2$]$^+$: 134.1.

Synthesis of R$_3$PN-9BBN (R = Et: 2-4, R = Cy: 2-5, R = Ph: 2-6; R = tBu: 2-7) These compounds were prepared in a similar manner and, thus, only a general synthetic protocol is given. A solution of 9-chloro-9-borabicyclo[3.3.1]nonane (78 mg, 0.5 mmol, 1.0 eq.) in toluene (3 mL) was added dropwise within five minutes to a solution of the respective phosphinimine (0.5 mmol, 1.0 eq.) in toluene (3 mL). The reaction mixture was stirred for one day at 90 °C (2-5, 2-7) or for six hours at ambient temperature (2-4, 2-6). All volatiles were removed in vacuo giving a white solid which was washed with n-hexane (2 x 1 mL). The remaining residue was extracted with n-hexane (5x5 mL). All volatiles were removed from the extract yielding 2-5, 2-6 and 2-7 as white solids. For 2-4, a white slush was obtained which was suspended in n-hexane. Remaining residue was removed by filtration and removal of all volatiles in vacuo gave 2-4 as a colourless oil. Single crystals of 2-6, suitable for X-ray single crystal structure determination, were obtained by slow diffusion of n-hexane into a toluene solution.

2-4: Yield: 97%, $^1$H NMR (toluene-ds, [ppm]): $\delta = 0.64$ (9H, dt, CH$_3$, $^3J_{HH} = 7.7$ Hz, $^3J_{PH} = 16.3$ Hz), 1.00 (6H, dq, CH$_2$, $^3J_{HH} = 7.7$ Hz, $^2J_{PH} = 11.7$ Hz), 1.11 - 1.18 (2H, m, CH), 1.41 - 1.49 (2H, m, BBN-CH$_2$), 1.85-2.01 (10H, m, BBN-CH$_2$); $^{11}$B{$^1$H} NMR (D$_8$-toluene, 26 °C, [ppm]): $\delta = 53.4$ (1B, s(br), $\Delta v_{1/2} = 294$ Hz); $^{13}$C{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 6.1$ (d, CH$_3$, $^2J_{PC} = 4.7$ Hz), 20.2 (d, $^1J_{PC} = 63.0$ Hz), 24.6 (m, BBN-CH$_2$), 30.6 (s(br), CH), 34.8 (m, BBN-CH$_2$); $^{31}$P{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 34.8$ (s); an elemental analysis was not performed due to the low melting point; DART MS: m/z: 253.2 (calcd. for [M]$^+$: 253.2), 135.1 (calcd. for [Et$_3$PNH$_3$]$^+$: 135.1), 134.1 (calcd. for [Et$_3$PNH$_2$]$^+$: 134.1.

2-5: Yield: 69%, $^1$H NMR (toluene-ds, [ppm]): $\delta = 0.84$ - 0.98 (9H, m, CH$_2$), 1.12 - 1.25 (8H, m, CH$_2$), 1.16 - 1.24 (2H, m, BBN-CH$_2$), 1.45 - 1.56 (6H, m, CH$_2$), 1.75 - 1.87 (3H, m, CH), 1.46 - 1.52 (2H, m, BBN-CH$_2$), 1.65 - 1.74 (7H, m, CH$_2$), 1.89 - 2.02 (10H, m, BBN-CH$_2$). $^{11}$B{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 53.1$ (s(br), $\Delta v_{1/2} = 452$ Hz); $^{13}$C{$^1$H} NMR (D$_8$-toluene, [ppm]): $\delta = 24.6$ (s, BBN-CH$_2$), 26.7 (d, CH$_2$, $^4J_{PC} = 1.7$ Hz), 27.3 (d, CH$_2$, $^1J_{PC} = 2.9$ Hz), 27.4 (d, CH$_2$, $^2J_{PC} = 11.5$ Hz), 31.3 (s(br), BBN-
CH), 34.9 (s, BBN-CH2), 36.3 (d, CH, $^1J_{PC} = 59.9$ Hz); $^{31}$P{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 22.8$ (s); elemental analysis for C$_{26}$H$_{47}$BNP: calcd.: C 75.2, H 11.4, N 3.4; found: C 74.9, H 10.9, N 3.4; DART MS: m/z: 416.3648 (calcd. For [MH]+: 416.3617).

2-6: Yield: 85%. $^1$H NMR (toluene-ds, [ppm]): $\delta = 1.40 - 1.48$ (2H, m, CH), 1.63 - 1.72 (2H, m, CH$_2$), 2.01 - 2.22 (10H, m, CH$_2$), 7.02 - 7.13 (9H, m, m-Ar, p-Ar), 7.72 - 7.80 (6H, m, o-Ar); $^{11}$B{$^1$H} NMR (D$_8$-toluene, 26 $^\circ$C, [ppm]): $\delta = 56.1$ (1B, s(br), $\Delta \nu_{1/2} = 378$ Hz). $^{13}$C{$^1$H} NMR toluene-ds, [ppm]): $\delta = 24.5$ (s, CH$_2$), 30.1 (s(br), CH), 34.6 (s, CH$_2$), 128.4 (d, m-Ar, $^3J_{PC} = 11.9$ Hz), 131.2 (d, p-Ar, $^4J_{PC} = 2.4$ Hz), 132.7 (d, o-Ar, $^2J_{CP} = 9.9$ Hz), 134.1 (d(br), i-Ar, $^1J_{CP} = 99.7$ Hz). $^{31}$P{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 22.8$ (s); elemental analysis for C$_{26}$H$_{47}$BNP: calcd.: C 75.2, H 11.4, N 3.4; found: C 74.9, H 10.9, N 3.4; DART MS: m/z: 416.3648 (calcd. For [MH]+: 416.3617).

2-7: Yield: 89%. $^1$H NMR (toluene-ds, [ppm]): $\delta = 1.23$ (27H, d, CH$_3$, $^3J_{PH} = 12.9$ Hz), 1.39 - 1.45 (2H, m, CH), 1.66 - 1.74 (2H, m, CH$_2$), 2.12 - 2.27 (10H, m, CH$_2$). $^{11}$B{$^1$H} NMR toluene-ds, [ppm]): $\delta = 51.8$ (1B, s(br), $\Delta \nu_{1/2} = 166$ Hz); $^{13}$C{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 24.9$ (s, CH$_2$), 29.6 (s, CCH$_3$), 31.3 (s(br)), 34.87 (s, CH$_2$), 39.8 (d, CCH$_3$, $^1J_{PC} = 53.2$ Hz). $^{31}$P{$^1$H} NMR (toluene-ds, [ppm]): $\delta = 6.5$ (1s); elemental analysis for C$_{20}$H$_{41}$BNP: calcd.: C 78.6, H 7.4, N 3.5; found: C 78.3, H 7.8, N 3.5; DART MS: m/z: 398.2 (calcd. for [MH]+: 398.2), 279.1 (calcd. for [Ph$_3$PNH$_3$]+: 279.1), 278.1 (calcd. for [Ph$_3$PNH$_2$]+: 278.1).

Synthesis of R$_3$PNB(C$_6$F$_5$)$_2$ 2-8 and 2-9 (R = Et: 2-8, R = Ph: 2-9) Both compounds were synthesized by analogous procedures and thus a general synthetic protocol is given. A solution of ClB(C$_6$F$_5$)$_2$ (190 mg, 0.5 mmol, 1.0 eq.) in toluene (3 mL) was added dropwise within five minutes to a solution of the respective phosphinimine (0.5 mmol, 1.0 eq.) in toluene (3 mL). The reaction mixture was stirred for one hour at ambient temperature. All volatiles were removed in vacuo giving, in the case of 2-8, a colourless slush which was dissolved in n-pentane (0.5 mL). A small amount of remaining residue was removed by filtration. Removal of all volatiles gave 2-8 as a colourless oil which solidified after storage for several days at −30 $^\circ$C (83% yield). For 2-9, a white solid was obtained which was washed with n-pentane (2 x 0.5 mL) and dried in vacuo yielding 2-9 as a white solid.

2-8: Yield: 83% $^1$H NMR (toluene-ds, [ppm]): $\delta = 0.62$ (9H, dt, CH$_3$, $^3J_{HH} = 7.8$ Hz, $^3J_{HP} = 16.8$ Hz), 0.62 (9H, dt, CH$_3$, $^3J_{HH} = 7.8$ Hz, $^3J_{HP} = 16.8$ Hz),
1.00 (6H, dq, CH$_2$, $^3J_{HH} = 7.8$ Hz, $^2J_{HH} = 11.8$ Hz); $^{11}$B$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = 33.8$ (s(br), $\Delta v_{1/2} = 315$ Hz); $^{13}$C$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = 5.4$ (d, CH$_3$, $^2J_{CP} = 5.3$ Hz), 18.3 (d, CH$_2$, $^1J_{CP} = 65.3$ Hz), 137.5 (m, C$_6$F$_5$), 141.1 (m, C$_6$F$_5$), 146.9 (m, C$_6$F$_5$), signals for boron-bound carbon atoms were not observed. $^{19}$F$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = -162.9$ (4F, m, m-F), $-155.7$ (2F, t, p-F, $^3J_{FF} = 20.2$ Hz), $-134.5$ (4F, m, o-F); $^{31}$P$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = 31.5$ (s); elemental analysis for C$_{18}$H$_{15}$BF$_{10}$NP: calcd.: C 45.3, H 3.2, N 2.9; found: C 45.1, H 3.5, N 2.9; DART MS: m/z: 478.1 (calcd. for [MH]$^+$: 478.1).

2-9: Yield: 92%; characterization data were previously reported.$^{36}$

2-10, 2-11, 2-12, 2-13: characterization data were previously reported.$^{36}$

Synthesis of borenium ion salts [R$_3$PNMe-9BBN][OTf] (R = Cy: 2-15, R = Et: 2-14, R = Ph: 2-16) A solution of MeOTf (82 mg, 0.5 mmol, 1.0 eq.) in toluene (3 mL) was added to a solution of the respective borane (0.5 mmol, 1.0 eq.) in toluene (3 mL). The reaction mixture was stirred for two hours at ambient temperature accompanied by the formation of a colourless precipitate. n-hexane (3 mL) was added to complete precipitation. The supernatant was removed and the remaining colourless solid was washed with n-hexane (3 x 3 mL) and dried in vacuo yielding the borenium ion salt as microcrystalline material.

2-14: Yield: 97% $^1$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 1.29 - 1.45$ (2H, m, BBN-CH$_2$), 1.35 (9H, dt, CH$_3$, $^3J_{HH} = 7.4$ Hz, $^3J_{HP} = 19.1$ Hz), 1.58 - 1.85 (6H, m, BBN-CH, BBN-CH$_2$), 1.94 - 2.06 (6H, m, BBN-CH$_1$, BBN-CH$_2$), 2.52 (6H, quart., CH$_2$, $^3J_{HH} = 7.4$ Hz, $^2J_{HP} = 11.6$ Hz), 3.18 (3H, d, NCH$_3$, $^3J_{HP} = 10.7$ Hz); $^{11}$B$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 61.7$ (s(br), $\Delta v_{1/2} = 430$ Hz); $^{13}$C$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 5.9$ (d, CH$_3$, $^2J_{CP} = 5.1$ Hz), 16.5 (d, CH$_2$, $^1J_{CP} = 56.3$ Hz), 22.8 (s, BBN-CH$_2$), 33.5 (s(br), BBN-CH, BBN-CH$_2$), 121.4 (quart., CF$_3$, $^1J_{CF} = 319.6$ Hz); $^{19}$F$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = -79.0$ (s); $^{31}$P$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 73.3$ (s); elemental analysis for C$_{16}$H$_{32}$PF$_3$NO$_3$PS: calcd.: C 46.1, H 7.7, N 3.4; found: C 46.6, H 7.8, N 3.3; ESI MS: m/z: 149.1 (calcd. for [Et$_3$PNMeH$_2$]$^+$: 149.1), 148.1 (calcd. for [Et$_3$PNMeH]$^+$: 148.1), no peak corresponding to the molecular ion was observed.
2-15 Yield: 95%; 1H NMR (CD2Cl2, [ppm]): δ = 0.62 - 2.20 (10H, m(br), BBN), 1.24 - 1.36 (2H, m, BBN), 1.75 - 1.90 (2H, m, BBN), 3.08 (3H, d, CH3, JHP = 13.1 Hz), 7.75 - 7.83 (12H, m, o-Ar, m-Ar), 7.85 - 7.93 (3H, m, p-Ar); 11B{1H} NMR (CD2Cl2, [ppm]): δ = 64.3 (s(br), Δν1/2 = 630 Hz); 13C{1H} NMR (CD2Cl2, [ppm]): δ = 22.5 (s, CH2-NN), 33.4 (s, CH2-NN), 37.6 (d, CH3, JCP = 3.3 Hz), 121.4 (quart., CF3, JCF = 321.6 Hz), 121.5 (d, i-Ar, JCP = 100.7 Hz), 130.8 (d, o/m-Ar, JCP = 13.3 Hz), 134.1 (d, o/m-Ar, JCP = 10.5 Hz), 136.0 (d, p-Ar, JCP = 3.0 Hz), signals for boron-bound carbon atoms were not observed; 19F{1H} NMR (CD2Cl2, [ppm]): δ = −78.9 (s); 31P{1H} NMR (CD2Cl2, [ppm]): δ = 43.9 (s); elemental analysis for C28H32PF3NO3PS: calcd.: C 58.0, H 8.7, N 2.4; found: C 57.6, H 8.7, N 2.5; ESI MS: m/z: 293.1 (calcd. for [Ph3PNMeH2]+: 293.1), 292.1 (calcd. for [Ph3PNMeH]+: 292.1), no peak corresponding to the molecular ion was observed.

2-16: Yield: 95%; 1H NMR (CD2Cl2, [ppm]): δ = 0.62 - 2.20 (10H, m(br), BBN), 1.24 - 1.36 (2H, m, BBN), 1.75 - 1.90 (2H, m, BBN), 3.08 (3H, d, CH3, JHP = 13.1 Hz), 7.75 - 7.83 (12H, m, o-Ar, m-Ar), 7.85 - 7.93 (3H, m, p-Ar); 11B{1H} NMR (CD2Cl2, [ppm]): δ = 64.3 (s(br), Δν1/2 = 630 Hz); 13C{1H} NMR (CD2Cl2, [ppm]): δ = 22.5 (s, CH2-NN), 33.4 (s, CH2-NN), 37.6 (d, CH3, JCP = 3.3 Hz), 121.4 (q, CF3, JCF = 321.6 Hz), 121.5 (d, i-Ar, JCP = 100.7 Hz), 130.8 (d, o/m-Ar, JCP = 13.3 Hz), 134.1 (d, o/m-Ar, JCP = 10.5 Hz), 136.0 (d, p-Ar, JCP = 3.0 Hz), signals for boron-bound carbon atoms were not observed; 19F{1H} NMR (CD2Cl2, [ppm]): δ = −78.9 (s); 31P{1H} NMR (CD2Cl2, [ppm]): δ = 43.9 (s); elemental analysis for C28H32PF3NO3PS: calcd.: C 58.0, H 8.7, N 2.4; found: C 57.6, H 8.7, N 2.5; ESI MS: m/z: 293.1 (calcd. for [Ph3PNMeH2]+: 293.1), 292.1 (calcd. for [Ph3PNMeH]+: 292.1), no peak corresponding to the molecular ion was observed.

2-17 A solution of MeOTf (82 mg, 0.5 mmol, 1.0 equiv) in toluene (3 mL) was added to a solution of 2-8 (0.5 mmol, 1 equiv) in toluene (3 mL). The reaction was stirred for 48 h at ambient temperature accompanied by the formation of a colourless precipitate. The supernatant was removed and the remaining colourless solid was washed with toluene (1 x 3 mL) and pentane (2 x 3 mL) and dried in vacuo yielding salt 2-17 as a microcrystalline solid in 83 % yield. Crystals suitable for x-ray diffraction analysis were obtained by slow diffusion of n-pentane into a saturated CH2Cl2 solution at −35 °C. 1H NMR (CD2Cl2, [ppm]): δ = 1.30 (9H, dt, CH2CH3, JHH = 7.6 Hz, JHP = 19.7 Hz); 2.40 (6H, dq, CH2CH3, JHH = 7.6 Hz, JHP = 11.4 Hz); 3.20 (3H,
d, NCH₃, ³JHH = 10.7Hz) ¹¹B{¹H} NMR (CD₂Cl₂, [ppm]): δ = 39.0 s(br), Δν₁/₂ = 700 Hz ¹³C{¹H} NMR (CD₂Cl₂, [ppm]): δ = 5.5 (d, CH₂CH₃, ³JPC = 5 Hz), 14.7 (d, CH₂CH₃, ¹JPC = 54 Hz), 110.4 (s(br), C₆F₅), 120.6 (1, q, CF₃, ¹JFC = 320 Hz), 138.2 (d, C₆F₅, ¹JFC = 260Hz), 143.6 (d, C₆F₅, ¹JFC = 260Hz), 146.3 (d, C₆F₅, ¹JFC = 247Hz ¹⁹F{¹H} NMR (CD₂Cl₂, [ppm]): δ = -78.9 (s; 3F, OSO₂CF₃); -131.3(m, 4F, α-C₆F₅); -149.8 (m, 2F, p-C₆F₅); -160.2 (m, 4F, m-C₆F₅); ³¹P{¹H} NMR (CD₂Cl₂, [ppm]): δ = 80.9 (s); elemental analysis for C₂₀H₁₈BF₁₃NO₃PS*C₇H₈: calcd.: C 37.5, H 2.8, N 2.2; found: C 37.3, H 3.1, N 2.3; DART MS: m/z: 492.1 (calcd. for M+: 492.1)

2-18: Yield: 82%; ¹H NMR (CD₂Cl₂, 26 °C, [ppm]): δ =1.27 (9H, d of t, CH₂CH₃, ³JHH = 7.6 Hz, ³JHP = 19.2 Hz); 2.23 (6H, s, Mes, o-CH₃), 2.24 (6H, s, Mes, o-CH₃); 2.26 (6H, d of q, CH₂CH₃, ³JHH = 2.9 Hz); 2.28 (3H, s, Mes, p-CH₃); (3H, s, Mes, p-CH₃), 3.15 (3H, d, NCH₃, ²JPH = 8.7 Hz); 6.81 (2H, Mes); 6.88 (2H, Mes) ¹¹B{¹H} NMR (CD₂Cl₂, 26 °C, [ppm]): δ = 45.6 s(br) ¹³C{¹H} NMR (CD₂Cl₂, 26 °C, [ppm]): δ = 24.1 (s, Cy), 24.6 (s, Cy), 25.9 (d, Cy, ³JPC = 5.4 Hz); 27.5 (d, Cy, ²JPC = 39.3 Hz), 29.4 (d, Cy, ²JPC = 13.3 Hz), 38.8 (d, CH₃, ¹JPC = 135.3 Hz); 40.8 (s, CH₃), 128.9 (s, Mes), 129.6 (s, Mes), 129.8 (s, Mes), 130.3 (s, Mes), 139.4 (s, Mes), 140.0 (s, Mes), 140.8 (s, Mes), 141.2 (s, Mes); signals for boron-bound carbon atoms were not observed; ¹⁹F{¹H} NMR (CD₂Cl₂, [ppm]): δ = -78.9 (s); ³¹P{¹H} NMR (CD₂Cl₂, [ppm]): δ = 22.1 (s); elemental analysis for C₃₈H₅₈BF₃NO₃PS*C₇H₈: calcd.: C 57.3, H 7.4, N 2.6; found: C 56.8, H 7.9, N 2.0; DART MS: m/z: 596.2990 (calcd. for M+: 596.2991)

2-19: Yield: 88% ¹H NMR (CD₂Cl₂, [ppm]): δ =1.05 - 1.21 (6H, m(br), Cy); 1.24 - 1.34 (3H, m, Cy), 1.63 - 1.78 (9H, m, Cy), 1.82-1.93 (6H, m(br), Cy), 1.98 - 2.09 (6H, m(br), Cy), 2.24 (9H, 2 overlapping s; 6H, Mes o-CH₃, and 3H, Mes p-CH₃, Mes); 2.27 (3H, s, Mes, p-CH₃); 2.29 (6H, s, Mes, o-CH₃); 2.66 (3H, quartet, Cy, 3JHH = 8.7 Hz); 3.07 (3H, d, NCH₃, ²JPH = 8.7 Hz); 6.81 (2H, Mes); 6.88 (2H, Mes) ¹¹B{¹H} NMR (CD₂Cl₂, 26 °C, [ppm]): δ = 57.5 s(br) ¹³C{¹H} NMR (CD₂Cl₂, [ppm]): δ = 24.1 (s, Cy), 24.6 (s, Cy), 25.9 (d, Cy, ³JPC = 5.4 Hz); 27.5 (d, Cy, ²JPC = 39.3 Hz), 29.4 (d, Cy, ²JPC = 13.3 Hz), 38.8 (d, CH₃, ¹JPC = 135.3 Hz); 40.8 (s, CH₃), 128.9 (s, Mes), 129.6 (s, Mes), 129.8 (s, Mes), 130.3 (s, Mes), 139.4 (s, Mes), 140.0 (s, Mes), 140.8 (s, Mes), 141.2 (s, Mes); signals for boron-bound carbon atoms were not observed; ¹⁹F{¹H} NMR (CD₂Cl₂, [ppm]): δ = -78.9 (s); ³¹P{¹H} NMR (CD₂Cl₂, [ppm]): δ = 72.7 (s); elemental analysis for C₃₈H₈₈BF₃NO₃PS*C₇H₈: calcd.: C 67.6, H 8.3, N 1.8; found: C 67.7, H 9.1, N 2.0; DART MS: m/z: 558.4402 (calcd. for M+: 558.4400)

2-20: Yield: 78%; ¹H NMR (CD₂Cl₂, [ppm]): δ =1.87 (6H, s, o-CH₃); 2.11 (3H, s, Mes, p-CH₃), 2.25 (3H, s, Mes, p-CH₃), 2.37 (6H, s, Mes, p-CH₃); 3.25 (3H, d, NCH₃, ³JPH = 11.2Hz); 6.38 (2H,s, m-
Mes); 6.85 (2H, s, m-Mes), 7.56-7.70 (12H, m, o/Mes), 7.77-7.83 (3H, m, p/Ph)

$^{11}$B$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 58.8$ (s(br), $\Delta v_{1/2} = 1200$ Hz); $^{13}$C$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 20.5$ (s, p-CH$_3$), 20.7 (s, p-CH$_3$), 22.9 (s, o-CH$_3$), 24.0 (s, o-CH$_3$), 24.6 (s, Cy), 41.7 (d, NCH$_3$, $^2$J$_{PC} = 2.3$ Hz), 118.3 (d, i-Ph, $^1$J$_{PC} = 100.3$ Hz), 121.0 (q, CF$_3$, $^1$J$_{PC} = 321.3$ Hz), 128.6 (s, m-Mes), 129.9 (s, m-Mes), 129.9 (d, m-Ph, $^3$J$_{PC} = 13.2$ Hz), 134.1 (d, o-Ph, $^2$J$_{PC} = 10.4$ Hz), 135.4 (d, p-Ph, $^4$J$_{PC} = 3.0$ Hz), 139.3 (s, o-Mes), 139.7 (s, p-Mes), 140.0 (s, p-Mes); signals for boron-bound carbon atoms were not observed; $^{19}$F$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = -78.8$, s; $^{31}$P$^{1}$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 47.7$ (s); elemental analysis for C$_{38}$H$_{40}$BF$_3$NO$_3$PS: calcd.: C 66.2, H 5.9, N 2.0; found: C 66.1, H 6.4, N 2.2; ESI MS: m/z: 539.3028 (calcd. for M$^+$: 539.3022)

**Synthesis of R$_2$PNHB(C$_6$F$_5$)$_2$ 2-21 and 2-22 (R = tBu 2-21, R = C$_5$H$_9$: 2-22):** Both compounds were synthesized by analogous procedures and thus a general synthetic protocol is given. To a solution of ClB(C$_6$F$_5$)$_2$ (190 mg, 0.5 mmol, 1.0 eq.) in toluene (3 mL) was added TMSN$_3$ (0.064 g, 1.1 equiv.) in 0.5 mL toluene. The reaction mixture was stirred for one hour at ambient temperature. A solution of the respective secondary phosphine (1.0 equiv.) in 0.5 mL toluene was then added and the reaction mixture was stirred 48 h. All volatiles were removed in vacuo and the resulting sticky residue was extracted with n-hexanes (2 x 3 mL), filtered through a Celite plug and further dried in vacuo to yield 2-21 and 2-22 as colourless oils which solidified after several hours at ambient temperature.

**2-21:** Yield: 76% $^1$H NMR (toluene-d$_8$, [ppm]): $\delta = 0.96$ (18H, d, tBu, $^3$J$_{PH} = 16$ Hz), 5.85 (1H, s(br), NH). $^{11}$B$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = 39.2$ (s) $^{19}$F$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = -131.2$ (2F, m, o-C$_6$F$_5$), −133.0 (2F, m, o-C$_6$F$_5$), −149.3 (1F, dm, p- C$_6$F$_5$) −153.1 (1F, dm, p- C$_6$F$_5$), −161.0 (1F, dm, m- C$_6$F$_5$) −162.3 (1F, dm, m- C$_6$F$_5$). $^{31}$P$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = 74.5$ (s).

**2-22:** Yield: 62 % $^1$H NMR (toluene-d$_8$, [ppm]): $\delta = 1.00$-1.89 (18H, m, C$_5$H$_9$), 5.37 (1H, s(br), NH). $^{11}$B$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = 38.8$ (s) $^{19}$F$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = -132.0$ (2F, m, o-C$_6$F$_5$), −132.9 (1F, m, o-C$_6$F$_5$), −150.0 (1F, dm, p- C$_6$F$_5$) −152.9 (1F, dm, p- C$_6$F$_5$), −161.2 (2F, dm, m- C$_6$F$_5$) −162.1 (2F, dm, m- C$_6$F$_5$). $^{31}$P$^{1}$H NMR (toluene-d$_8$, [ppm]): $\delta = 54.0$ (s).

**2-23** A solution of MeOTf (82 mg, 0.5 mmol, 1.0 equiv) in toluene (3 mL) was added to a solution of 2-21 (0.5 mmol, 1 equiv) in toluene (3 mL). The reaction was stirred for 48 h at ambient temperature accompanied by the formation of a colourless precipitate. The supernatant was removed and the
remaining colourless solid was washed with toluene (1 x 3 mL) and pentane (2 x 3 mL) and dried in vacuo yielding salt 2-17 as a microcrystalline solid in 83 % yield.

2-24 Yield: 99%; A solution of 2-21 (101 mg, 0.2 mmol) was heated to 110 °C in toluene (2 mL) for 48 h. Volatiles were removed in vacuo. Crystals suitable for x-ray diffraction analysis were obtained by slow diffusion of n-pentane into a saturated CH₂Cl₂ solution at – 35 °C. ¹H NMR (tol-d₈, [ppm]): δ = 0.72 (9H, d, tBu, ³JPH = 16 Hz), 0.88 (9H, d, tBu, ³JPH = 16 Hz), 2.23 (1H, d, NH, ³JPH = 16 Hz) ¹¹B¹H NMR (tol-d₈, [ppm]): δ = 4.3 (s) ¹³C¹H NMR (tol-d₈, [ppm]): δ = 26.5 (s, tBu), 26.8 (s, tBu), 36.8 (d, tBu), 37.2 (s, tBu), 37.3 (s, tBu), 37.7 (s, tBu); 109.0 (t, C₆F₅), 110.0 (t, C₆F₅), 136.8 (m, C₆F₅), 139.3 (m, C₆F₅), 141.7 (m, C₆F₅), 143.3 (m, C₆F₅), 145.0 (m, C₆F₅), 145.9 (m, C₆F₅). ¹⁹F¹H NMR (tol-d₈, [ppm]): δ = –125.8 (1F, m, C₆F₄), –129.9 (1F, m, C₆F₄), –133.9 (2F, m, o-C₆F₅), –146.9 (1F, tm, C₆F₄), –155.1 (1F, m, C₆F₄), –155.3 (1F, m(br), BF), –155.1 (1F, t, p-C₆F₅), –164.5 (2F, m, m-C₆F₅).

31P¹H NMR (tol-d₈, [ppm]): δ = 85.3 (s)

2-25 To a solution of 2-24 (50 mg, 0.11 mmol) dissolved in bromobenzene (2 mL) [Et₃Si(tol)][B(C₆F₅)₄] (86 mg, 0.11 mmol, 1 equiv.) was added and the resulting oily suspension was stirred overnight. A dark solid precipitate had formed by the following day. The supernatant was decanted and the precipitate was washed with bromobenzene (1 mL), toluene (1 x 1 mL) and pentane (3 x 1 mL) resulting in 2-25. Crystals suitable for x-ray diffraction analysis were obtained by slow diffusion of n-pentane into a saturated CH₂Cl₂ solution at – 35 °C. ¹H NMR (CD₂Cl₂, [ppm]): δ = 1.04 (18H, d, tBu, ³JPH = 16 Hz), 5.85 (1H, d, NH, ²JPH = 17 Hz) ¹¹B¹H NMR (CD₂Cl₂, [ppm]): δ = -16.3 (s) ¹⁹F¹H NMR (CD₂Cl₂, [ppm]): δ = -117.3 (1F, m, C₆F₄), –119.0 (1F, m, C₆F₄), –129.0 (2F, m, o-C₆F₅), –132.0 (8F, m, o-B(C₆F₅)₄), –135.5 (1F, m, C₆F₄), –137.0 (1F, C₆F₄), –143.2 (1F, p-C₆F₅), –158.1 (2F, m, m-C₆F₅), –162.0 (4F, m, p-B(C₆F₅)₄), –166.0 (8F, m, m-B(C₆F₅)₄). ³¹P¹H NMR (CD₂Cl₂, [ppm]): δ = 101.0 (s)
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<td>triclinic</td>
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<td>(P2_1/c)</td>
<td>(P-1)</td>
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Table 2.5 Crystallographic data and details of the structure refinement of compounds 2-16, 2-17, 2-20

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### Table 2.7 Crystallographic data and details of the structure refinement of compounds 2-24*, 2-26

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References


Chapter 3: Synthesis of Chlorophosphonium Dication

[(SIMes)PClPh₂][B(C₆F₅)₄]₂ and its Catalytic Activity in the Hydrodeoxygenation of Ketones

3.1 Introduction

3.1.1 Cationic Main Group Lewis Acid Catalysts

Lewis acids mediate a wide variety of stoichiometric and catalytic transformations. Quintessential examples of main group Lewis acids include group 13 compounds such as BH₃, BF₃ and AlMe₃, which possess a vacant acceptor p-orbital. These classical compounds were known well before their ability to mediate organic transformations was harnessed. Their utility as reagents and catalysts in organic transformations was discovered subsequently.

The design of new compounds specifically to act as Lewis acid catalysts is a more recent development. Particularly in the last decades of the twentieth century and into the twenty-first century, the exploration of both the lighter and heavier main group elements in catalysis has gained substantial interest. Especially with respect to the activation of small molecules such as dihydrogen, carbon dioxide, carbon monoxide, ammonia, and ethylene, these catalysts have been able to both mimic and augment the reactivity of transition metals. More powerful and sophisticated main group Lewis acids have been developed utilizing electron-withdrawing substituents such as perfluorinated aryl groups to increase Lewis acidity, as in the case of B(C₆F₅)₃, enabling catalysis and frustrated Lewis pair (FLP) reactivity. Electrophilic borenium cations have also been developed which derive their Lewis acidity instead from a positive charge and thus do not need strongly electron-withdrawing substituents to be effective catalysts. Borenium cations based on 9-BBN ligated by an N-heterocyclic carbene or triazole substituent have proven effective catalysts for the hydrogenation of a variety of unsaturated compounds. This development has significantly increased the potential scope of boron Lewis acids for catalysis. Among group 14 cations, both stoichiometric and catalytic silylium reagents have been found particularly useful for challenging C-F bond activations.
3.1.2 Cationic Pnictogen Lewis Acid Catalysts

In contrast to Group 13 cations, group 15 pnictogen cations are generally more chemically robust and the heavier elements exhibit stable III and V oxidation states. A variety of P(III) phosphonium cations have been synthesized both as ligands and for use as catalysts themselves.\textsuperscript{20,21} Polycationic phosphonium species, where additional cationic charges may formally reside either on the ligands or the phosphorus atom, have also been synthesized.\textsuperscript{20}

In the case of phosphorus (V) cations of the form [R\textsubscript{4}P]\textsuperscript{+}, the tendency to attract anionic ligands X\textsuperscript{-} to form neutral phosphoranes R\textsubscript{4}PX is evidence for considerable Lewis acidity and electrophilicity. This Lewis acidity has been exploited in the development of fluoride ion sensors\textsuperscript{22} or as catalysts for (cyclo)addition reactions to polar or activated unsaturated molecules.\textsuperscript{1,23} More recently, focus in the Stephan group has been on enhancing this Lewis acidity by preparing more electrophilic phosphonium cations (EPCs) such as [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF]\textsuperscript{+} (Figure 3.2A), [(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}PhPF]\textsuperscript{+} and [(C\textsubscript{6}F\textsubscript{5})Ph\textsubscript{2}PF]\textsuperscript{+}\textsuperscript{24,25}. It has been demonstrated that the low-lying $\sigma^*$ anti-bonding orbital\textsuperscript{24} permits these species to act as effective Lewis acid catalysts for the hydrodefluorination of fluoroalkanes,\textsuperscript{24,26,27} hydrodeoxygenation of ketones,\textsuperscript{28} dehydrocoupling of alcohols and silanes,\textsuperscript{29} hydrosilylation of olefins,\textsuperscript{29,30} ketones,\textsuperscript{4} imines,\textsuperscript{4} and nitriles,\textsuperscript{4} isomerization of 1-hexene,\textsuperscript{30} polymerization of isobutylene\textsuperscript{30} and THF,\textsuperscript{27} Friedel-Crafts dimerization of 1,1-diphenylethylene and transfer\textsuperscript{29} and direct\textsuperscript{31} hydrogenation of olefins. Both Lewis acidity indicators and catalytic activities of these cations demonstrate a direct positive correlation with increasing number of C\textsubscript{6}F\textsubscript{5} substituents.\textsuperscript{25}
As in the case of group 13 Lewis acids, however, the dependence of these catalysts on perfluorinated aryl substituents to attain sufficient Lewis acidity to perform targeted catalytic transformations limited the range of potential EPC catalysts of this design. Thus, in analogy to the strategy by which group 13 hydrogenation catalysts lacking perfluorinated aryl substituents were developed, the Stephan group targeted phosphorus cations with increased formal charge which mitigated the necessity for strongly electron-withdrawing substituents.

Three distinct synthetic approaches were developed to incorporate additional cationic charges into these EPC species. The first approach utilized commercially-available polyphosphines to derive multiple phosphonium centres within a single molecule, as in Figure 3.2 B and 3.2 C. The second approach incorporated a cationic charge on a pyridinium centre on the ligand (Figure 3.2 D). The third approach featured an imidazolium substituent with a delocalized cationic charge (Figure 3.2 E), in direct analogy to borenium cations of the type depicted in Figure 3.1.

![Figure 3.2: Monocationic EPC A and frameworks for dicationic EPCs (B-E)](image)

### 3.2.1 Synthesis of Phosphorane [(SIMes)PCl₂Ph₂][B(C₆F₅)₄] 3-4

With a much wider array of potential catalysts now attainable through facile synthetic methods, it was of interest to study the effects of differing substituents on Lewis acidity and on catalytic activity. In particular, the dication depicted in Figure 3.2 D, synthesized according to Scheme 3.1, offered three facile avenues of variation. This dication was accessed via reaction of Ph₂PCl with the common carbene...
SIMes, resulting in a phosphonium cation-type adduct, whereupon the chloride counterion was replaced by the weakly-coordinating \([B(C_6F_5)_4]\) anion through reaction with an equivalent of \([\text{Et}_3\text{Si(tol)}]\) \([B(C_6F_5)_4]\) to generate the new phosphonium cation 3-1.\(^{36}\) Using oxidation protocols with XeF\(_2\) yielded difluorophosphorane 3-2, followed by fluoride ion abstraction with a second equivalent of \([\text{Et}_3\text{Si(tol)}]\) \([B(C_6F_5)_4]\) yielded dication 3-3 (Scheme 3.1).\(^{36}\)

The first facile avenue of variation featured analogous synthetic strategies using various carbenes in reaction with Ph\(_2\)PCl. The second avenue of variation utilized differing chlorophosphines R\(_2\)PCl resulting in variation of the other organic substituents at the phosphorus atom. The third avenue of variation involved changing the fluoride substituent, either by substitution from the fluorophosphonium dication directly or by the use of a non-fluorinating oxidation agent to introduce a different substituent. While other members of our group have since developed protocols to substitute the fluoride atom with phenoxy and siloxy moieties and examined the effect of these different groups on the stability and activity of the resulting EPC catalysts,\(^{37}\) this chapter will focus on the first EPC developed through the use of a chlorinating oxidation agent leading to the isolation of a dicationic chlorophosphonium complex.

Scheme 3.1: Synthesis of fluorophosphonium dication

Phosphonium dications of either type \([\text{SIMesR}_2\text{PR}']\) (R = Ph, R’ = alkyl or aryl) or \([\text{SIMesR}_2\text{PX}]\) (X = Cl, Br, I) were initially targeted. Treating the phosphonium cation 3-1 with I\(_2\), MeI, MeOTf, or PhCH\(_2\)Br did not result in a reaction. Formal oxidation by methylation agents would involve nucleophilic attack of the phosphonium cation at the carbon atom, and it is postulated that the positive charge and bulky carbene substituent rendered 3-1 too poorly nucleophilic to undergo this reaction. A similar reaction pathway was envisioned for reaction with I\(_2\). As these efforts were unsuccessful, efforts were concentrated on the synthesis of a chlorophosphonium dication via a dichlorophosphorane precursor.
The chlorine atom is substantially larger and notably less electronegative than fluorine, with an atomic radius of 1.75 Å versus that of 1.47 Å for the fluorine atom, and a Pauling electronegativity value of 3.16 for chlorine in comparison to 3.98 for fluorine. The P-Cl bond is also substantially weaker than the P-F bond, with a bond dissociation enthalpy of 289(42) kJ/mol versus 439(96) kJ/mol, and the bond substantially longer, in the range of 2.03 Å for P-Cl bonds in contrast to 1.54 Å for P-F bonds. Particularly in the case of elements with various oxidation states such as phosphorus, these values can vary substantially with oxidation state, geometry, and formal charge; however the trend between P-F and P-Cl bonds remains relevant to this discussion. The lowest-energy σ* anti-bonding orbital oriented opposite the most electronegative substituent at the phosphorus atom accepts electron density to permit activation of substrates by EPCs and thus it could be expected that substitution of P-F for P-Cl would have a significant effect on reactivity in catalysis. It could be postulated that the less electronegative chlorine atom would raise the energy of the σ* antibonding orbital, thus hindering an initial activation step between the EPC and a substrate molecule but facilitating cleavage of the activated substrate from the phosphorus atom. Calculations have not yet been performed comparing P-F and P-Cl EPCs to verify these postulates.

Ample precedent exists for oxidative chlorination of neutral phosphines using Cl₂, SO₂Cl₂, or C₂Cl₆. Reaction of SOCl₂ with phosphine oxides has also been shown to yield dichlorophosphoranes. Due to the inherent dangers of using Cl₂ gas and the toxicity of C₂Cl₆, SO₂Cl₂ was chosen as the safest and least harmful chlorinating agent. Reaction of phosphenium cation 3-1 in DCM with one equivalent of SO₂Cl₂ from a 1.0M DCM solution resulted in rapid precipitation of a microcrystalline solid, which was shown by NMR spectroscopy, mass spectrometry and X-ray structural analyses to be the cationic dichlorophosphorane 3-4 (Scheme 3.2). 3-4 was isolated in 96% yield and exhibited a ³¹P NMR shift at -63.9 ppm, within the range of chemical shifts expected for dihalophosphoranes. Rapid isolation of this product was necessary as allowing the reaction mixture to remain in DCM solution for extended periods of time resulted in degradation of product 3-4. Nonetheless, a solid-state structure was obtained by cooling a saturated solution of 3-4 in CH₂Cl₂ to -35 °C (Figure 3.3). This structure exhibited an approximately trigonal bipyramidal geometry with P-Cl bond lengths of 2.198(1) Å and 2.187(1) Å. The Cl-P-Cl angle of 164.7(1)° deviates further from linearity than the F-P-F angles of the structurally characterized difluorophosphoranes [(SIMes)PF₂R₂][B(C₆F₅)₄] (R = Me: 170.9(1)°; R = Et: 168.8(1)°).
Scheme 3.2: Synthesis of cationic dichlorophosphorane 3-4

Figure 3.3: POV-ray depiction of 3-4 with H atoms omitted for clarity. C: black; P: orange; Cl: green; N: blue

In an attempt to discern the cause of the degradation of 3-4 in solution, the reaction mixture was monitored over a period of twenty-four hours by $^{31}$P NMR spectroscopy (Figure 3.4). The spectra reveal that much of species 3-4 is no longer present after one hour in solution, while after five hours the signal has completely disappeared. The minor resonance observed at 13.9 ppm was assigned to the analogous phosphine oxide cation previously identified from the stoichiometric reaction of fluorophosphonium dication [(SIMes)PF$_2$R$_2$][B(C$_6$F$_5$)$_4$] with acetophenone, while the minor resonance at 87.0 ppm could not be assigned. The major product of the decomposition exhibited a signal at 44.0ppm. While this product could not be separated from the mixture and definitively identified, it is postulated that it may be the dication [(SIMes)PClPh$_2$][B(C$_6$F$_5$)$_4$][Cl] based on the similarity of its chemical shift in the $^{31}$P
NMR spectrum to the shift assigned to dication [(SIMes)PClPh₂][B(C₆F₅)₄]₂ 3-5, discussed in section 3.2.2 of this thesis, which exhibits a ³¹P NMR signal at 47.4 ppm in CD₂Cl₂ solution.

Figure 3.4 Changes in ³¹P NMR spectrum of reaction mixture to synthesize 3-2 over time (DCM)

3.2.2 Synthesis of Dication [(SIMes)PClPh₂][B(C₆F₅)₄]₂

Scheme 3.3: Synthesis of dication 3-5

Reaction of 3-4 in toluene with one equivalent of [Et₃Si(tol)][B(C₆F₅)₄] resulted in the isolation of dication [(SIMes)PClPh₂][B(C₆F₅)₄]₂ in 60% yield. This species exhibited a ³¹P {¹H} NMR resonance
at 47.4 ppm (Figure 3.5), differing significantly from the fluorophosphonium dication analogue 3-3 which resonated at 78.1 ppm in the $^{31}$P{$^1$H} NMR spectrum. The expected $^1$H and $^{13}$C{$^1$H} NMR resonances were observed for the bound SIMes ligand and the phenyl groups, indicating equivalence of the mesityl groups on the carbene and of the phenyl groups bound to the phosphorus atom.

![Figure 3.5: $^{31}$P{$^1$H} NMR spectrum of dication 3-5 in DCM](image)

A solid-state structure (Figure 3.6) of dication 3-5 was obtained by diffusion of $n$-pentane into a saturated DCM solution of 3-5 at -35 °C over a period of weeks. In the solid state, 3-5 exhibits a P-Cl bond length of P–Cl 1.972(2) Å, significantly longer than the reported P-Cl bond lengths for cyclic phosphonium monocations and dications reported by Burford$^{41}$ but shorter than the bond length of the P-Cl cation reported by Schmidpeter$^{42}$. As expected these bond lengths are significantly shortened from the P-Cl bond lengths determined for the phosphorane precursor 3-4.
3.3.1 Deoxygenation of Carbonyls and Et₃PO by EPC 3-3

The reduction or functionalization of unsaturated compounds has been an area in which main group catalysts have been particularly prolific.⁴³ Full reduction of carbonyl functionalities, however, is a transformation that has proven challenging for homogeneous main group catalysts.

Because of the ubiquity of ketone functionalities in organic molecules, hydrodeoxygenation of ketones is a widely-applied protocol in synthesis and has found more recent applications in targeting biofuels.¹¹
Classic protocols for deoxygenation of ketones such as the Barton-McCombie ($R_3SnH$),$^{12}$ Clemmensen ($Zn/Hg, HCl$),$^{13}$ or Wolff-Kishner reductions ($N_2H_4, KOH$)$^{14}$ generally require harsh reaction conditions, use of stoichiometric amounts of toxic reagents, and show limited functional group tolerance. Recent heterogeneous catalysts such as $PtO_2$,$^{15}$ and $Ni/Al_2O_3$,$^{16}$ have been described which utilize $H_2$ gas as the reducing agent and a recent report has also described the use of $Pd/C$,$^{17}$ as a heterogeneous catalyst for the reduction of aromatic ketones using polymethylhydrosiloxane (PMHS) as a source of two formal equivalents of hydride.

In attempting to use the Gutmann-Beckett and Childs tests to gauge the relative Lewis acidity of dication \textit{3-3}, it was observed by members of the Stephan group, Dr. Michael Holthausen and Meera Mehta, that instead of forming an adduct with \textit{3-3} both $Et_3PO$ and crotonaldehyde underwent clean abstraction of an oxygen atom (Scheme 3.4 A)$^{36}$. In a subsequent test with slightly greater than one equivalent of acetophenone, it was observed that \textit{3-3} reacted to form the corresponding phosphine oxide and difluorophosphorane (Scheme 3.4 B). It was then demonstrated that \textit{3-3} could effect the catalytic reduction of ketones to alkyl functionalities in excellent yields in the presence of a slight excess of silanes such as $Et_3SiH$ (Scheme 3.4 C)$^{28}$ EPC $[(C_6F_5)_3PF]^+$ effected the same catalysis with similar activity. A comparison of these two EPCs was carried out by mixing $[(C_6F_5)_3PF_2]$ with \textit{3-3}, which resulted in abstraction of the fluoride ion to form \textit{3-2}, the difluorophosphorane precursor to \textit{3-3}$^{35}$ This competition experiment clearly demonstrated that dication \textit{3-3} was more fluorophilic than $[(C_6F_5)_3PF]^+$.

Investigating the catalytic utility of EPCs without P-F bonds was of interest to demonstrate that additional electron-withdrawing substituents at the phosphorus centre could achieve similar catalytic activities. Additionally, in certain cases considerable amounts of \textit{3-3} were degraded during catalysis, thus the investigation of ketone deoxygenations with \textit{3-5} as a catalyst was of interest. In addition, the broad range of substrates would allow a comprehensive gauging of the effect on catalytic activity of replacing the fluoride ion substituent of EPC \textit{3-3} with the chloride ion substituent of \textit{3-5}.
Scheme 3.5: A) Stoichiometric abstraction of an oxygen atom from Et$_3$PO and fluoride from difluorophosphorane by 3-3. B) Stoichiometric abstraction of an oxygen atom from benzaldehyde by 3-3 C) Catalytic Deoxygenation of ketones with 3-3

3.3.2 Computed Mechanism of Deoxygenation of Ketones by EPC [(C$_6$F$_5$)$_3$PF]$^+$

As mentioned above, the hydrosilylation of alkenes, alkynes,$^{44}$ imines, ketones and nitriles catalyzed by EPC [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] has been previously reported$^{24,44,45}$ and computational and experimental data supported a mechanism involving interaction of the EPC with silane. This hydrosilylation mechanism
is analogous to the mechanism established for B(C₆F₅)₃-mediated hydrosilylation of carbonyl compounds established by Piers⁴⁶-⁴⁸ and Oestreich.⁴⁹-⁵¹

The Grimme group has probed the mechanism of deoxygenation of the simple ketone acetophenone in the presence of Et₃SiH with EPC [(C₆F₅)₃PF][B(C₆F₅)₄] as a catalyst via DFT calculations⁵²,⁵³-⁶⁰ (Figure 3.7) employing the B2PLYP-D3/def2-QZVP level of theory.

**Figure 3.7** Predicted mechanisms for the deoxygenation of benzophenone with EPC [(C₆F₅)₃PF][B(C₆F₅)₄]

Analogously to the B(C₆F₅)₃-mediated hydrosilylation pathway, the initial step involves the interaction of the Lewis acid with the hydridic hydrogen atom on Et₃SiH, rendering the silicon centre more electrophilic. Two possible subsequent pathways for deoxygenation were considered. One possible mechanism involves the S_N2-like nucleophilic attack by the oxygen atom of the initial hydrosilylated intermediate PhCH(OSiEt₃)CH₃ D at the silicon centre of the silane-EPC adduct A. This reaction generates (C₆F₅)₃PFH B and [(Et₃Si)₂OCHPhMe]⁺ E, which is exergonic by 5.4 kcal mol⁻¹ with a free energy barrier of 23.8 kcal mol⁻¹. Subsequent hydride delivery from A prompts elimination of (Et₃Si)₂O and gives ethylbenzene, regenerating the catalyst.
An alternative pathway involves reaction of the transiently generated \((\text{Et}_3\text{Si})\text{OCPhMe}^+\) \(\text{C}\) with \(\text{Et}_3\text{SiH}\) to generate \((\text{Et}_3\text{Si})_2\text{OCHPhMe}^+\) \(\text{E}\) which again abstracts hydride from \(\text{A}\) to yield the product ethylbenzene, \(\text{Et}_3\text{SiOSiEt}_3\) and regenerates \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\) \(\text{A}\). Calculations predict the transformation of \(\text{C}\) to \(\text{E}\) is exergonic by 6.7 kcal mol\(^{-1}\) with an activation barrier of 17.7 kcal mol\(^{-1}\). By these computations, the latter pathway is energetically favorable, however, it may well be that variations in the catalyst, substrate and silane could reverse the energetic preference and thus either reaction mechanism may be operative.

It is noteworthy that in closely related chemistry, \(\text{B}(\text{C}_6\text{F}_5)_3\) has been shown to catalyze the deoxygenation of unsaturated cyclic ethers and silyl ethers\(^{61-66}\) affording allylic and homoallylic alcohols\(^{67}\) and siloxanes, respectively.\(^{68}\) In addition \(\text{B}(\text{C}_6\text{F}_5)_3\) has also been used to dehydrocouple silanes with alcohols\(^{61-63,69}\) to give silyl ethers.

### 3.3.3 Comparison of the Catalytic Activity of 3-3 and 3-5 in the Deoxygenation of Ketones

A range of ketones investigated in deoxygenation reactions mediated by 3-3 were reduced using catalyst 3-5 to further compare the Lewis acidity and activity of these two catalysts in this transformation. Deoxygenation reactions were performed under identical conditions to those at which Ph.D. student Meera Mehta performed the analogous reactions with catalyst 3-3 (Table 3.1). 1 mole % catalyst 3-5 was added to solutions of the ketone substrate and 2.1 (Table 3.1, Entries 1-8) or 3.1 (Table 3.1, Entries 9 and 10) equivalents of \(\text{Et}_3\text{SiH}\) at room temperature in dichloromethane, mixed thoroughly and monitored at room temperature by \(^1\text{H}\) NMR spectroscopy and \(^19\text{F}\) NMR spectroscope in the case of 4-fluorobenzophenone (Entry 1) and 1,1,1-trifluorobenzophenone (Entry 7). These reactions resulted in the reduced products shown in Table 3.1. Reported yields were determined via \(^1\text{H}\) NMR spectroscopy by integration of \(\text{CH}_2\) resonances corresponding to the protons on the carbon atom which underwent deoxygenation against the methyl protons of 1.0 equivalent of toluene as an internal standard. Substrates 1-8 underwent complete deoxygenation to yield the corresponding aliphatic products in excellent yields. In the cases of 4-methoxybenzophenone (Entry 5) and 1,2-bis(4-methoxyphenyl)ethanone (Entry 8), yields of the deoxygenated products isolated by column chromatography are reported in parentheses. One equivalent of silyl ether \(\text{Et}_3\text{SiOSiEt}_3\) was formed as a by-product of the deoxygenation reactions.
Table 3.1 Catalytic deoxygenation of ketones with catalysts 3-3 and 3-5

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Note: [a] Conversion values are approximate.

References:

1. [catalyst] (1.0 mol%) + 2.1 or 3.1 Et3SiH → Et3SiOSiEt3

Chemical structures are shown for each entry.
Acetophenone (Entry 1) was deoxygenated to ethylbenzene with conversions of greater than 99% in two hours by 3-5 and 5 hours by 3-3. Benzophenone (Entry 2) was deoxygenated to diphenylmethane with conversions of greater than 99% in five hours by both catalysts. In the cases of substrate entries 3-5, which feature an electron-withdrawing halogen atom in the para- (Entries 3 and 4) or ortho-positions (Entry 5) of one phenyl ring, excellent yields were achieved for both catalysts in 1-5 hours, with 3-5 exhibiting faster deoxygenation in the case 4-fluorobenzophenone and 2-chlorobenzophenone. Entries 6, 7 and 9 feature electron donating methyl (Entry 6) or methoxy (Entries 7, 9) substituents on the phenyl rings and were also deoxygenated in excellent yields in 2-5 hours by both 3-3 and 3-5. The notable exception was the deoxygenation of Entry 6, 2-methylbenzophenone, which yielded only 56% of the deoxygenated product after a reaction time of 72 hours using catalyst 3-5. No reason for the reduced activity of 3-5 in the deoxygenation of this substrate is readily evident, and repetition of this reaction under the same conditions yields similar results. It is possible that the steric congestion caused by the methyl group affects the reactive site during the catalysis with EPC 3-5 more than EPC 3-3, however no reason is obvious for this effect, as the computed mechanism depicted in Figure 3.6 does not involve direct interaction of the catalyst with the substrate. In experiments undertaken with 3-3, using longer reaction times and 3.2 equivalents of silane, the reduction of the methoxy-substituted benzophenone derivatives proceeds further, with methoxy-ether cleavage affording \( \text{PhCH}_2(C_6H_4OSiEt}_3) \). This reaction, however, was not probed with 3-5.

As mentioned in the introduction to this chapter, hydrodefluorination of alkyl fluorides occurs under the same conditions with strongly Lewis acidic EPC catalysts as deoxygenation reactions. This made 1,1,1-trifluoroacetophenone (Entry 8) a particularly interesting substrate to analyze, as this features both ketone and trifluoromethyl functionalities. While it was possible to observe moderate yields of the hydrosilylated ketone with the trifluoromethyl group left intact (Scheme 3.6) when 3.2 equivalents of catalyst 3-3 were used, it was not possible to observe significant quantities of 1,1,1-trifluoroethylbenzene in the \(^1\text{H}\) or \(^19\text{F}\) NMR spectra, nor was it possible to isolate this product. This indicates that at least in the case of 1,1,1-trifluoroacetophenone, the reaction pathway leading to hydrosilylated intermediate D (Figure 3.6) is favoured, as a cationic intermediate such as C would be far less likely to undergo hydrodefluorination via abstraction of a fluoride ion. Correspondingly, the observation of the initial hydrosilylated product indicated that hydrosilylation is favoured over hydrodefluorination. With a significant excess (seven equivalents) of Et\(_3\)SiH, it was possible to effect both deoxygenation and
hydrodefluorination of 1,1,1-trifluoroacetophenone to attain ethylbenzene in moderate (3-5: 56%) or good yields (3-3: 81%).

**Scheme 3.6** Hydrosilylation of 1,1,1-trifluoroacetophenone with catalyst 3-3

Similarly, while the hydrosilylated products of the aryl-substituted ketones were not observed, significant quantities of the hydrosilylated products of aliphatic ketone substrates 3-methyl-2-butanone (Entry 10) and 4-heptanone (Entry 11) were observed. While fully deoxygenated 2-methylbutane was observed in 95% yields in twenty-four hours using both catalysts 3-3 and 3-5, significant quantities of heptane were not observed under these reaction conditions, with 3-heptene, a product of an elimination reaction, being observed instead after further reaction of the hydrosilylated product. Significant amounts of olefin polymerization were also observed by NMR spectroscopy, as well as possible other olefin isomers after prolonged reaction times.

Overall, while some individual ketone substrates showed differing yields of the corresponding deoxygenated products using EPC catalysts 3-3 and 3-5, and differing reaction times were necessary in some cases, a clear trend in catalytic activity was not established. In the deoxygenation of ketones, chloro-substituted dicationic catalyst 3-5 performs comparably to fluoro-substituted dication 3-3. This indicates that while chloro-substituted EPCs may perform just as well as fluoro-substituted catalysts, the substitution of the P-F bond for the significantly weaker bond to the larger, less electronegative chlorine atom is not a significant enough factor to either hinder or enhance catalyst efficiency in the deoxygenation of ketones.

### 3.4 Conclusions

Using SO₂Cl₂ as a chlorinating oxidizing agent, phosphonium cation 3-1 could be converted to dichlorophosphorane 3-4 and subsequently to chlorophosphonium dication 3-5 via abstraction of a chloride ion with [Et₃Si(tol)][B(C₆F₅)₄]. 3-5 represents the first example of a carbene-stabilized chlorophosphonium dication and establishes that chlorophosphonium EPCs are a readily-synthesized
alternative to fluorophosphonium EPCs. The isolation of dichlorophosphorane intermediate 3-4 did prove more challenging than isolation of its difluorophosphorane analogue 3-2, with NMR studies showing progressive degradation of 3-4 in DCM solution. Nonetheless, 3-5 proved much more stable than its precursor and was isolated cleanly.

3-5 is an efficient EPC catalyst for the deoxygenation of ketones in the presence of Et$_3$SiH, with comparable activity to its fluoro-substituted dication analogue 3-3. While not all ketone substrates were deoxygenated with identical efficiencies by catalysts 3-3 and 3-5, no clear trend in reactivity between the two catalysts was evident. The only substrate examined for both catalysts for which profoundly different catalytic efficiency was observed was 2-methylbenzophenone, for which deoxygenation proceeded much more slowly with 3-5 than with 3-3. Hydrosilylated products of aliphatic ketones are observable using both catalysts with approximately one equivalent of Et$_3$SiH, indicating that in the case of these substrates deoxygenation proceeds through an initial hydrosilylation step, while for diaryl-substituted ketones the corresponding hydrosilylated intermediates were not observed and only fully deoxygenated products could be isolated. Interestingly, for PhC(O)CF$_3$, the initial hydrosilylation product was observed without activation of C-F bonds, but the fully deoxygenated product with C-F bonds intact could not be observed.

3.5 Experimental Details

3.5.1 General

All preparations and manipulations were carried out under an anhydrous N$_2$ atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercially available reagents such as SO$_2$Cl$_2$ (1M, CH$_2$Cl$_2$), XeF$_2$, Et$_3$SiH, Ph$_2$PCl, ketones and aldehydes were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise. [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$]$^{70}$ 1,3-dimesityl-4,5-dihydropyrazol-3-ium-2-ylidene,$^{71}$ [(SIMes)PPh$_2$][B(C$_6$F$_5$)$_4$],$^{36}$ and [(SIMes)PFPh$_2$][B(C$_6$F$_5$)$_4$]$^{26}$ 3-3 were prepared following procedures described in literature. CH$_2$Cl$_2$, Et$_2$O, $n$-pentane, and toluene were dried using an Innovative Technologies solvent purification system. C$_6$H$_5$F and CD$_2$Cl$_2$ (Aldrich) were deoxygenated, distilled over CaH$_2$, then stored over 4 Å molecular sieves before use. C$_6$D$_5$Br (Aldrich) was deoxygenated and stored over 4 Å molecular sieves before use. Reactions were monitored using NMR
spectroscopy. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian Agilent DD2 500 MHz spectrometer, and Varian Agilent DD2 600 MHz spectrometer. Data for $^1$H NMR spectroscopy is reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, dm = doublet of multiplets, b = broad), coupling constant (Hz), integration. Data for $^{13}$C NMR is reported in terms of chemical shift (δ / ppm). High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART). Mass spectroscopy experiments were run for isolated products and reaction mixtures, however in some cases the high fragmentation of compounds or volatility did not allow for mass peak identification.

**X-ray Diffraction Studies.** Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) Data reduction was performed using the Bruker SMART$^{72}$ software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). Structure solutions were found with the SHELXS-97 package using the direct method and were refined with SHELXL-97$^{73}$ against $F^2$ using first isotropic and anisotropic thermal parameters for all non-hydrogen atoms.

### 3.5.2 Syntheses of Compounds 3-4 and 3-5

**Synthesis of [(SIMes)PCl$_2$Ph$_2$][B(C$_6$F$_5$)$_4$] 3-4**

![Chemical structure](image)

0.11 mL SO$_2$Cl$_2$ solution (1.0M in CH$_2$Cl$_2$, 0.11 mmol, 1 eq.) was added to a solution of [(SIMes)PPh$_2$][B(C$_6$F$_5$)$_4$] (129 mg, 0.11 mmol, 1.0 eq.) in C$_6$D$_5$Br (1 mL). Upon standing for 30 min a colourless microcrystalline solid precipitated from the yellow solution. The supernatant was decanted and the residue was washed with toluene (2 x 2 mL) and pentane (2 x 2 mL) and dried *in vacuo* yielding [(SIMes)PCl$_2$Ph$_2$][B(C$_6$F$_5$)$_4$] as colourless solid (131 mg, 96% yield). Single crystals of [(SIMes)PCl$_2$Ph$_2$][B(C$_6$F$_5$)$_4$], suitable for X-ray single crystal structure determination, were obtained by cooling a saturated CH$_2$Cl$_2$ solution at −35 °C. While NMR data assignable to [(SIMes)PCl$_2$Ph$_2$][B(C$_6$F$_5$)$_4$] was obtained, even in the case where the product was purified by multiple
recrystallizations notable amounts of Ph₂PCl and [(SIMes)PPh₂][B(C₆F₅)₄] were observed in solution, indicating some decomposition of the product. ¹H NMR (CD₂Cl₂, [ppm]): δ = 2.31 (12H, s, o-Me), 2.35 (6H, s, p-Me), 4.55 (4H, s(br), CH₂), 7.09 (4H, s, m-H), 7.43 (4H, m, Ph), 7.60-7.81 (4H, m, Ph), 7.99 (2H, m, Ph). ¹¹B{¹H} (CD₂Cl₂, [ppm]): δ = −16.7 (s). ¹³C{¹H} (CD₂Cl₂, [ppm]): δ = 19.0 (d, o-CH₃, 3JCP = 4.4 Hz), 21.6 (s, p-Me), 51.5 (s, CH₂), 125.9 (d, i-Ph, 1JCP = 2.5 Hz), 129.6 (d, m-Mes, 3JCP = 10.6 Hz), 129.5 (d, m-Ph, 3JCP = 6.7 Hz), 131.3 (s, m-Mes), 131.3 (s, p-Ph), 132.4 (d, o-Ph, 2JCP = 24.5 Hz), 135.7 (s, o-Mes), 136.2 (d(br), C₆F₅, 1JCF = 244 Hz), 138.1 (d(br), C₆F₅, 1JCF = 247 Hz), 143.2 (s, p-Mes), 148.9 (d(br), C₆F₅, 1JCF = 241 Hz), 158.9 (s, C₂). ¹⁹F{¹H} NMR (CD₂Cl₂, 26 °C): δ = −167.6 (8F, m, m-F), −163.7 (4F, t, p-F), −133.1, (8F, m, o-F). ³¹P{¹H} NMR (CD₂Cl₂, 26 °C): δ = −63.9 ppm.

Elemental analysis for C₅₇H₃₆BF₂₀Cl₂N₂P: calcd.: C 55.1, H 2.9, N 2.3; found: C 54.4, H 3.2, N 2.4; ESI MS: m/z: 561.2 (calcd. for M⁺: 561.2).

Synthesis of [(SIMes)PCl₂Ph₂][B(C₆F₅)₄] 3-5

Freshly prepared [Et₃Si(tol)][B(C₆F₅)₄] (98 mg, 0.11 mmol, 1.0 eq.) was added portionwise to a suspension of [(SIMes)PCl₂Ph₂][B(C₆F₅)₄] (137 mg, 0.11 mmol, 1.0 eq.) in 2 mL toluene. The reaction mixture was stirred for two hours at ambient temperature giving a yellow solid and a yellowish supernatant. The supernatant was decanted and the residue was washed with toluene (2 x 2 mL) and pentane (2 x 2 mL) and dried in vacuo yielding 3-5 as a yellow solid (116 mg, 60% yield).

¹H NMR (CD₂Cl₂, [ppm]): δ = 2.21 (12H, s, o-Me), 2.24 (6H, s, o-Me), 4.60 (4H, s, CH₂), 6.81 (4H, s, m-H), 7.59 (4H, m, o-Ph), 7.67 (4H, td, m-Ph), 8.00 (2H, tt, p-Ph, 3JHH = 7.5 Hz, 4JHH = 1.5 Hz). ¹¹B{¹H} (CD₂Cl₂, [ppm]): δ = −16.7 (s). ¹³C{¹H} (CD₂Cl₂, [ppm]): δ = 19.1 (s, o-Me), 21.4 (s, p-Me), 55.5 (d, CH₂, 3JCP = 4.7 Hz), 111.2 (d, i-Ph, 1JCP = 91.2 Hz), 126.0 (s, i-Mes), 132.0 (s, m-Mes), 132.6 (d, m-Ph, 3JCP = 13.7 Hz), 133.3 (d, o-Ph, 2JCP = 14.1 Hz), 135.2 (s, o-Mes), 137.1 (d(br), C₆F₅, 1JCF = 241 Hz), 139.0 (d(br), C₆F₅, 1JCF = 244 Hz), 140.7 (d, p-Ph, 4JCP = 3.6 Hz), 145.6 (s, p-Mes), 149.0 (d(br), C₆F₅, 1JCF = 241 Hz), 155.5 (d, C₂, 1JCP = 86.5 Hz). ¹⁹F{¹H} NMR (CD₂Cl₂, [ppm]): δ = −167.3 (8F, m, m-F), −163.4 (4F, m, p-F), −133.1, (8F, m, o-F). ³¹P{¹H} NMR (CD₂Cl₂, [ppm]): δ = 47.4 ppm. Elementary analysis for C₈₁H₃₆B₂F₄₀N₂P: calcd.: C 51.6, H 1.9, N 1.5; found: C 52.4, H 2.3, N 1.5; ESI MS: m/z: 263.2 (calcd. for M⁺: 263.2).
3.5.3 Catalytic Hydrodeoxygenation of Ketones

General Procedure for Ketone Hydrosilylation

All reactions were carried out under identical conditions on a 0.1 - 0.2 mmol scale. In a glove box, 1 mol % of the respective catalyst (3-3: 1.9 mg, 0.0010 mmol; 3-5: 1.9 mg, 0.0010 mmol) was added to a solution of Et$_3$SiH (18 µL, 0.21 mmol for substrate Entries 1-7, 9; 26 µL, 0.31 mmol for substrate Entries 10,11; 59 µL, 0.70 mmol for substrate 9) in CD$_2$Cl$_2$ (0.7 mL). One equivalent (0.10 mmol) of the respective substrate was then added. The reaction mixture was transferred to a NMR tube, sealed and monitored by $^1$H and $^{13}$C NMR spectroscopy and in the cases of substrates 3 and 8, $^{19}$F NMR spectroscopy. An internal standard of toluene was added to determine degree of conversion. For less volatile products, reaction mixtures were worked-up by evaporating the di(triethylsilyl) ether by-product. To avoid loss of product under reduced pressure the solution was occasionally monitored by $^1$H NMR. For the substrates that could not be isolated, NMR data for the crude reaction mixture is presented, in which the bis(triethylsilyl) ether by-product can be observed. Upon completion of catalysis, $^{31}$P NMR reveals that both catalysts $[(\text{SIMes})\text{PFPh}_2][\text{B(C}_6\text{F}_5)_4]$$_2$ 3-3 and $[(\text{SIMes})\text{PClPh}_2][\text{B(C}_6\text{F}_5)_4]$$_2$ 3-5 undergo significant decomposition to $[(\text{SIMes})\text{PPh}_2][\text{B(C}_6\text{F}_5)_4]$, observed as a singlet at 14.1 ppm in the $^{31}$P NMR spectrum, and $[(\text{SIMes})\text{PF}_2\text{Ph}_2][\text{B(C}_6\text{F}_5)]$, observed as a peak as a triplet at -62.9 ppm ($^1J_{PF} = 735$ Hz) in the $^{31}$P NMR spectrum. $^{11}$B or $^{19}$F NMR spectroscopy did not indicate any decomposition of the borate anion for either catalyst.

Characterization Data for Hydrosilylation and Hydrodeoxygenation Products of Ketones

Reaction of Catalyst 5 with Acetophenone

Catalyst (3-3) (10 mg) was dissolved in CD$_2$Cl$_2$ (0.7 mL), an excess of acetophenone was added. The solution was allowed to sit for an hour, before $^{31}$P NMR was run. The $^1$H NMR revealed a mixture of products and the organic decomposition product could not be identified.
Table 3.1-1 & Table 3.1-8: Ethylbenzene 74

\[ \text{1H NMR (CD}_2\text{Cl}_2, [ppm]): } \delta = 1.29 (3H, t, \text{CH}_2\text{CH}_3, 3J_{HH} = 8 \text{ Hz}), 2.70 (2H, q, \text{CH}_2\text{CH}_3, 3J_{HH} = 8 \text{ Hz}), 7.26 (5H, m, \text{Ph}). \]

\[ \text{13C} \{\text{1H} \} \text{ NMR CD}_2\text{Cl}_2, [ppm]): } \delta = 16.4 (s, \text{CH}_3), 29.8 (s, \text{CH}_2), 126.4 (s, \text{Ph}), 128.7 (s, \text{Ph}), 129.2 (s, \text{Ph}), 145.3 (s, \text{Ph}) \]

Table 3.1-2: Diphenylmethane 75

\[ \text{1H NMR (CD}_2\text{Cl}_2, [ppm]): } \delta = 3.98 (2H, s, \text{CH}_2), 7.20 (6H, m, \text{Ph}), 7.29 (4H, m, \text{Ph}). \]

\[ \text{13C}\{\text{1H} \} \text{ NMR CD}_2\text{Cl}_2, [ppm]): } \delta = 41.9 (s, \text{CH}_2), 126.0 (s, \text{Ph}), 128.4 (s, \text{Ph}), 128.8 (s, \text{Ph}), 141.4 (s, \text{Ph}) \text{. DART MS: } m/z: ](\text{calcd. for M+NH}_4^+: 186.1287). \]

Table 3.1-3: 1-Benzyl-4-fluorobenzene 75, 76
$^1$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 3.97$ (2H, s, CH$_2$), 7.00 (2H, m, Ph), 7.20 (5H, m, Ph), 7.30 (2H, m, Ph).

$^{13}$C $\{^1$H$\}$ NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 41.6$ (s, CH$_2$), 115.7 (d, Ph, $^3$J$_{CF} = 21$ Hz), 126.8 (s, Ph), 129.3 (d, Ph, $^2$J$_{CF} = 34$ Hz), 130.9 (s, Ph), 137.8 (s, Ph), 141.8 (s, Ph), 162.0 (d, Ph, $^1$J$_{CF} = 243$ Hz).

$^{19}$F NMR (CD$_2$Cl$_2$, [ppm]): $\delta = -118.1$ (s ppm).

Table 3.1-4: 1-Benzyl-4-bromobenzene

$^1$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 3.94$ (2H, s, CH$_2$), 7.11 (2H, m, Ph), 7.20 (2H, m, Ph), 7.22 (1H, m, Ph), 7.30 (2H, m, Ph), 7.43 (2H, m, Ph).

$^{13}$C NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 42.0$ (s, CH$_2$), 120.6 (s, Ph), 127.1 (s, Ph), 129.4 (s, Ph), 129.7 (s, Ph), 131.4 (s, Ph), 132.3 (s, Ph), 141.3 (s, Ph), 141.5 (s, Ph).

Table 3.1-5: 1-Benzyl-2-chlorobenzene

$^1$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 4.13$ (s, 2H), 7.22 (m, 6H), 7.30 (m, 2H), 7.40 (m, 1H).

$^{13}$C NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 39.7$ (s, CH$_2$), 126.8 (s, Ph), 127.5 (s, Ph), 128.3 (s, Ph), 129.0 (s, Ph), 129.5 (s, Ph), 130.1 (s, Ph), 131.7 (s, Ph), 134.7 (s, Ph), 139.4 (s, Ph), 140.3 (s, Ph). DART MS: m/z: 220.08995 (calcd. for M+NH$_4^+$: 220.08930).

Table 3.1-6: 1-Benzyl-2-methylbenzene

$^1$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 2.28$ (s, 3H), 4.02 (s, 2H), 7.17 (m, 7H), 7.30 (m, 2H).

$^{13}$C NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 20.0$ (s, CH$_3$), 40.0 (s, CH$_2$), 126.6 (s, Ph), 127.0 (s, Ph), 129.0 (s, Ph), 129.3 (s, Ph), 130.5 (s, Ph), 130.8 (s, Ph), 137.2 (s, Ph), 139.8 (s, Ph), 141.3 (s, Ph). DART MS: m/z: 200.14314 (calcd. for M+NH$_4^+$: 200.14392).

Table 3.1-7: 1-Benzyl-4-methoxybenzene

Isolated Yield = 73%. $^1$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 3.77$ (3H, s, OCH$_3$), 3.92 (2H, s, CH$_2$), 6.84 (2H, m, Ph), 7.12 (2H, m, Ph), 7.19 (3H, m, Ph), 7.28 (2H, m, Ph).

$^{13}$C NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 41.8$ (s, CH$_2$), 56.0 (s, OCH$_3$), 114.6 (s, Ph), 126.7 (s,
Ph), 129.2 (s, Ph), 129.5 (s, Ph), 130.6 (s, Ph), 134.3 (s, Ph), 142.7 (s, Ph), 158.9. **DART MS:** m/z: 216.13914 (calcd. for M+NH₄⁺: 216.13884).

(4-Benzylphenoxy)triethylsilane from reaction of 4-methoxybenzophenone with 3.1 equivalents of Et₃SiH

(Isolated Yield = 60%). **¹H NMR (CD₂Cl₂, [ppm]):** δ = 0.54 (6H, q, CH₂CH₃, ³J_HH = 7.9 Hz), 0.94 (9H, t, CH₂CH₃, ³J_HH = 7.9 Hz, 9H), 3.90 (2H, s, CH₂), 6.75 (2H, m, Ph), 7.06 (2H, m, Ph), 7.18 (3H, m, Ph), 7.27 (2H, m, Ph). **¹³C NMR (CD₂Cl₂, [ppm]):** δ = 6.9 (s, CH₂CH₃), 7.2 (s, CH₂CH₃), 41.5 (s, CH₂), 115.7 (s, Ph), 126.5 (s, Ph), 129.0 (s, Ph), 129.3 (s, Ph), 130.5 (s, Ph), 134.1 (s, Ph), 142.4 (s, Ph), 154.6 (s, Ph). **²⁹Si NMR (119 MHz, CD₂Cl₂):** δ = −37.0 (s) ppm. **DART MS:** m/z: 184.1 (calcd. for M+NH₄⁺: 184.1).

Table 3.1- 8: Triethyl(2,2,2-trifluoro-1-phenylethoxy)silane

(Isolated yield: 74%). **¹H NMR (CD₂Cl₂, [ppm]):** δ = 0.61 (6H, q, CH₂CH₃, ³J_HH = 7.9 Hz, 6H), 0.90 (9H, t, CH₂CH₃, ³J_HH = 7.9 Hz), 4.97 (1H, q, CH(OSiEt₃)CF₃, ²J_HF = 6.7 Hz, 1H), 7.37 (3H, m, Ph), 7.47 (2H, m, Ph). **¹³C NMR (CD₂Cl₂, [ppm]):** δ = 5.0 (s, CH₂CH₃), 6.7 (s, CH₂CH₃), 73.9 (q, CH(OSiEt₃)CF₃, ²J_CF = 31.8 Hz), 125.0 (q, CF₃, ¹J_CF = 282.3 Hz), 128.2 (s, Ph), 128.8 (s, Ph), 129.7 (s, Ph), 136.1 (s, Ph). **¹⁹F NMR (CD₂Cl₂, [ppm]):** δ = −78.8 (d, ³J_HF = 7.2 Hz); **²⁹Si NMR (119 MHz, CD₂Cl₂):** δ = 24.6 (s) ppm. **DART MS:** m/z: 308.16629 (calcd. for M+NH₄⁺: 308.165751).

Table 3.1- 9: 1,2-Bis(4-methoxyphenyl)ethane

(Isolated Yield = 35%). **¹H NMR (CD₂Cl₂, [ppm]):** δ = 2.83 (4H, s, CH₂), 3.76 (6H, s, CH₃), 6.81 (4H, m, Ph), 7.09 (4H, m, Ph). **¹³C NMR (CD₂Cl₂, [ppm]):** δ = 38.0 (s, CH₂), 55.4 (s, OCH₃), 114.4 (s, Ph), 130.2 (s, Ph), 134.7 (s, Ph), 158.8 (s, Ph); **DART MS:** m/z: 260.16538 (calcd. for M+NH₄⁺: 260.16505).
Table 3.1-10: Triethylsilyl((3-methylbutan-2-yl)oxy)silane

\[
\text{OSiEt}_3
\]

\(^1\)H NMR (CD\(_2\)Cl\(_2\), [ppm]): \(\delta = 0.53\) (6H, q, CH\(_2\)CH\(_3\), \(^3\)J\(_{HH}\) = 7.9 Hz), 0.93 (15H, m, CH\(_3\), OSi(CH\(_2\)CH\(_3\))\(_3\)), 1.09 (3H, dd, \(^3\)J\(_{HH}\) = 31.0, 6.2 Hz, CH\(_3\)), 1.58 (1H, m, CH(CH\(_3\))\(_2\)), 3.57 (1H, m, CH\(_3\)CH(OH)(OSiEt\(_3\))). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), [ppm]): \(\delta = 5.6\) (s, CH\(_2\)CH\(_3\)), 7.3 (CH\(_2\)CH\(_3\)), 18.2 (s, CH\(_3\)); 18.3 (s, CH\(_3\)), 18.5 (s, CH\(_3\)), 20.4 (s, CH\(_3\)), 20.6 (s, CH\(_3\)), 35.6 (s, CH); 36.1 (s, CH), 73.5 (s, CH\(_3\)C(H)OSi(CH\(_2\)CH\(_3\))\(_3\)). \(^{29}\)Si NMR (CD\(_2\)Cl\(_2\), [ppm]): \(\delta = 14.9\) ppm.

Table 3.1-10: Isopentane

\[
\text{CH}_3\text{C}(\text{H})\text{OSi}(\text{CH}_2\text{CH}_3)_3
\]

\(^1\)H NMR (CD\(_2\)Cl\(_2\), [ppm]): \(\delta = 0.87\) (3H, m (overlapping d), CH\(_3\)), 0.88 (6H, d, \(^3\)J\(_{HH}\) = 6.8 Hz, CH\(_3\)), 1.17 (2H, m, CH\(_2\)), 1.30 (2H, m, CH\(_2\)); 1.55 (1H, m, CH); \(^{13}\)C\(^{1}\)H NMR (CD\(_2\)Cl\(_2\), [ppm]): \(\delta = 12.1\) (s, CH\(_3\)), 22.6 (s, CH\(_3\)), 30.5 (s, CH(CH\(_3\))\(_2\)), 32.3 (s, CH\(_3\)CH\(_2\))

Table 3.1-11(Heptan-4-yloxy)triethylsilane

\[
\text{CH}_2\text{CH}_3\text{C}(\text{H})\text{OSi}(\text{CH}_2\text{CH}_3)_3
\]

Isolated Yield = 83%. \(^1\)H NMR (CD\(_2\)Cl\(_2\), [ppm]) \(\delta = 0.52\) (6H, q, \(^3\)J\(_{HH}\) = 8.0 Hz, CH\(_2\)CH\(_3\)), 0.93 (15H, t and overlapping m, CH\(_3\), t : \(^3\)J\(_{HH}\) = 8.0 Hz, ), 1.39 (8H, m, CH\(_2\)), 3.67 (1H, m, CH(CH\(_3\))OSiEt\(_3\)). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), [ppm]) \(\delta = 72.7, 40.2, 19.2, 14.7, 7.3, 5.6\). \(^{29}\)Si NMR (CD\(_2\)Cl\(_2\), [ppm]) \(\delta = 14.9\) (s) ppm. HRMS (DART Ionization, m/z): calcd. for C\(_{13}\)H\(_{31}\)OSi, \([\text{M}^+\text{H}^+]\): 231.21442; found: 231.21496.

Olefin Polymerization of 4-heptanone

\[
\text{Olefin Polymerization of 4-heptanone}
\]
Reaction Mixture (1H CD₂C₂)

1 hr

5 hr

24 hr

72 hr

0.0  9.5  9.0  8.5  8.0  7.5  7.0  6.5  6.0  5.5  5.0  4.5  4.0  3.5  3.0  2.5  2.0  1.5  1.0  0.5  0.0  -0.5

Reaction Mixture 72 hr (13C{1H} NMR CD₂C₂)

-54.00

20  210  200  190  180  170  160  150  140  130  120  110  100  90  80  70  60  50  40  30  20  10  0  -10
### 3.5.4. Crystallographic Details

Table 3.4 Crystallographic data and details of the structure refinement of compounds 3-4 and 3-5

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(52) The final free energies (in kcal mol⁻¹) are calculated at the B2PLYP-D3/def2-QZVP level of theory using TPSS-D3/def2-TZVP + COSMO(CH2Cl2) computed geometries and thermal corrections and more reliable COSMO-RS(CH2Cl2) solvation free energies. For more information, please see Supporting Information.


(73) Sheldrick, G.M. SHELXTL-97, Program for Crystal Structure Determination, Gottingen, Germany, 1997


Chapter 4: Synthesis and Lewis Acid Catalytic Activity of Ferrocenyl-Derived Phosphonium Cations

4.1 Introduction

4.1.1 Easily-Synthesized Electrophilic Phosphonium Cations

The utility of electrophilic phosphonium cations (EPCs) as Lewis acid catalysts for a range of catalytic transformations has been demonstrated. These transformations include the hydrodefluorination of fluoroalkanes,2-5 hydrodeoxygenation of ketones,6 dehydrocoupling of alcohols and silanes,7 hydrosilylation of olefins,7,8 ketones,9 imines,9 and nitriles,9 isomerization of 1-hexene,8 polymerization of isobutylene9 and THF,4 Friedel-Crafts dimerization of 1,1-diphenylethylene10 and transfer7 and direct11 hydrogenation of olefins. The focus of efforts in continued development of EPC Lewis acid catalysts have been to broaden the scope of transformations achievable, to increase catalytic efficiency, and to expand the architectures of EPCs. For the latter aim, it was sought to synthesize robust, catalytically-efficient EPCs from cheap, commercially-available starting materials in a minimum number of synthetic steps. The abundance of commercially-available phosphine ligands typically used for transition metal catalysts presents a wide range of potential EPC variants synthesizable in relatively few steps using established protocols.

As noted in the previous chapter, proximal dicationic charges were shown to enhance catalytic activity of these EPCs3-6,12. Several dicationic architectures have been explored by the Stephan group, featuring either dual cationic phosphorus centres or the incorporation of a ligand bearing an additional cationic charge, as described in the previous chapter of this thesis.3-6,12 A selection of these architectures is shown in Figure 4.1 (structures B-E).
4.1.2 Ferrocene Derivatives as Lewis Acid Catalysts

We have noted the previous work of Oestreich, who described the synthesis of ferrocenylsilylum cations which are unique Lewis acid catalysts (Figure 4.2). These ferrocenylsilylum cations exhibit a Z-type interaction between the iron(II) centre and the cationic silicon atom. With few exceptions, previously characterized silylum cations reported prior to this example were stabilized by electron donation from arene solvents; stabilization by donation from a metal centre is highly unusual. These cations were demonstrated to catalyze Diels-Alder reactions of a variety of substrates, although it was noted that the degree of electron-deficiency at the silicon centre did not necessarily correlate with catalyst performance. Recently, the Oestreich group also reported planar chiral variants of these catalysts accessed by functionalization of the Cp ring at the position adjacent to the silyl group.
4.2 Ferrocenyl Phosphonium Cations

4.2.1 Synthesis of Ferrocenyl Fluorophosphonium Cations

Reaction of diphenylphosphinoferrocene and 1,1’-bis(diphenylphosphino)ferrocene (dppf)\(^{23,24}\) using one or two equivalents of xenon difluoride, respectively, resulted in oxidation of the P(III) centres in the ferrocene derivatives, yielding quantitatively ferrocenyl mono- and bis-diphenyldifluorophosphoranes, \(\text{CpFe}(\eta^5-\text{C}_5\text{H}_4\text{PF}_2\text{Ph}_2)\) \textbf{4-1} and \(\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{PF}_2\text{Ph}_2)_2\) \textbf{4-2}, respectively (Scheme 4.1). The \(^{31}\text{P}\) NMR spectrum for \textbf{4-1} exhibits a triplet resonance at \(-50.1\)
ppm, while the associated doublet resonance in the $^{19}$F NMR spectrum appeared at $-42.7$ ppm. ($J_{PF} = 656$ Hz). The corresponding $^{31}$P and $^{19}$F NMR spectra for 4-2 are very similar, showing a triplet signal at $-51.5$ ppm and a doublet signal at $-42.8$ ppm, respectively with measured $J_{PF}$ coupling of $662$ Hz. Interestingly, the P-F couplings in 4-1 and 4-2 are significantly smaller than those observed in Fe($\eta^5$-C$_5$H$_4$PF$_4$)$_2$ (817 Hz, 977 Hz).$^{26}$

Clear differences between the two compounds were only observed by $^1$H NMR and $^{13}$C NMR spectroscopies. In the $^1$H NMR spectrum, the higher symmetry of 4-2 results in only two distinct resonances for the Cp protons in a 1:1 ratio at 4.10 ppm and 4.62 ppm, while 4-1 exhibits three resonances in the due to the inequivalence of the Cp rings, with the five protons of the unsubstituted Cp ring appearing at 3.94 ppm, and two resonances assigned to the $\beta$ and $\alpha$ protons of the substituted Cp ring at 4.50 ppm and 4.83 ppm, respectively. X-ray diffraction analysis of single crystals of 4-1 confirmed a pseudo-trigonal bipyramidal geometry at phosphorus with the two fluorine atoms occupying the axial positions with a F–P–F angle of 177.0(1)$^\circ$ and P-F bond lengths averaging 1.677(5) Å, typical of aryl fluorphosphoranes (Figure 4.3).$^2$

![Figure 4.3](image)

**Figure 4.3** POV-ray depiction of 4-1 with H atoms omitted for clarity. C: black; P: orange; F: magenta; Fe: brown

Subsequent reaction of 4-1 and 4-2 using one or two equivalents of [SiEt$_3$(tol)][B(C$_6$F$_5$)$_4$], respectively (Scheme 4.1), resulted in abstraction of fluoride ion from the difluorophosphoranes yielding the B(C$_6$F$_5$)$_4$ salts of the ferrocenyldiphenylfluorophosphonium cation, [CpFe($\eta^5$–C$_5$H$_4$PF$_2$)][B(C$_6$F$_5$)$_4$] 4-3 and ferrocenylbis-(diphenylfluorophosphonium)
dication, \([\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{PFPh}_2)_2]\) \([\text{B}(\text{C}_6\text{F}_5)_4]_2\) 4-4, respectively (Scheme 4.1). The \(^{31}\text{P}\{^1\text{H}\}\) and \(^{19}\text{F}\{^1\text{H}\}\) NMR spectra of 4-3 and 4-4 are very similar, with \(^{31}\text{P}\{^1\text{H}\}\) doublet resonances appearing at 102.8 and 102.9 ppm and doublets in the \(^{19}\text{F}\) NMR spectra at –112.4 ppm for 4-3 and at –119.6 ppm for 4-4. The observed \(^1J_{\text{PF}}\) coupling constants are characteristic of fluorophosphonium cations, 998 Hz for 4-3 and 1002 Hz for 4-4. Signals in the \(^1\text{H}\) NMR spectra of 4-3 and 4-4 are shifted downfield compared to those of the phosphorane precursors, consistent with the decreased shielding due to the cationic charges on the phosphorus centres.

Scheme 4.1 Syntheses of ferrocenyl phosphonium salts 4-3 and 4-4

Crystallographic studies of single crystals of 4-3 and 4-4 confirmed the proposed formulations (Figure 4.4). In 4-3 and 4-4, the fluorophosphonium centres are pseudo-tetrahedral. In 4-3 the P-F bond is 1.574(3) Å, while in 4-4 the P-F bonds are shorter, averaging 1.545(2) Å. In both cases observed bond metrics are typical of fluorophosphonium cations. As in previous structurally-characterized fluorophosphonium EPCs,\(^3-6,12\) dication 4-4 has a slightly shorter P-F bond length than monocation 4-3. Unsurprisingly the phosphonium moieties in 4-4 are oriented so as to maximize the distance between the cationic centres in the solid state.
Figure 4.4 – POV-ray depictions of cations 4-2 (top) and 4-3 (bottom) with H atoms omitted for clarity. C: black; P: orange; F: magenta; Fe: brown.

4.2.2 Redox Activity of Ferrocenyl Fluorophosphonium Cation 4-3

The isolation of the Fe(III) analogue of 4-3 would present a unique example of an EPC dication with positive charges formally residing on the phosphorus and iron atoms. Oxidation reactions of the Fe(II) centre of 4-3 were thus pursued. A variety of chemical oxidation agents were added to solutions of cation 4-3, with Ag(I) species exhibiting the most promise. Efforts to generate the Fe(III) species by the addition of AgX (X = F, Cl) to 4-3 exhibited the colour change characteristic of Fe(II) to Fe (III) oxidation as DCM and toluene suspensions changed from a
light orange colour to a deep turquoise (Scheme 4.2). However, all efforts to isolate the oxidized species were fraught with difficulty and ultimately unsuccessful.

Scheme 4.2 Attempted oxidation of the Fe(II) centre in 4-3 to the Fe (III) analogue.

Electrochemical oxidation of 4-3 was also investigated. 4-3 was dissolved in a dry CH₂Cl₂ solution containing 0.1M [nBu₄N][PF₆] and after two hours ³¹P and ¹⁹F NMR spectra were obtained. Gratifyingly, only trace amounts of phosphorane 4-2, the product of fluoride abstraction from the PF₆ anion by 4-3, were observed by NMR spectroscopy. Under a flow of nitrogen gas, a dry CH₂Cl₂ solution of 4-3 with 0.1M [nBu₄N][PF₆] as the supporting electrolyte was analyzed by cyclic voltammetry. Cyclic voltammograms were obtained at scan rates of 5, 10, 20, 50, 100 and 200 mV/s versus a glassy carbon working electrode. 4-3 exhibited a quasi-reversible oxidation wave, but began to decompose in solution.

Figure 4.5 Cyclic Voltammogram of 4-3 obtained in CH₂Cl₂ with 0.1M [nBu₄N][PF₆] as electrolyte and referenced against ferrocene (glassy carbon working electrode, step = 5mV, scan rate = 200 mV/s).
4.3.1 Synthesis of Ferrocenyl Phosphonium Cation $\text{[PhMeP(}\eta^5\text{-C}_5\text{H}_4\text{)}_2\text{Fe}[\text{B(C}_6\text{F}_5\text{)}_4]]$

Efforts to increase the Lewis acidity of phosphonium cations had to this point focused on the two strategies detailed previously to minimize electron density at the phosphorus atom: the incorporation of strongly inductively electron-withdrawing substituents, or the incorporation of positively charged substituents. A third approach conceived to render phosphonium centres more electron-deficient and Lewis acidic was to incorporate phosphonium centres into rigid molecular architectures which would induce significant geometric deviation from tetrahedral geometry. This would reduce effective orbital overlap between the ipso-Cp carbon atoms and the phosphorus atom, potentially rendering the phosphorus atom more Lewis acidic and reactive. To achieve such geometric strain, the most obvious route was to design species wherein two or more of the atoms bonded to the phosphorus centre were connected by a linkage forming an angle of significantly less than the 109.5 ° expected for an ideally tetrahedral phosphonium cation. For example, methylation of phenylphosphine-bridged ferrocenophane 4-525 resulted in the previously-reported ferrocenophane 4-6 (Figure 4.6) featuring a phosphonium bridge. This cation exhibited a C-P-C bond angle between the ipso carbon atoms of the cyclopentadienide rings and the phosphorus atom of 99.8(4) °.27

Figure 4.6 The methylphosphonium salt 4-6 synthesized by Manners et. al.

Attempts to synthesize additional fluorophosphonium cations derived from a phosphinoferrocenophane were undertaken. To this end, the species PhP(η^5-C_5H_4)_2Fe 4-5 was prepared following slightly modified literature methods.27,28 Addition of a solution of XeF_2 to a solution of 4-5 in dichloromethane rapidly yielded an insoluble, intractable dark solid, suggesting the possibility of polymeric products. Similarly, attempts to form the fluorophosphonium cation directly by fluoronium ion transfer from Selectfluor or fluoropyridines were also unsuccessful. Manners has noted that the chlorophosphine analogue CIP(C_5H_4)_2Fe is unstable at temperatures above -20°C.28 Nonetheless, compound 4-5 could be methylated upon addition of MeOTf
generating the OTf salt [PhMeP(η⁵-C₅H₄)₂Fe][O₂SCF₃] 4-6 (Scheme 4.3) reported by Manners. Although this species was not isolated, treatment of the solution of 4-6 with one equivalent of [Et₃Si(tol)][B(C₆F₅)₄] effected anion exchange providing access to the new salt [PhMeP(η⁵-C₅H₄)₂Fe][B(C₆F₅)₄] 4-7 (Scheme 4.3). 4-7 exhibited a singlet in the ³¹P NMR spectrum at 35.6 ppm (Figure 4.7), nearly identical to that of the OTf salt reported by Manners.²⁷

![3¹P NMR spectrum of isolated product (CD₂Cl₂)](image)

**Figure 4.7** ³¹P NMR spectrum of isolated salt 4-7

It has been observed that most phosphonium cations catalytically active as their [B(C₆F₅)₄] salts are often inactive as OTf salts,¹ hence the synthesis of 4-7. The formulation of 4-7 and the quaternization of the phosphorus centre were confirmed crystallographically (Figure 4.8). The structure of [PhMeP(η⁵-C₅H₄)₂Fe][B(C₆F₅)₄] exhibited a C-P-C bond angle between the ipso carbon atoms of the cyclopentadienide rings and the phosphorus atom of 100.8(2) °, very similar to the solid-state structure reported for 4-6.²⁷

![Scheme 4.3 Syntheses of ferrocenyl phosphonium salt 4-7](image)
Figure 4.8 – POV-ray depiction of cation of 4-7, with H atoms omitted for clarity. C: black; P: orange; Fe: light brown.

### 4.4 Lewis Acid Catalysis with Compounds 4-3, 4-4, and 4-7

#### 4.4.1 An Overview of Lewis Acid Catalysis Mediated by Compounds 4-3, 4-4, and 4-7

Having generated several ferrocene-derived phosphonium cations, the catalytic activities of the salts 4-3, 4-4 and 4-7 were probed (Scheme 4.4). Consistent with the observed reactivity of established EPCs of types A, B, C, D, and E,\(^3\)\(^-\)\(^6\)\(^,\)\(^1\)\(^2\) dication 4-4 was shown to quantitatively catalyze Friedel-Crafts dimerization of 1,1-diphenylethylene, dehydrocoupling of phenol and triethylysilane, and deoxygenation of acetophenone in the presence of 2.1 equivalents of HSiEt\(_3\) as a hydride source. While relatively weakly Lewis acidic EPCs have demonstrated the ability to catalyse the former two reactions, it generally requires more strongly Lewis acid EPCs to effect deoxygenation of ketones. More weakly Lewis acidic EPCs, and even the borane Lewis acid \(\text{B(C}_6\text{F}_5)_3\), show reduced ability to mediate ketone deoxygenation or in some cases only achieve hydrosilylation.\(^1\)\(^6\)

Compound 4-4 also mediated the hydrodefluorination of 1-fluoropentane in the presence of HSiEt\(_3\) in 55% yield after 7 days at 25\(^\circ\)C. The relatively poorer activity in this latter process is attributed to the high bond energy of the C-F bond, requiring a particularly strong Lewis acid. While the computed mechanism for hydrodefluorination by EPC [(C\(_6\)F\(_5\))\(_3\)PF][B(C\(_6\)F\(_5\))\(_4\)] does not involve direct C-F bond activation by the phosphonium cation,\(^2\) it can be postulated that this more Lewis acidic EPC interacts more strongly with the hydridic hydrogen atom of Et\(_3\)SiH, thus
inducing greater positive charge at the silicon atom and rendering it more fluorophilic and thus a better C-F bond activation agent.

In contrast, the monocation 4-3 was less reactive in each of these catalytic processes, requiring heating to 50 °C to catalyze 10% dimerization of diphenylethylene. Nonetheless, 4-3 did catalyze the dehydrocoupling of phenol and triethylsilane (97%) albeit over the course of 7 days. Similarly, heating 4-3 for 3 days only catalyzed the deoxygenation of acetophenone to 27% yield. At the same temperature 4-3 exhibited essentially no ability to mediate hydrodefluorination, converting only 1% of 1-fluoropentane to pentane. Interestingly, neither 4-3 nor 4-4 catalyzed the hydrosilylation of olefins with either Et$_3$SiH or PhSi(Me$_2$)H, in contrast to other EPCs.

In stark contrast to 4-3 and 4-4, compound 4-7 showed neither catalytic nor stoichiometric activity in any of these transformations. This is consistent with our previous observations that electron-withdrawing substituents are essential to lower the energy of the σ* LUMO enhancing the electron acceptor properties of such phosphonium cations.$^2$ In addition, ferrocene is comparatively sterically demanding and may inhibit access to the σ* LUMO on the phosphorus atom.

\[ 
\begin{align*}
\text{PhOH} + \text{Et}_3\text{SiH} & \xrightarrow{\text{<cat> (2mol%)}} \text{PhOSiEt}_3 \\
\text{PhCOCH}_3 + 2 \text{Et}_3\text{SiH} & \xrightarrow{\text{<cat> (2mol%)}} \text{PhCH}_3(\text{Et}_3\text{Si})_2\text{O} \\
\text{F-C}_4\text{H}_9 & \xrightarrow{\text{<cat> (2mol%)}} <1\% (96h, 50^\circ\text{C})
\end{align*}
\]

\textbf{Scheme 4.4} Transformations mediated by Lewis acidic EPCs 4-3, 4-4 and 4-7
4.4.2 Study of Deoxygenation of Ketones with Compounds 4-3 and 4-4

To further probe the reactivity of 4-3 and 4-4 in deoxygenation of ketones, a broader range of substrates was investigated (Table 4.1). The deoxygenation of ketones in the presence of slight excesses of silanes is a process for which EPCs, in particular strongly Lewis acidic EPCs, have proven significantly more capable than the prototypical borane Lewis acid catalyst B(C₆F₅)₃. As discussed in the previous chapter of this thesis, many classic methods of ketone deoxygenation such as the Barton-McCombie reaction using trialkyltinhydrides, and the Clemmensen (Zn/Hg, HCl) or Wolff-Kishner (H₄N₂, KOH) reductions generally require stoichiometric amounts of toxic reagents and show poor functional group tolerance. While more recent heterogeneous catalysts for this process such as PtO₂, Ni/Al₂O₃ or Pd/C use H₂ as the reducing agent, development of homogeneous metal-free catalysts nonetheless offer significant advantages. For this reason it was chosen to undertake a more comprehensive study of the ketone deoxygenation activity of catalysts 4-3 and 4-4. With the analysis of a broader scope of substrates, it was also sought to establish more clearly how these ferrocenylphosphonium cations compared with other EPCs in terms of catalytic activity, and whether they exhibited any differences in functional group compatibility compared to the dications of type B examined in our previous comprehensive study of ketone deoxygenations by EPCs.

Catalyst 4-4 proved capable of carrying out deoxygenation of a range of substrates at ambient temperatures over the course of 24-120 h (Table 4.1). For example, acetophenone was deoxygenated to ethyl benzene during a 1-day treatment with Et₃SiH and the catalyst 4-4. In contrast, the analogous use of 4-3 as the catalyst was much less efficient in this case, giving a 27% yield of ethylbenzene together with some PhCH₂(OSiEt₃)CH₃ after 4 days at 50 °C. Benzophenone is deoxygenated to diphenylmethane in the presence of silane and either 4-3 or 4-4 although 4-3 requires 7 days at 50 °C for complete conversion whereas 4-4 is requires 5 days at 25°C. The para-substituted aromatic ketones PhC(O)C₆H₄X (X = F, Br, OMe) and 2,4,6-iPrPhC(O)CH₃ are reduced using either 4-3 and 4-4 as the catalyst (Table 2). The ketone MeOC₆H₄C(O)CH₂C₆H₄OMe was effectively reduced under similar conditions. Aliphatic ketones PhC(O)C₆H₁₁ and CH₃C(O)CH(CH₃)₂ were also deoxygenated, although for the latter, a reduced yield of the deoxygenated product was obtained. This results from competing elimination pathways giving small amounts of alkene products. PhC(O)CF₃ underwent reaction in the presence of catalyst 4-4 at 50 °C, however only the hydrosilylation product was obtained. In contrast, the corresponding reaction with 4-3 gave minimal conversion.
Table 4.1. Catalytic deoxygenation of ketones mediated by 4-3 and 4-4

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</tbody>
</table>
Comparing these activities to those previously reported, we note that the phosphonium dications of types B, C, and D have shown to be active catalysts for ketone deoxygenation under similar conditions. In general, the dicationic catalysts are significantly more active than 4-3 or 4-4, effecting the catalysis at ambient temperatures. Interestingly, dicationic catalysts of type C with bridges of one or two carbon atoms proved generally more active in catalysis than 4-4. On the other hand, type C cations connected by alkyl chains consisting of 3-5 carbon atoms are less active than 4-4, suggesting that enhanced reactivity results from the enforced proximity of the two phosphonium centres. In contrast, this is not the case for 4-4 where, at least in the solid state, the cationic centres on each Cp-ring are oriented so as to maximize the separation of the charged centers. Nonetheless, the presence of the second phosphonium centre in 4-4 inductively enhances the Lewis acidity of this cation, although it is unlikely that these centres act in a cooperative fashion. As a result, 4-4 exhibits catalytic activity that certainly exceeds that of the cation [Ph₃PF][B(C₆F₅)₄]²⁻ but is somewhat less than that of diphosphonium dications derived from Ph₂P(CH₂)ₙPPh₂ (n = 1, 2), or of dication types B or D, where the proximity of the cationic centres is imposed by more rigid frameworks.

4.5 Conclusions

The species [CpFe(η⁵-C₅H₄PFPh₂)][B(C₆F₅)₄] 4-3 and [Fe(η⁵-C₅H₄PFPh₂)₂] [B(C₆F₅)₄]₂ 4-4, are easily prepared from commercially available or easily synthesized phospine precursors by oxidation with XeF₂ and subsequent fluoride abstraction. These Lewis acids are effective catalysts for Friedel-Crafts dimerization of 1,1-diphenylethylene, dehydrocoupling of phenol and triethylsilane, hydrodefluorination of 1-fluoropentane and the deoxygenation of a series of ketones. The present systems show activities that are comparable to several previously reported EPC catalysts, although the monocation 4-3 showed lower activity than the dication 4-4. This further indicates the enhanced Lewis acidity that results from a dicationic Lewis acidic phosphonium cation.

The ferrocenophane methylphosphonium species 4-7 was also synthesized, although the corresponding fluorophosphonium cation could not be accessed. Unsurprisingly, this cation was inactive for Lewis
acid catalysis, despite evidence of geometric distortion about the phosphonium centre observed in the solid-state structure. This inactivity is in accordance with our observations that monocationic phosphonium species lacking a strongly electronegative substituent to lower the energy of the $\sigma^*$ orbital are insufficiently electrophilic to promote these types of catalysis.

4.6 Experimental Details

4.6.1 General

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques or a nitrogen-filled glove box (MBRAUN). All solvents (including deuterated solvents) were dried using an Innovative Technologies solvent purification system or over CaH$_2$ and distilled, deoxygenated then stored over 4 Å molecular sieves before use. Fe($\eta^5$-C$_5$H$_4$PPh$_2$)$_2$, XeF$_2$, HSiEt$_3$, 1,1-diphenylethylene, PhOH, MeO$_3$SCF$_3$, and all ketones were commercially available and used as received. [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$]$^{30}$ and Fe($\eta^5$–C$_5$H$_4$)$_2$PPh $^{31}$ were prepared according to literature known methods. $^1$H, $^{13}$C, $^{11}$B and $^{31}$P NMR spectra were recorded on a Bruker Avance III or a Bruker Avance 500 spectrometer. $^1$H NMR data, referenced to external Me$_4$Si, are reported as follows: chemical shift ($\delta$/ppm), coupling constant (Hz), normalized integrals. $^{13}$C{$^1$H} NMR chemical shifts ($\delta$/ppm) are referenced to external Me$_4$Si. Assignments of individual resonances were done using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer. Elemental analyses (C, H, N) were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyser. Catalytic trial were performed in 5 mm NMR tubes using 0.75 mL of CD$_2$Cl$_2$. NMR spectra were obtained on a Bruker Avance III 400 MHz, Varian Mercury 300 MHz, Agilent DD2 600 MHz, or Agilent DD2 500 MHz spectrometer. Spectra were referenced to residual toluene-d$_8$ ($^1$H = 2.08 for methyl; $^{13}$C = 20.40 for CH$_3$), CD$_2$Cl$_2$ ($^1$H = 5.32, $^{13}$C = 54.0), or C$_6$D$_5$Br ($^1$H = 7.28 ppm for meta proton; $^{13}$C = 122.4 ppm for ipso carbon). Chemical shifts are listed in ppm and coupling constants are listed in Hz. NMR assignments are supported by additional 2D experiments. High-resolution mass spectrometry (HRMS) was performed in house.
X-ray Diffraction Studies: Crystals were coated in paratone oil and mounted in a cryo-loop. Data were collected on a Bruker APEX2 X-ray diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å). The temperature was maintained at 150(2) K using an Oxford cryo-stream cooler for both, initial indexing and full data collection. Data were collected using Bruker APEX-2 software and processed using SHELX and Olex2 an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved by direct methods within the SHELXTL package and refined with Olex2.

4.6.2 Syntheses of Compounds 4-1, 4-2, 4-3, 4-4, 4-5

Synthesis of CpFe(η^5-C_5H_4PF_2Ph_2) 4-1 A solution of XeF_2 (34 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of phenylphosphinoferrocene (74 mg, 0.20 mmol) in CH_2Cl_2 (1 mL). Effervescence was immediately observed. After stirring for 2 h volatiles were removed in vacuo resulting in an orange solid in quantitative yield (81 mg, yield >99 %). X-ray quality crystals were obtained by cooling a saturated solution of the product in CH_2Cl_2 to -35°C. ^1H NMR (CD_2Cl_2, [ppm]): 3.94 (s, 5H, Cp), 4.50 (s, 2H, Cp CH), 4.83 (2H, s, Cp CH), 7.44-7.50 (m, 6H, p-Ph, m-Ph), 7.96-8.08 (m, 4H, o-Ph) ^13C{^1H} NMR (CD_2Cl_2, [ppm]): 70.2 (Cp C_β), 72.8 (d, Cp C_α, 2J_PC = 15 Hz), 76.0 (br m, Cp C_ ipso), 128.9 (d, Ph, C_α, 2J_PC = 17 Hz), 131.8 (s, Ph, C_β) 134.2 (m). Resonances for ipso-carbon atoms on phenyl, Cp moieties were not observed. ^19F{^1H} NMR (CD_2Cl_2, [ppm]): -42.7 (d, 1J_PF = 656 Hz) ^31P{^1H} NMR (CD_2Cl_2, [ppm]): -50.1 (t, 1J_PF = 656 Hz); Elemental Analysis for C_{22}H_{19}F_{2}P: calcd.: C: 64.7, H 4.7, found: C: 63.1, H: 4.9; HRMS (ESI-QTOF^+): m/z 387.0596 ([CpFe(η^5-C_5H_4POPh_2)]) (calc.: 387.0601).

Synthesis of Fe(C_5H_4PF_2Ph_2) 2 4-2 A solution of XeF_2 (68 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of 1,1’-bis(diphenylphosphino)ferrocene (111 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) Effervescence was immediately observed. After stirring for 1-2 mins. a yellow solid precipitated from the solution. This was filtered and washed with n-pentane (2 x 1 mL) and dried in vacuo to give 118 mg of product (94% yield). ^1H NMR (CD_2Cl_2, [ppm]): 4.10 (m, 4H, Cp, H_α), 4.62 (m, 4H, Cp CH_β), 7.47 (m, 12H, p-Ph, m-Ph), 8.00 (m, 8H, o-Ph) ^13C{^1H} NMR (CD_2Cl_2, [ppm]): 74.6 (dt, Cp C_β, 3J_PC = 15 Hz, 4J_FC = 2 Hz), 77.2 (dt, Cp C_α, 2J_PC = 18 Hz, 3J_FC = 10 Hz), 129.0 (td, i-Ph, 2J_PC = 17 Hz, 4J_FC = 2 Hz), 132.1 (s, i-Ph) 134.6 (dt, m-Ph, 2J_CF = 13 Hz, 2J_CFC = 10 Hz), 138.5 (td, i-Ph, 1J_PC = 182 Hz, 2J_FC = 28 Hz) Resonances for ipso carbon atoms on Cp moieties were not observed. ^19F{^1H} NMR
(CD2Cl2, [ppm]): -42.8 (d, JPF = 662 Hz) 31P{1H} NMR (CD2Cl2, [ppm]): -51.5 (t, JPF = 662 Hz); 
Elemental Analysis for C34H28F4P2: calcd.: C 64.8, H 4.5, found: C: 64.9, H: 4.8; HRMS (ESI-QTOF*): m/z 587.0987 ([Fe(η5-C5H4P(OH)Ph2) (η5-C5H4POPh2)]) (calc.: 587.0992)

Synthesis of [CpFe(η5-C5H4PFPh2)][B(C6F5)4] 4-3 To a solution of 41mg (0.10 mmol) 4-1 in toluene was added 93 mg of freshly prepared [Et3Si(tol)][B(C6F5)4] (0.095 mmol). Stirring for 3 h resulted in precipitation of a dark yellow oil. Washing with toluene (1 x 0.5 mL) and pentane (3 x 0.5 mL) and drying in vacuo resulted in 90 mg of 4-3 as a dull orange solid (84% yield). X-ray quality crystals were obtained by slow diffusion of n-pentane into a saturated solution of 4-3 in dichloromethane at -35º C,

1H NMR (CD2Cl2, [ppm]): 4.50 (s, 5H, Cp), 4.64 (m, 2H, Cp, Hα), 5.07 (m, 2H, Cp, Hβ), 7.79-7.85 (m, 8H, o-Ph, m-Ph), 7.99 (t, 2H, p-Ph, , 3JHH = 7 Hz) 11B NMR (CD2Cl2, [ppm]): -16.7 13C{1H} NMR (CD2Cl2, [ppm]): 72.3 (s, Cp), 75.2 (d, Cp C), 2JPC = 17 Hz), 77.9 (d, Cp C), 3JPC = 13 Hz), 131.3 (d, Ph, JPC = 14 Hz), 133.5 (d, Ph, JPC = 13 Hz), 138.5 (s, Ph) signals for ipso-carbon atom not observed. 19F{1H} NMR (CD2Cl2, [ppm]): -112.5 (d, JPF = 998 Hz). 31P{1H} NMR (CD2Cl2, [ppm]): 102.9 (d, JPF = 998 Hz) Elemental Analysis for C46H19BF21PFe: calcd.: C: 51.5, H: 1.8, found: C: 51.0, H: 1.5; HRMS (ESI-QTOF*): m/z 387.0596 ([CpFe(η5-C5H4POPh2)] (calc.: 387.0601)

Synthesis of [Fe(η5-C5H4PFPh2)][B(C6F5)4] 4-4 To a solution of 63mg (0.10 mmol) 2 in 2 mL toluene was added 186 mg freshly prepared [Et3Si(tol)][B(C6F5)4] (0.19 mmol). Stirring for 3 h resulted in precipitation of a dark yellow oil. Washing with toluene (1 x 0.5 mL) and pentane (3 x 0.5 mL) and drying in vacuo resulted in 156 mg of 4-4 as a dull orange solid (80% yield). X-ray quality crystals were obtained by slow diffusion of n-pentane into a saturated solution of 4-4 in dichloromethane at -35º C,

1H NMR (CD2Cl2, [ppm]): 4.51 (m, 4H, Cp CHα), 5.19 (m, 4H, Cp CHβ), 7.47 (m, 12H, p-Ph, m-Ph), 7.72 (m, 4H, Ph), 7.79 (m, 4H, Ph), 8.04 (m, 2H, p-Ph) 11B NMR (CD2Cl2, [ppm]): -16.7 13C{1H} NMR (CD2Cl2, [ppm]): 74.6 (dt, Cp C), 2JPC = 17 Hz, 4JPC = 2 Hz), 77.2 (dt, Cp C), 2JPC = 18 Hz, 3JPC = 10 Hz), 129.0 (td, i-Ph, 2JPC = 17 Hz, 4JPC = 2 Hz), 132.1 (s, i-Ph) 19F{1H} NMR (CD2Cl2, [ppm]): -42.8 (d, JPF = 662 Hz). 31P{1H} NMR (CD2Cl2, [ppm]): -51.5 (t, JPF = 662 Hz); Elemental Analysis for C32H23B2F2P2Fe: calcd.: C: 50.5, H: 1.5, found: C: 51.0, H: 1.5; HRMS (ESI-QTOF*): m/z 587.0987 ([Fe(η5-C5H4P(OH)Ph2) (η5-C3H4POPh2)]) (calc.: 587.0992)
**Synthesis of [PhMeP(η⁵-C₅H₄)₂Fe][B(C₆F₅)₄] 4-7** To a solution of Fe(η-C₅H₄)₂PPh in 2 mL toluene was added a solution of MeO₃SCF₃ in 0.5 mL toluene. Successive precipitations yielded induced by addition of n-pentane resulted in 0.050 g of the product (80% yield). ¹H NMR (CD₂Cl₂, [ppm]): 2.39 (d, 3H, CH₃, ²Jₚₗ = 14 Hz), 4.50 (m, 2H, Cp), 4.80 (m, 2H, Cp), 5.06 (m, 2H, Cp), 5.11 (m, 2H, Cp), 7.79-7.85 (m, 4H, o-Ph, m-Ph), 7.99 (t, 1H, p-Ph, ³Jₜₜ = 7 Hz) ¹³B{¹H} NMR (CD₂Cl₂, [ppm]): -16.7 ¹³C {¹H} NMR (CD₂Cl₂, [ppm]): 12.1 (d, Me, ¹Jₚₗ = 221 Hz), 72.3 (s, Cp), 75.2 (d, Cp, ²Jₚₗ = 17 Hz), 77.9 (d, Cp, ³Jₚₗ = 13 Hz), 131.3 (d, Ph, Jₚₗ = 14 Hz), 133.5 (d, Ph, Jₚₗ = 13 Hz), 138.5 (s, Ph) signals for ipso carbon atom not observed. ³¹P{¹H} NMR (CD₂Cl₂, [ppm]): 35.6. **Elemental Analysis** for C₄₁H₁₆BF₂₀P: calcd.: C: 49.9 H: 1.6 found: C: 50.2, H: 1.9; **HRMS (ESI-QTOF⁺):** m/z 307.0343 (Ph(Ο)P(η⁵-C₅H₄)₂Fe) (calc.: 307.0339)

**4.6.3 Lewis Acid Catalysis**

**Friedel-Crafts dimerization of 1,1-diphenylethylene with 3, 4 and 7 as catalysts**

![Friedel-Crafts dimerization](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conditions</th>
<th>Conversion</th>
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<tbody>
<tr>
<td>4-3</td>
<td>(2 mol%, 50°C, 4 d)</td>
<td>10%</td>
</tr>
<tr>
<td>4-4</td>
<td>(2 mol%, rt, 2 d)</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>4-7</td>
<td>(2 mol%, 50°C, 3 d)</td>
<td>0%</td>
</tr>
</tbody>
</table>

Catalyst 4-3 (2.1 mg, 2 mol%), 4-4 (3.9 mg, 2 mol%) or 4-7 (2.2 mg, 2 mol%) were added to a solution of 1,1-diphenylethylene (18 mg, 0.1 mmol) in CD₂Cl₂ (0.7 mL). The reaction mixtures were either left at ambient temperature (4-4) or heated to 50 °C for 2-4 days (4-3, 4-7) and monitored by ¹H NMR spectroscopy. After the reaction catalyzed by 4-4 had been observed to go to completion by ¹H NMR spectroscopy, all volatiles were removed from the reaction mixture *in vacuo* and the remaining residue was suspended in n-pentane. The mixture was filtered through a Celite plug and the solvent was removed *in vacuo* resulting in isolated 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene as a colourless solid (15.9 mg, 88% yield). The isolated product was re-dissolved in C₆D₆; NMR data is reported in this solvent.¹[S3]
$^1$H NMR (C$_6$D$_6$, [ppm]): $\delta = 1.48$ (3H, s, CH$_3$), 3.02 (1H, d, CH$_2$, $^3$J$_{HH} = 14$ Hz), 3.42 (1H, d, CH$_2$, $^3$J$_{HH} = 14$ Hz), 6.90 - 7.23 (19H, m); $^{13}$C($^1$H) (C$_6$D$_6$, [ppm]): $\delta = 29.1$ (1C, s, CH$_3$), 51.5 (1C, s, CH$_2$), 61.4 (1C, s, CPh), 61.8 (1C, s, CPh), 125.4 (1C, s, Ph), 125.9 (1C, s, Ph), 126.0 (1C, s, Ph), 126.3 (1C, s, Ph), 127.3 (1C, s, Ph), 127.3 (2C, s, Ph), 127.9 (2C, s, Ph), 128.0 (2C, s, Ph), 128.3 (2C, s, Ph), 128.3 (2C, s, Ph), 129.1 (2C, s, Ph), 129.3 (2C, s, Ph), 147.9 (1C, s, Ph), 149.1 (1C, s, Ph), 149.4 (1C, s, Ph), 149.7 (1C, s, Ph), 151.0 (1C, s, Ph).

Dehydrocoupling of Et$_3$SiH and Phenol with 3, 4 and 7 as catalysts.

$$\text{PhOH} + \text{Et}_3\text{SiH} \xrightarrow{<2\%\text{cat}>_{\text{CD}_2\text{Cl}_2}} \text{PhOSiEt}_3$$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conditions</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-3</td>
<td>(7 d, 50 °C):</td>
<td>97% conversion</td>
</tr>
<tr>
<td>4-4</td>
<td>(1 d, rt):</td>
<td>&gt;99% conversion</td>
</tr>
<tr>
<td>4-7</td>
<td>(3 d, 50 °C):</td>
<td>0% conversion</td>
</tr>
</tbody>
</table>

Catalyst 4-3 (2.1 mg, 2 mol%), 4-4 (3.9 mg, 2 mol%) or 4-7 (2.2 mg, 2 mol%) were added to a solution of Et$_3$SiH (17 µL, 0.10 mmol) and PhOH (9.4 mg, 0.10 mmol) in CD$_2$Cl$_2$ (0.7 mL) at ambient temperature. The reaction mixtures were either left at ambient temperature (4-4) or heated to 50 °C for 2-4 days (4-3, 4-7) and monitored by NMR spectroscopy. After the reaction catalyzed by 4-4 had been observed to go to completion by NMR, all volatiles were removed in vacuo and the remaining residue was suspended in n-pentane. The mixture was filtered through a Celite plug and the solvent was removed in vacuo giving triethyl(phenoxy)silane as a colourless oil (16.2 mg, 78% yield).[83]

$^1$H NMR (CD$_2$Cl$_2$, [ppm]): $\delta = 0.75$ (6H, quart. of d., CH$_2$, $^3$J$_{HH} = 8$ Hz), 0.96 (9H, t, CH$_3$, $^3$J$_{HH} = 8$ Hz), 6.85 (1H, t, p-Ph, $^3$J$_{HH} = 7$ Hz), 6.89 - 6.94 (2H, m, o-/m-Ph), 7.07 - 7.15 (2H, m, o-/m-Ph); $^{13}$C($^1$H) (C$_6$D$_6$, [ppm]): $\delta = 5.4$ (3C, s, CH$_2$), 6.9 (3C, s, CH$_3$), 120.3 (2C, s, o-/m-Ph), 121.7 (1C, s, p-Ph), 129.8 (2C, s, o-/m-Ph), 156.2 (1C, s, t-Ph).
Hydrodefluorination of fluoropentane in the presence of Et$_3$SiH using 4-3, 4-4 and 4-7 as catalysts.

Catalyst 4-3 (2.1 mg, 2 mol%), 4-4 (3.9 mg, 2 mol%), or 4-7 (2.0 mg, 2 mol%) were added to a solution of Et$_3$SiH (17 µL, 0.10 mmol) and fluoropentane (9 mg, 0.10 mmol) in CD$_2$Cl$_2$ (0.7 mL). The reaction mixture containing catalyst 4-4 was left at ambient temperature and monitored at intervals by $^1$H, $^{13}$C and $^{19}$F NMR spectroscopy over seven days, while the reaction mixtures of 4-3 and 4-7 were heated to 50 °C for 4 days. Conversion was determined by means of $^{19}$F NMR spectroscopy (consumption of fluoropentane and formation of Et$_3$SiF).[S3]

$^{19}$F NMR spectrum of reaction mixture (CD$_2$Cl$_2$)

$^{19}$F NMR spectrum of reaction with catalyst 4-4 after 7 d at ambient temperature showing 1-fluoropentane product, unreacted Et$_3$SiF, and resonances for B(C$_6$F$_5$)$_4$ anion (P-F doublet of dication too small to be seen in this view).
4.7  Hydrodeoxygenation of Ketones

4.7.1  General Procedure for Ketone Hydrodeoxygenation

All reactions were carried out under identical conditions on a 0.1 mmol scale. In a glove box the respective catalysts (2 mol%, 4-3: 2.1 mg, 4-4: 3.9 mg) were added to a solution of Et₃SiH (0.21 mmol – 2.1 equiv.) in CD₂Cl₂ (0.7 mL). 0.10 mmol (one equiv.) of the respective substrate was then added. The reaction mixture was transferred to a NMR tube, sealed and monitored by ¹H NMR ¹³C NMR spectroscopy in all cases as well as ¹⁹F NMR spectroscopy in the case of 4-fluorobenzophenone. When catalyst 4-4 was used >90% deoxygenation was observed for most substrates. 1-benzyl-4-methoxybenzene was isolated by filtering the reaction mixture through Celite and removing bis(triethylsilyl) in vacuo. For other samples, toluene was added as an internal standard to determine degree of conversion after the times reported herein. The bis(triethylsilyl) ether by-product can be observed in the ¹H and ¹³C NMR spectra of the reaction mixtures.

4.7.2  Spectroscopic Data of Isolated Products of Deoxygenation and Hydrosilylation

**Ethylbenzene**

\[ \text{C} \ \text{H}_3 \ | \ \text{C} \ \text{H}_2 \ | \ \text{C} \ \text{H}_3 \]

¹H NMR (400 MHz, CD₂Cl₂ [ppm]): \( \delta = 1.29 \) (3H, t, CH₂CH₃, \( ^3J_{HH} = 8 \) Hz); 2.70 (2H, q, CH₂CH₃, \( ^3J_{HH} = 8 \) Hz); 7.26 (5H, m, Ph); ¹³C {¹H} NMR (100 MHz, CD₂Cl₂ [ppm]): \( \delta = 16.4 \) (s, CH₃); 29.8 (s, CH₂); 126.4 (s, Ph); 128.7 (s, Ph); 129.2 (s, Ph); 145.3 (s, Ph)

**1-Benzyl-4-fluorobenzene**

\[ \text{C} \ \text{H}_3 \ | \ \text{C} \ \text{H}_2 \ | \ \text{C} \ \text{H}_3 \]

¹H NMR (500 MHz, CD₂Cl₂ [ppm]) : \( \delta = 3.97 \) (2H, s, CH₂); 7.00 (2H, m, Ph); 7.20 (5H, m, Ph); 7.30 (2H, m, Ph); ¹³C {¹H} NMR (126 MHz, CD₂Cl₂ [ppm]): \( \delta = 41.6 \) (s, CH₂); 115.7 (d, Ph, \( ^3J_{CF} = 21 \) Hz); 126.8 (s, Ph); 129.3 (d, Ph, \( ^2J_{CF} = 34 \) Hz); 130.9 (s, Ph); 137.8 (s, Ph); 141.8 (s, Ph); 162.0 (d, Ph, \( ^1J_{CF} = 243 \) Hz); ¹⁹F {¹H} NMR (376 MHz, CD₂Cl₂ [ppm]): \( \delta = -118.1 \) (s ppm).
1-Benzyl-4-bromobenzene

\[
\begin{align*}
\text{1H NMR (500 MHz, CD}_2\text{Cl}_2 \text{[ppm]} & : \delta = 3.94 (2H, s, CH_2); 7.11 (2H, m, Ph); 7.20 (2H, m, Ph); 7.22 (1H, m, Ph); 7.30 (2H, m, Ph); 7.43 (2H, m, Ph); \quad 13C NMR (126 MHz, CD}_2\text{Cl}_2 \text{[ppm]} : \delta = 42.0 (s, Ph); 120.6 (s, Ph); 127.1 (s, Ph); 129.4 (s, Ph); 129.7 (s, Ph); 131.4 (s, Ph); 132.3 (s, Ph); 141.3 (s, Ph); 141.5 (s, Ph)
\end{align*}
\]

1,2-Bis(4-methoxyphenyl)ethane

\[
\begin{align*}
\text{1H NMR (500 MHz, CD}_2\text{Cl}_2 \text{[ppm]} & : \delta = 2.83 (4H, s, CH_2); 3.76 (6H, s, CH_3); 6.81 (4H, m, Ph); 7.09 (4H, m, Ph) \quad 13C NMR (126 MHz, CD}_2\text{Cl}_2 \text{[ppm]} : \delta = 38.0 (s, CH_2); 55.4 (s, OCH_3); 114.4 (s, Ph); 130.2 (s, Ph); 134.7 (s, Ph); 158.8 (s, Ph); \text{DART MS: m/z: 260.16538 (calcd. for M+NH}_4^+ \text{: 260.16505).}
\end{align*}
\]

1-Benzyl-4-methoxybenzene

Isolated Yield = 81%.  
\[
\begin{align*}
\text{1H NMR (500 MHz, CD}_2\text{Cl}_2 \text{[ppm]} & : \delta = 3.77 (3H, s, OCH_3); 3.92 (2H, s, CH_2); 6.84 (2H, m, Ph); 7.12 (2H, m, Ph); 7.19 (3H, m, Ph); 7.28 (2H, m, Ph); \quad 13C NMR (126 MHz, CD}_2\text{Cl}_2 \text{[ppm]} : \delta = 41.8 (s, CH_2); 56.0 (s, OCH_3); 114.6 (s, Ph); 126.7 (s, Ph); 129.2 (s, Ph); 129.5 (s, Ph); 130.6 (s, Ph); 134.3 (s, Ph); 142.7 (s, Ph); 158.9 \text{DART MS: m/z: 216.13914 (calcd. for M+NH}_4^+ \text{: 216.13884).}
\end{align*}
\]

Isopentane

\[
\begin{align*}
\text{1H NMR (400 MHz, CD}_2\text{Cl}_2 \text{[ppm]} & : \delta = 0.87 (3H, m (overlapping d), CH_3); 0.88 (6H, d, } 3J_{HH} = 6.8 \text{ Hz, CH}_3; 1.17 (2H, m, CH}_2; 1.30 (2H, m, CH}_2; 1.55 (1H, m, CH); \quad 13C{^1H} \text{NMR (100 MHz, CD}_2\text{Cl}_2 \text{[ppm]} : } \delta = 12.1 (s, CH}_3; 22.6 (s, CH}_3; 30.5 (s, CH(CH}_3)_2; 32.3 (s, CH}_3CH}_2,
\end{align*}
\]
Diphenylmethane\textsuperscript{6}

\begin{center}
\includegraphics[width=0.2\textwidth]{diagram1.png}
\end{center}

\textsuperscript{1}H NMR (500 MHz, CD_2Cl_2 [ppm]): \(\delta = 3.98\) (2H, s, CH_2); 7.20 (6H, m, Ph); 7.29 (4H, m, Ph); \textsuperscript{13}C\textsuperscript{1}H NMR (126 MHz, CD_2Cl_2 [ppm]): \(\delta = 41.9\) (s, CH_2); 126.0 (s, Ph); 128.4 (s, Ph); 128.8 (s, Ph); 141.4 (s, Ph). DART MS: m/z: (calcd. for M+NH\textsubscript{4}⁺: 186.12827).

Phenylcyclohexylmethane\textsuperscript{6}

\begin{center}
\includegraphics[width=0.2\textwidth]{diagram2.png}
\end{center}

\textsuperscript{1}H NMR (500 MHz, CD_2Cl_2 [ppm]): \(\delta = 1.21\) (2H, m, Cy); 1.51 (2H, m, Cy); 1.69 (6H, m, Cy); 1.89 (1H, m, Cy); 2.50 (2H, d, \(^3\)JHH = 7.1Hz, CyCH_2); 7.18 (3H, m, Ph); 7.27 (2H, m, Ph); \textsuperscript{13}C\textsuperscript{1}H NMR (126 MHz, CD_2Cl_2 [ppm]): \(\delta = \) EI MS: m/z: (calcd. for M⁺: 174.1405). DART MS: m/z: 174.1405 (calcd. for M⁺: 174.1409).

1-Benzyl-4-methoxybenzene\textsuperscript{6}

\begin{center}
\includegraphics[width=0.2\textwidth]{diagram3.png}
\end{center}

Isolated Yield = 80%. \textsuperscript{1}H NMR (500 MHz, CD_2Cl_2 [ppm]): \(\delta = 3.77\) (3H, s, OCH_3); 3.92 (s, 2H, CH_2); 6.84 (2H, m, Ph); 7.12 (2H, m, Ph); 7.19 (3H, m, Ph); 7.28 (2H, m, Ph); \textsuperscript{13}C NMR (126 MHz, CD_2Cl_2 [ppm]): \(\delta = 41.5\) (s, CH_2), 55.7 (s, OCH_3); 114.6 (s, Ph); 126.7 (s, Ph); 129.2 (s, Ph); 129.5 (s, Ph); 130.5 (s, Ph); 134.2 (s, Ph); 142.7 (s, Ph); 158.9 (s, Ph). DART MS: m/z: 216.13914 (calcd. for M+NH\textsubscript{4}⁺: 216.13884).

1-Ethyl-2,4,6-triisopropylbenzene\textsuperscript{35}

\begin{center}
\includegraphics[width=0.2\textwidth]{diagram4.png}
\end{center}

\textsuperscript{1}H NMR (400 MHz, CD_2Cl_2 [ppm]): \(\delta = 1.27\) (3H, t, CH_2CH_3, \(^3\)JHH = 8 Hz); 1.30 (12H, d, \(^3\)JHH = 7 Hz, CH_3); 1.32 (6H, d, \(^3\)JHH = 7 Hz, CH_3); 2.71 (2H, q, CH_2CH_3, \(^3\)JHH = 8 Hz) 2.79 (2H, sept, \(^3\)JHH = 7 Hz, CH(CH_3)_2); 2.95 (1H, sept, \(^3\)JHH = 7 Hz, CH(CH_3)_2); 7.10 (2H, s, Ph); \textsuperscript{13}C NMR (126 MHz, CD_2Cl_2 [ppm]): \(\delta = 7.4\) (s, CH_3); 7.6 (s, CH_3); 22.1 (s, CH_2CH_3); 24.7 (s, CH_2); 25.0 (s, CH_2); 32.0 (s, CH); 35.4 (s, CH); 122.0 (s, Ph); 144.1 (s, Ph); 150.5 (s, Ph); one quaternary carbon atom not observed
Hydrosilylation of 2,2,2-trifluoroacetophenone to triethyl(2,2,2-trifluoro-1-phenylethoxy)silane\textsuperscript{6}

\[ \text{Et}_3\text{SiO} \begin{array}{c} \text{CF}_3 \\ \end{array} \]

\begin{align*}
\textsuperscript{1}H \text{ NMR} (400 \text{ MHz, CD}_2\text{Cl}_2 \text{ [ppm]}) & : \delta = 0.63 (6\text{H, q, }^3J_{HH} = 8 \text{ Hz, CH}_2\text{CH}_3); 0.98 (9\text{H, t, }^3J_{HH} = 8 \text{ Hz, CH}_2\text{CH}_3); 5.04 (1\text{H, q, }^3J_{HF} = 7 \text{ Hz, CH}); 7.44 (3\text{H, m, Ph}); 7.53 (2\text{H, m, Ph}); \\
\textsuperscript{13}C \text{ NMR} (126 \text{ MHz, CD}_2\text{Cl}_2 \text{ [ppm]}) & : \delta = 4.9 (s, \text{CH}_2\text{CH}_3); 6.7 (s, \text{CH}_2\text{CH}_3); 73.9 (q, ^2J_{CF} = 32 \text{ Hz}); 124.9 (q, ^1J_{CF} = 282 \text{ Hz}); 128.1 (s, \text{Ph}); 128.8 (s, \text{Ph}); 129.6 (s, \text{Ph}); 136.7 (s, \text{Ph}); \\
\textsuperscript{19}F \{\textsuperscript{1}H\} \text{ NMR} (564 \text{ MHz, CD}_2\text{Cl}_2 \text{ [ppm]}) & : \delta = -78.8 (d, ^3J_{HF} = 7 \text{ Hz}); \text{DART MS: m/z} = 308.16629 \text{ (calcd. for M+NH}_4^+; 308.165751). \end{align*}
Table 4.4 Crystallographic data and details of the structure refinement of compounds 4-1, 4-3, 4-4 and 4-7

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References


(10) Bayne, J. M.; Stephan, D. W. *Chemical Society Reviews* 2016, 45, 765-774


(34) Repeated attempts to obtain satisfactory elemental analysis of 1 led consistently to low C values. This is attributed to incomplete combustion, presumably a result of the formation of metal-carbide.

Chapter 5

Interactions of Trifluoromethyl and Palladium(II) Functionalities with Proximal Phosphonium Cations Within a 1,8-Disubstituted Naphthyl Framework

5.1 Introduction

5.1.1 Modelling Reaction Pathways by Calculation and Synthesis of Intermediates

In recent decades the rapid proliferation of computational modelling of reaction pathways has emerged as a powerful tool to understanding how and why chemical reactions happen and informing development of new catalysts.\(^1\) Calculations can also beget visual simulations of the progress of reactions by permitting researchers to use video animation of molecular and atomic movements for communication and pedagogical purposes. Synthetic chemists often use calculations to discern reaction pathways, to explain selectivity, to justify solvent effects, or to estimate or corroborate kinetic and thermodynamic data, among other purposes.

Nonetheless, while computations have diminished reliance on experimental methods to corroborate postulated reaction pathways, experiments remain essential to supporting calculated mechanisms. NMR studies such as isotopic labelling allow researchers to trace the transfer of atoms between molecules. In the case of catalytic processes, examining the corresponding stoichiometric reactions can lend credence to calculated mechanisms. Varying the stoichiometries and physical conditions can yield thermodynamic and kinetic data, while synthesizing and trapping intermediates or models of intermediates in chemical reactions is a valuable method for supporting calculated reaction pathways.\(^2\) Particularly in catalytic processes, where reactions often proceed rapidly through multiple steps, experimentally observing systems in which a substrate molecule is interacting with a catalyst is useful in validating computationally-predicted intermediates. Where an intermediate can be synthesized and structural data obtained by such methods as x-ray diffraction, experiments can provide a snapshot of a chemical species occurring along the path between reactants and products.
Isolation of transition states is infeasible by definition, but trapping or synthesizing compounds which model or approach transition states can yield similarly valuable information. Changing of conformations, elongation of bonds, or the diminishment of distance between two reactive sites can all indicate progress towards a particular transition state or intermediate. Thermodynamic data can also be extracted by these means for chemical reaction steps to obtain information about mechanisms.

The synthesis of intermediates along reaction pathways, or compounds that model intermediates or transition states can also provide data on which to base further computations. Thus, while the degree of reliance on experimental evidence has diminished, synthesis and calculation are complementary techniques which together can provide enhanced clarity of chemical reaction mechanisms.

5.1.2 Trapped Intermediates and Reactive Species Models in Main Group Catalysis

The growth of the field of main group catalysis has generated the corresponding investigations into the mechanisms by which this catalysis occurs. The seminal report by Piers that B(C₆F₅)₃ can catalyze the hydrosilylation of carbonyl functionalities on aromatic compounds initiated a wide range of subsequent applications of this electron-deficient borane in Lewis acid and FLP catalysis. Numerous additional Lewis acid catalysts based on boron or other main group elements have been developed. Much of this catalysis is initiated by the Lewis acid catalyst interacting with C-H, C-X or Si-H bonds, weakening the bond to the substrate and rendering the carbon or silicon atom electrophilic. In the case of hydrosilylation of carbonyl moieties, the Si-H activation mechanism was somewhat counterintuitive, as electrophilic boron centres are generally strongly oxophilic. Nonetheless, experimental and calculated evidence overwhelmingly support Piers’ mechanistic proposal of activation of the Si-H bond, rather than the C=O bond, by B(C₆F₅)₃ (Figure 5.1 A). It was not until 2014, however, that an x-ray structure of an elusive Et₃SiH adduct of an electrophilic borane, the heterocyclic 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene (Figure 5.1C) was isolated by the Piers group. The next year, the Chen group isolated and crystallographically characterized the Et₃SiH adduct of the heavier congener of B(C₆F₅)₃, Al(C₆F₅)₃ (Figure 5.1B).
Figure 5.1 Putative Et$_3$SiH adduct of B(C$_6$F$_5$)$_3$ (A) and structurally-characterized Et$_3$SiH adducts of Al(C$_6$F$_5$)$_3$ (B) and 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene (C).

The isolation of these silane adducts of borane and alane Lewis acids permitted study of previously unobserved intermediates along the hydrosilylation reaction pathway. The metric parameters of the solid-state structures gave definitive Si-H, B-H and Al-H bond distances and allowed Piers and Chen to measure the geometric distortions of the boron, aluminum, and silicon centres. IR and NMR spectral data provided further insights. Dissolution of adduct C gave the expected equilibrium of free borane/silane versus the adduct (Scheme 5.1). Piers and co-workers recorded variable-temperature NMR spectra of the adduct and observed a clear temperature dependence of the $^{19}$F NMR chemical shift of the fluorine nucleus closest to the boron atom on the boraindene core. This allowed them to determine the ratios of the free silane/free borane versus adduct C at different temperatures. Titration of the borane with various amounts of silane at different temperatures permitted them to determine an equilibrium constant for the adduct formation process from which they determined $\Delta H^\circ$ and $\Delta S^\circ$ values for this equilibrium.

Scheme 5.1 Equilibrium between adduct C and free silane and borane.

Chen and co-workers focused their analysis on properties of the solid-state structure and on effecting catalysis from the isolated Et$_3$Si-H-Al(C$_6$F$_5$)$_3$ adduct. They found a secondary interaction between the meta-fluorine atom of one of the C$_6$F$_5$ rings on a neighbouring Al(C$_6$F$_5$)$_3$ and the Al centre in the solid state, an interaction not previously discerned. They also found that adduct complex B effects
hydrodefluorination of Ph$_3$CF as a pre-catalyst (a fluoride-bridged analogue of this complex forms and is the active catalyst). They also examined substituent redistribution reactions of other silanes.

These two examples highlight some of the ways in which isolation and structural characterization of catalytic reaction intermediates can provide mechanistic and thermodynamic information. In the case of adduct C, although this borane was not the common B(C$_6$F$_5$)$_3$, it was a sufficiently close analogue to reasonably assume that information garnered from its study would apply to B(C$_6$F$_5$)$_3$-mediated reactions as well.

### 5.2.1 Naphthyl Phosphonium Cations

Our group has recently developed electrophilic phosphonium cation (EPC) Lewis acid catalysts that effect hydrodefluorination, hydrosilylation, deoxygenation and dehydrocoupling reactions using silane reductants. Mechanisms analogous to the B(C$_6$F$_5$)$_3$-mediated reactions have been calculated for these transformations, involving initial activation of the Si-H bond by the EPC.

We have thus far been unsuccessful in observing R$_3$Si-H interactions with phosphonium cations in solution, nor have attempts to crystallize adducts in the solid state been successful. It was of interest to model this putative intermediate by synthesizing a compound in which an electrophilic phosphonium centre was held in close proximity to a silane.

The naphthalene scaffold is readily functionalized at the 1- and 8-positions. Indeed, we have used this scaffold to synthesize dication 5-1, where two phosphonium centres are in close proximity, from 1,8-bis(diphenylphosphino)naphthalene. This work was done primarily by post-doctoral fellow Dr. Michael Holthausen and Ph.D. student Julia Bayne. This dication exhibited reactivity unique from other EPCs. In combination with $t$Bu$_3$P, 5-1 formed a rare phosphorus-phosphorus FLP. This author’s contribution to this research was in the synthesis and structural characterization of a C-H activated product of this FLP. When 5-1 in combination with two equivalents of $t$Bu$_3$P was reacted with 1,3,5-cycloheptatriene, a unique C-H activation was effected to form the bicyclic product 5-2 (Scheme 5.2). One equivalent of $[t$Bu$_3$PH$][B$(C$_6$F$_5$)$_4$] was formed and 5-1 was reduced to 1,8-bis(diphenylphosphino)naphthalene. Although the solid-state structure of 5-2 could not be obtained, the solid-state structure of the cation with a BF$_4$ (5-2b) anion was successfully discerned (Figure 5.2). In the solid state 5-2 exhibits the phosphonium moiety in the sterically-favoured exo-position relative to the bicyclic framework.
Scheme 5.2 C-H activation of 1,3,5-cycloheptatriene by phosphorus-phosphorus FLP to produce 5-2

Figure 5.2: POV-ray depiction of cation of salt 5-2. H atoms are omitted for clarity. C: black; P: orange.

5.2.2 Attempted Synthesis of Naphthylphosphonium-Silanes

While 1,8-bis(diphenylphosphino)naphthalene can be readily accessed from 1,8-dibromonaphthalene via lithiation, obtaining asymmetrically 1,8-disubstituted naphthalenes in good yields is more challenging. The iPrMgCl*LiCl “turbo Grignard” reagent allows for selective lithiation of one aryl-X bond (X = I, Br, Cl) where multiple aryl-X bonds are in close proximity. Use of this reagent proved an effective way to mono-lithiate 1,8-diiodonaphthalene or 1,8-dibromonaphthalene. Subsequent reaction with Ph₂PCl permitted installation of one diphenylphosphate moiety and isolation of 1-bromo-8-diphenylphosphinonaphthalene 5-3 or 1-iodo-8-diphenylphosphinonaphthalene 5-4 (Scheme 5.3). Lithiation of either species with nBuLi in toluene and addition of Me₂SiHCl or Ph₂SiHCl resulted in phosphinosilanes 5-5 and 5-6 (Scheme 5.3).


5-5 exhibited a $^{31}$P{$^1$H} NMR chemical shift at $-15.1$ ppm while 5-6 exhibited a chemical shift at $-19.9$ ppm in CDCl$_3$ (Figure 5.3). Solid-state structures were obtained for both compounds (Figure 5.4). In both cases, the Si-H hydrogen atom was located on the difference map. Steric interference is postulated to cause the silyl and phosphino moieties to bend away from each other, distorting the trigonal planar geometry about the naphthyl carbon atoms at the 1- and 8-positions.

**Scheme 5.3** Synthesis of phosphinosilanes 5-5 and 5-6.

**Figure 5.3** $^{31}$P{$^1$H} NMR spectrum of 5-5 (top) and 5-6 (bottom, with minor impurities)
Deriving the corresponding phosphonium cation from either of these phosphinosilanes proved synthetically challenging. Oxidation of the phosphorus centre with one equivalent of XeF$_2$ gave a mixture of products, with the difluorophosphorane present in only minor amounts as determined by $^{31}$P and $^{19}$F NMR spectroscopy (Scheme 5.4). The fluorophilicity of the silicon centre caused degradation of the Si-H bond, with fluorosilane 5-7 the only structurally-characterized product isolated from these reactions (Figure 5.5). Interestingly, in contrast to 5-5 and 5-6 where the Si-H bond was oriented in the direction of the phosphine moiety, in 5-7 the Si-F bond was oriented in the opposite direction, indicating a possible interaction of the phosphine lone pair with the Si-F $\sigma^*$ antibonding orbital. Computational or experimental verification of this potential interaction has not yet been investigated.

Scheme 5.4 Formation of 5-7.

Figure 5.4: POV-ray depiction of 5-5 (left) and 5-6 (right). Silicon-bound H atoms are shown but all other H atoms are omitted for clarity. C: black; P: orange; Si: pink; H: white
Figure 5.5: POV-ray depiction of 5-7. H atoms are omitted for clarity. C: black; P: orange; Si: pink; F: magenta

Attempts to access the phosphonium cation directly from 5-5 or 5-6 via electrophilic fluorination agents such as fluoropyridines or N-fluorobenzenesulphonimide were unsuccessful. A different synthetic target was therefore investigated to examine mechanisms of EPC-mediated bond activation.

5.3.1 Synthesis and X-ray Crystallographic and NMR Spectroscopic Analysis of a 1,8-substituted (Trifluoromethyl)naphthylphosphonium Cation

As mentioned in the introduction to this chapter, EPC catalysts have also been effective in C-F bond activation in hydrodefluorination or Friedel-Crafts C-C bond formation processes.\textsuperscript{32,33} An electrophilic phosphonium cation proximal to a CF\textsubscript{3} group would potentially permit examination of this bond activation process. To this end, synthesis of a 1,8-disubstituted naphthyl compound featuring these two functionalities was targeted.

Installation of trifluoromethyl functionalities on arenes is considerably more challenging than installation of phosphino or silyl groups. Again, the selective functionalization of each of the 1- and 8-positions presented a synthetic challenge. 1,8-asymmetrically disubstituted naphthalenes featuring a Lewis acidic functionality have notably been reported by Bourissou.\textsuperscript{34-37} These were derived from 1,8-dibromonaphthalene, however the initial lithium-bromine exchange reaction using n-BuLi gave relatively low yields of the product resulting from monolithiation. Though we also targeted a synthetic route starting from commercially-available 1,8-dibromonaphthalene, a higher-yielding protocol was desired.
Installation of the inert CF$_3$ group prior to functionalization with the phosphine was also necessary, as the phosphine would likely be intolerant of the reaction conditions necessary for CF$_3$ installation. The prior reported synthetic protocol for the preparation of 1-bromo-8-trifluoromethylnaphthalene 5-8\textsuperscript{38} in our hands resulted in isolation of this product only in $>$5% yields. In addition, no $^{19}$F NMR resonance was reported in this protocol.

Hartwig et. al. reported efficient one-pot temperature-selective, copper-mediated trifluoromethylation of aryl-X bonds (X = Br,I). At 50 °C substitution of aryl-iodine bonds by a CF$_3$ group occurs but aryl-bromine bonds remain intact.\textsuperscript{39} Although synthesis of 5-8 was not reported using this method the analogous protocol was attempted. Addition of iPrMgCl*LiCl to a THF solution of 1,8-dibromonaphthalene cooled to −35 °C followed by addition of I$_2$ resulted in the asymmetrically-substituted 1-bromo-8-iodonaphthalene in good yield (Scheme 5.5). Following Hartwig’s protocol for trifluoromethylation of arenes resulted in isolation of 5-8 in 75% yield (Scheme 5.5). The $^{19}$F NMR resonance corresponding to the CF$_3$ group appeared at −49.8 ppm. A solid-state structure was obtained (Figure 5.6). Lithiation of 5-8 with $n$-BuLi in toluene at −35 °C followed by reaction with either Ph$_2$PCl or (C$_6$F$_5$)$_2$PBr resulted in 5-9 and 5-10, respectively, after work-up.

![Scheme 5.5 Synthesis of 5-9 and 5-10](image)

5-9 exhibited a quartet resonance at −2.5 ppm in the $^{31}$P{$^1$H} NMR spectrum with a coupling constant of 110 Hz, and the corresponding doublet at −51.0 ppm in the $^{19}$F{$^1$H} NMR spectrum. This large coupling constant is attributed to through-space coupling between the phosphorus and fluorine atoms.
5-10 exhibited a complex multiplet at $-34.7$ ppm in the $^{31}\text{P}{}^{1}\text{H}$ NMR spectrum that could be deconvoluted to a quartet of quintets with a through-space coupling of 120 Hz to the trifluoromethyl group and coupling to the four ortho-C$_6$F$_5$ fluorine nuclei. The corresponding doublet appears at $-52.1$ ppm in the $^{19}\text{F}{}^{1}\text{H}$ NMR spectrum. Through-space coupling is again postulated to account for the large coupling constant between the phosphorus and fluorine atoms. Further characterization by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy was undertaken, however the expected quartet in the $^{13}\text{C}$ NMR spectrum corresponding to the CF$_3$ carbon atom was not located. A $^{13}\text{C}{}^{19}\text{F}$ HSQC spectrum was obtained and a cross-peak at 119.8 ppm on the $^{13}\text{C}$ NMR axis corresponding to the CF$_3$ resonance at $-51.0$ ppm enabled the identification of the CF$_3$ carbon atom (Figure 5.6.)

![Figure 5.6: POV-ray depiction of 5-8. H atoms are omitted for clarity. C: black; F: magenta; Br: red.](image)
As 5-10 features C₆F₅ substituents, the corresponding fluorophosphonium cation could be expected to be significantly more Lewis acidic than a fluorophosphonium cation derived from 5-9. Oxidation of 5-10 with XeF₂ yielded phosphorane 5-11 which exhibits a triplet of quartets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -50.3 ppm with a $^1J_{PF}$ coupling constant of 729 Hz and a significantly weaker coupling than precursor 5-10 to the CF₃ fluorine atoms of 14 Hz (Scheme 5.6). Subsequent abstraction of a fluoride ion with [Et₃Si(tol)][B(C₆F₅)₄] resulted in the isolation of phosphonium cation 5-12, with the diagnostic $^{31}\text{P}\{^1\text{H}\}$ NMR resonance appearing as a doublet at 64.6 ppm with a P-F coupling constant of 1010 Hz. Coupling to the fluorine nuclei of the CF₃ moiety was no longer observed at room temperature. The CF₃ $^{19}\text{F}$ resonance appears as a singlet in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum at -58.9 ppm. Strangely, the resonance for the fluorine atom bound directly to the phosphorus atom was not observed in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum at room temperature. A solid-state structure of 5-12 was obtained (Figure 5.8).

Scheme 5.6 Synthesis of 5-11 and 5-12
Two-dimensional NMR methods were used to locate the resonance of the fluorine atom bound to the phosphonium centre. A $^{31}$P-$^{19}$F HSQC NMR experiment was undertaken with the help of Dr. Darcy Burns and the team at the University of Toronto NMR facility. A doublet resonance correlating to the phosphorus atom was detected at $-102.2$ ppm from the $^{31}$P-$^{19}$F HSQC NMR experiment (Figure 5.9).

**Figure 5.9** $^{31}$P-$^{19}$F HSQC NMR spectrum of 5-12 showing the correlation of the P-F nuclei.

Low-temperature NMR studies were also undertaken both to verify the chemical shift of the P-F $^{19}$F nucleus and to ascertain if an interaction could be observed between a C-F fluorine atom and the cationic
phosphonium centre of 5-12. If an interaction was present and it was of sufficient strength to hinder rotation about the C\textsubscript{napthyl}-C\textsubscript{trifluoromethyl} bond, the fluorine nuclei of the CF\textsubscript{3} moiety could be expected to be rendered inequivalent. Reducing the thermal energy of the system would provide an opportunity to reach a point where the strength of a putative P-F interaction might be sufficient to hinder C-C bond rotation and allow observation of inequivalent CF\textsubscript{3} fluorine nuclei by $^{19}\text{F}$ NMR spectroscopy. $^{19}\text{F}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic measurements of 5-12 in CD\textsubscript{2}Cl\textsubscript{2} were taken at 25 °C, 0 °C, –20 °C, –40 °C, –60 °C and –80 °C (Figure 5.10).

Gratifyingly, in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum obtained at –80 °C the doublet resonance for the P-F $^{19}\text{F}$ nucleus was clearly visible at –100.4 ppm exhibiting a $^1J_{PF}$ coupling constant of 970 Hz (Figure 5.9). In addition, a smaller doublet resonance at –122.9 ppm with a $^1J_{PF}$ coupling constant of 1070 Hz was observed. These signals integrated in an approximately 4:1 ratio. The $^{31}\text{P}$ NMR spectrum obtained at –80 °C showed the corresponding doublet resonances in approximately a 4:1 ratio, with the larger resonance at 59.3 ppm exhibiting the corresponding $^1J_{PF}$ coupling constant of 970 Hz and the smaller resonance at 70.3 ppm exhibiting a $^1J_{PF}$ coupling constant of 1070 Hz. These data clearly identify two distinct fluorophosphonium chemical species present at –80 °C. Whether these are geometric or rotational isomers, or if the more abundant species does indeed exhibit a reduced P-F coupling due to interaction of the corresponding \(\sigma^*\) orbital with a CF\textsubscript{3} fluorine atom is undetermined. It is worth noting that both the $^{31}\text{P}$ NMR chemical shift of 64.6 ppm and the $^1J_{PF}$ coupling constant of 1010 Hz observed at room temperature for this cation lie between the values observed for the chemical shifts and coupling constants of the species present at –80 °C.
Figure 5.10 Variable-temperature $^{19}$F$\text{H}$ NMR (left) and $^{31}$P$\text{H}$ NMR (top right) spectra of 5-12, and boxed region of $^{19}$F$\text{H}$ NMR spectrum obtained at $-80\,\text{°C}$ showing the two P-F doublet resonances (bottom, right) at $-100.4$ and $-122.9$ ppm.

The solid-state metric parameters were analyzed for evidence of an interaction between a fluorine atom of the CF$_3$ substituent and the phosphonium centre. The P-F bond length in the solid state averaged 1.544(4) Å, within the range previously observed for fluorophosphonium cations.\textsuperscript{19,20,40,41} However, the two molecules in the asymmetric unit exhibited small but significant differences in the C–F bond lengths of the CF$_3$ functionality. The two CF$_3$ groups each exhibited three differing C–F bond lengths, of 1.374(10), 1.349(9), and 1.333(10) Å for one molecule and 1.358(10), 1.341(10) and 1.323(11) Å for the other. The longest C–F bond in each was to the fluorine atom oriented toward the phosphonium centre. These bonds averaged 1.366 Å in length, compared to 1.337 (av.) Å for the other four C–F bonds. While the variation in bond lengths are not definitive of an interaction and may be due to packing effects, it cannot be overlooked that in both molecules the C–F bond to the fluorine atom oriented to allow a potential interaction with the phosphonium centre is elongated well beyond the standard error for this structure, consistent with a reduction in bond order due to donation into the P-F σ* orbital of the
phosphonium centre. The distances between this fluorine atom and the phosphorus atom are 2.615(5) Å and 2.597(6) Å. This is within the sum of the van der Waals radii of phosphorus and fluorine, 3.27 Å.\textsuperscript{42}

### 5.4.1 Atoms in Molecules (AIM) Analysis of Cation 5-12

The structural and spectroscopic evidence described above was insufficient to either prove or disprove the presence of a P-CF\textsubscript{3} interaction in 5-12. We then turned to theoretical methods to study the electronic structure in the vicinity of the proximal [(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}PF]+ and CF\textsubscript{3} functionalities. The Quantum Theory of Atoms In Molecules (QTAIM or AIM) offered a useful means to assess whether an electronic interaction existed between the phosphorus atom and a fluorine atom of the CF\textsubscript{3} functionality in 5-12.

AIM was primarily developed by Professor Richard Bader at McMaster University beginning in the early 1960s.\textsuperscript{43,44} Within this framework, a topological analysis of electron density in a molecule affords insight into indicate bonding, structure, and divisions between atoms within molecules. Analysis of the electron density (\(\rho\)) is complemented by analyzing the gradients (\(\nabla \rho\)), the first derivative, or \(\nabla^2 \rho\), the Laplacian or second derivative of the electron density.\textsuperscript{44} Electron densities can be obtained from both theoretical calculations and from experiments such as x-ray diffraction analysis.\textsuperscript{43,44} Topological features of the electron density are indicative of bonding interactions. For example, for a pair of nuclei there is only one gradient path that begins at one nucleus and ends at the other. Traversing this “bond path” from one nucleus, electron density decreases until it reaches a minimum, or bond critical point, then increases until it reaches the other nucleus.\textsuperscript{44} When the bond critical point is approached from any other direction except along the bonding path, this point is a maximum in electron density. Two other points with topologically interesting properties are the ring critical point and the cage critical point. A ring critical point lies at a minimum of electron density along two intersecting paths across a cyclic molecule or moiety, while a cage critical point lies at a minimum along three intersecting points in a three-dimensional cage structure. Properties of these critical points can provide useful information about the electronic structure of a molecule. The value of \(\rho\) is usually greater along stronger bonds. The value of the Laplacian, \(\nabla^2 \rho\), is generally less than zero at bonding critical points of covalent bonds and greater than zero at bond critical points of non-covalent interactions.\textsuperscript{44}

A geometry optimization of 5-12 was undertaken using the crystallographically-determined coordinates as the input geometry. To complement this analysis, an AIM analysis was performed. A bond critical point was indeed located between the fluorine atom bound to the CF\textsubscript{3} group and the phosphorus atom.
As described above, the presence of this bond critical point is indicative of an interaction between the phosphonium centre and this C-F fluorine atom. The electron density at this bond critical point was 0.0207 au and the $\nabla^2 \rho$ assumes a value of 0.071, both of which are indicative of a weak, non-covalent interaction (Figure 5.11). As a further corroboration of this observation, a ring critical point was found in the six-membered ring formed by the three carbon atoms in the naphthyl backbone, the phosphorus atom, the CF$_3$ carbon atom, and the CF$_3$ fluorine atom interacting with the phosphorus centre (Figure 5.12). The electron density at this ring critical point was 0.01084 au and $\nabla^2 \rho$ was 0.0563.

While small, these interactions clearly demonstrate the ability of an electron-deficient phosphonium centre to interact with aliphatic C-F bonds, leading to the activation observed in catalytic hydrodefluorination reactions and Friedel-Crafts-type C-C coupling. The interaction observed was aided by the enforced proximity afforded by placing phosphonium cation and CF$_3$ functionalities at the 1- and 8-positions of a naphthalene scaffold; while the interaction was not as definitive as the Si-H-B and Si-H-Al interactions of the Lewis acid-silane complexes reported by Piers and Chen, 5-12 nonetheless remains the first example of a molecule showing structural evidence of C-F activation by a main group Lewis acid.
Figure 5.11 Contour map of the electron density (black) of 5-13 in the F-P-F plane, overlaid with the gradient of the electron density (blue). Bond critical points are shown as blue points and ring critical points as orange points. Centred in the image is the bond critical point between the CF$_3$ fluorine atom (right) and the phosphonium centre.

5.5.1 Ambiphilic Ligands

It was also of interest to investigate the interaction of an electron-rich transition metal centre with an electrophilic phosphonium cation. Molecules featuring electronic donation from a transition metal atom to a main group element have been known since at least the 1970s, but recent applications in catalysis have spurred interest in these complexes. Using electrophilic main group atomic centres as Z-type ligands has burgeoned in recent years. The strength of the metal→ligand bonding in these complexes varies widely. Most complexes exhibiting a Z-type interaction feature a ligand which has one or more electron-donor atoms as well as an electron acceptor. These ligands are termed ambiphilic ligands.
This electron donor is known as a buttress and exhibits a traditional X- or L-type bond with the metal, helping to maintain the metal donor atom proximate to the main group acceptor atom to favour interaction. Examples of main group centres into which electron-rich metals have donated include boron,"^48" aluminum,"^45" antimony,"^50" and tellurium,"^51" compounds, with empty p-orbitals and \( \sigma^* \) orbitals used to accept electron density from the d-electrons of transition metals. Electron-rich metals such as Pd(0), Pt(0), Rh(I) or Au(I) are most common in complexes of ambiphilic ligands, though more electron-deficient transition metal centres such as Pd(II)^"52-54" and Pt(II)^"54,55" have been utilized."^47-50,52"

### 5.5.2 Synthesis of a Naphthylphosphonium Cation Pendant to a Pd(II) Complex

To the best available knowledge, there are no complexes wherein a phosphonium cation acts as a Z-type ligand reported in the literature. In collaboration with undergraduate student Ruben Mirzoyan, efforts to synthesize a complex with a transition metal centre held in close proximity to a phosphonium cation were undertaken. A 1,8-disubstituted naphthyl framework was targeted, with a Pd(II) centre and phosphonium cation in those positions. Although Pd(II) is not an optimal electron donor, previous Pd(II) complexes of ambiphilic ligands induced metal-to-ligand electron donation by use of donor buttresses to anchor the Pd(II) centre in close proximity to the boron acceptor atoms."^52-54" Additionally, oxidative addition iodonaphthalene compounds to Pd(0) offered a facile synthetic route to install Pd on a functionalized naphthalene scaffold which would act as a rigid buttress.

Oxidation of 1-iodo-8-(diphenylphosphino)naphthalene with XeF\(_2\) to phosphorane 5-13 was undertaken. This step was carried out prior to installation of the Pd metal centre to avert oxidation of Pd(II) to Pd(IV) by the strong oxidizing agent XeF\(_2\). 5-13 was characterized by \( ^{31}\)P and \( ^{19}\)F NMR spectroscopy. This molecule was less stable than expected, thus immediately after isolation, oxidative addition of Pd(PPh\(_3\))\(_4\) was undertaken resulting in Pd(II) complex 5-14 (Scheme 5.7). Abstraction of fluoride ion with TMSOTf resulted in the isolation of cation 5-15 in moderate yield (Scheme 5.7). Characterization of 5-15 by multinuclear NMR spectroscopy was undertaken, and a solid-state structure was obtained by single-crystal x-ray diffraction analysis. 5-15 exhibited the expected doublet in the \( ^{31}\)P NMR spectrum at 96.4 ppm with a \( ^1\)J\(_{PF}\) coupling constant of 1040 Hz as well as a doublet at 18.6 ppm with a coupling constant of 39 Hz attributed to the \( ^{31}\)P nuclei of the two remaining PPh\(_3\) ligands (Figure 5.12). The phosphorus-bound \( ^{19}\)F nucleus resonates as a doublet of triplets in the \( ^{19}\)F NMR spectrum at \(-111.5\) ppm and the corresponding 1039 Hz coupling to the cationic phosphorus nucleus and 39 Hz coupling to the PPh\(_3\) ligands are observed (Figure 5.12). This latter coupling was of particular interest, as a 39 Hz
coupling constant was deemed unlikely to arise from through-bond coupling over the six bonds separating the fluorine atom from the phosphorus atoms of the bound PPh\textsubscript{3} ligands, raising the probability of a different interaction.

**Scheme 5.7** Synthesis of fluorophosphonium cation 5-15 bearing a proximal Pd(II) centre

**Figure 5.12** $^{31}\text{P}$ (top) and $^{19}\text{F}$ NMR (bottom) spectra of 5-15 with $^{19}\text{F}$-$^{31}\text{PPh}_3$ coupling shown (insets).
Figure 5.13 POV-ray depiction of cation of 5-15. H atoms are omitted for clarity. C: black; F: magenta; P: orange; Pd: turquoise; I: violet.

X-ray diffraction-quality crystals were obtained by vapour diffusion of n-pentane into a saturated solution of 5-15 in DCM. The solid-state structure of 5-15 (Figure 5.13) shows the fluorine ligand bound to the phosphonium centre to be oriented in the direction of the Pd atom. The distance between the Pd and phosphonium centres is observed to be 2.807(2) Å, significantly less than the sum of the van der Waals radii (3.03 Å). The P-F bond length of 1.546(3) Å is not elongated compared to similar structurally-characterized fluorophosphonium compounds. The Pd and P atoms are tilted away from each other in the solid-state, indicating that a Z-type metal-to-ligand donation is unlikely. As a Pd(II) d⁸ complex, the dₓ² orbital in the apical position would be expected to be populated and the dₓ²-y² orbital unpopulated. Nonetheless, the coupling of the ¹⁹F nucleus to the ³¹P nuclei of the PPh₃ ligands presented evidence of an interaction.

It would seem that this putative interaction can arise only from donation of electron density from the F atom into an empty orbital of the Pd atom, or donation of electron density from Pd d-orbitals into a σ* orbital of the F atom. Due to the extreme unlikelihood of this latter possibility, it is postulated that the interaction is donation from the F atom to Pd, forming a bridging interaction and leading to the observed...
coupling between the $^{19}$F nucleus and $^{31}$P nuclei of the PPh$_3$ ligands. Computations may be helpful in supporting this postulate.

### 5.6 Conclusions

Asymmetric disubstitution of the naphthalene scaffold at the 1- and 8-positions offers the possibility of enforcing proximity of various functionalities to phosphonium centres. Such intramolecular proximity might yield insight into the interactions of these functionalities with phosphonium cations. Silyl and trifluoromethyl functional groups were targeted, as Si-H and aliphatic C-F bonds have been activated by EPCs in catalysis and compounds modelling reactive intermediates in these cycles could yield valuable mechanistic information.

The use of the “turbo Grignard” reagent proved effective for the selective functionalization of 1,8-dibromonaphthalene or 1,8-diiodonaphthalene, allowing asymmetric functionalization. 1,8-disubstituted naphthalene compounds 5-5 and 5-6 were synthesized, featuring proximal silyl and phosphine functionalities, however accessing the corresponding fluorophosphonium cations proved unsuccessful. Compound 5-12, featuring an electrophilic fluorophosphonium cation centre proximal to a CF$_3$ functionality was successfully synthesized, and computations undertaken on the geometry-optimized structure indicated a weak interaction between one carbon-bound fluorine atom and the phosphonium centre. The solid-state structure of 5-12 and low-temperature NMR studies offered hints of such an interaction.

Similarly, a Pd functionality was installed adjacent to a fluorophosphonium cation in an attempt to induce a Z-type interaction. While this was not observed, coupling between the P-F $^{19}$F nucleus and the P atoms of the PPh$_3$ ligands was observed by NMR spectroscopy, suggesting the presence of an interaction between the fluorine nucleus and the Pd centre.

### 5.7 Experimental Details

#### 5.7.1 General

All preparations and manipulations were carried out under an anhydrous N$_2$ atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercially-available reagents such as 1,8-dibromonaphthalene, 1,8-diiodonaphthalene, CuI, 1,10-
phenanthroline, TMSCF, XeF₂, I₂, silanes, Ph₂P(Cl, Pd(PPh₃)₄, TMSOTf, and nBuLi, iPrMgCl*LiCl solutions were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise. [Et₃Si(tol)][B(C₆F₅)₄] was prepared following a procedure described in the literature. 1-bromo-8-(diphenylphosphino)naphthalene and 1-iodo-8-(diphenylphosphino)naphthalene were prepared using modified literature procedures substituting iPrMgCl*LiCl for n-BuLi. DCM, n-pentane, and toluene were dried using an Innovative Technologies solvent purification system. CD₂Cl₂ (Aldrich) was deoxygenated, distilled over CaH₂, then stored over 4 Å molecular sieves before use. C₆D₅Br (Aldrich) was deoxygenated and stored over 4 Å molecular sieves before use. Reactions were monitored using NMR spectroscopy. Reagent-grade DMF was used without drying. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian Agilent DD2 500 MHz spectrometer, and Varian Agilent DD2 600 MHz spectrometer. Data for ¹H NMR spectroscopy is reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, dm = doublet of multiplets, b = broad), coupling constant (Hz). Data for ¹³C NMR is reported in terms of chemical shift (δ / ppm). High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART).

**X-ray Diffraction Studies.** Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoKα radiation (λ = 0.71073 Å) Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). Structure solutions were found with the SHELXS-97 package using the direct method and were refined with SHELXL-97 against F² using first isotropic and anisotropic thermal parameters for all non-hydrogen atoms.
5.6.2 Syntheses

Synthesis of \([t\text{Bu}_3\text{P}(\text{C}_7\text{H}_7)][\text{BF}_4]\) 5-2

Tropylium salt \([\text{C}_7\text{H}_7][\text{BF}_4]\) (79 mg, 0.44 mmol, 1.0 equiv.) was added portionwise to a solution of \(t\text{-Bu}_3\text{P}\) (98 mg, 0.44 mg, 1.0 equiv.) in \(\text{CH}_3\text{CN}\) (5 mL). After stirring for 15 min at ambient temperature, the brownish reaction mixture was filtered over a Kimwipe plug. \(\text{Et}_2\text{O}\) (15 mL) was added resulting in the formation of a copious amount of white precipitate. The supernatant was removed and the residue was washed with \(\text{Et}_2\text{O}\) (3 x 3 mL) and dried in vacuo yielding 5-2 as colourless, polycrystalline material (142 mg, 85% yield). Single crystals of 5-2, suitable for x-ray single crystal structure determination, were obtained by slow diffusion of n-pentane into a \(\text{CH}_2\text{Cl}_2\) solution at \(-35\) °C. \(^1\text{H NMR (C}_6\text{D}_5\text{Br, [ppm]})\): \(\delta = 0.07-0.10\) (1H, m, CHP), 1.16 (27H, d, t-Bu, 3JHP = 14.2 Hz), 3.01 - 3.05 (2H, m, CH), 5.99 - 6.04 (2H, m, CH), 6.10 - 6.14 (2H, m, CH); \(^{11}\text{B\{1H\} NMR (C}_6\text{D}_5\text{Br, [ppm]})\): \(\delta = -0.6\) (s); \(^{13}\text{C\{1H\} NMR (C}_6\text{D}_5\text{Br, [ppm]})\): \(\delta = 18.3\) (1C, d, CHP, \(\text{J}_{\text{CP}} = 55.6\) Hz), 29.6 (9C, s, CCH), 40.8 (3C, d, CCH, \(\text{J}_{\text{CP}} = 29.3\) Hz), 42.4 (2C, s(br), CH), 125.2 (2C, s, CH), 125.7 (2C, d, \(3/4\text{J}_{\text{CP}} = 4.0\) Hz, CH); \(^{19}\text{F\{1H\} NMR (C}_6\text{D}_5\text{Br, [ppm]})\): \(\delta = -151.2\) (s); \(^{31}\text{P\{1H\} NMR (C}_6\text{D}_5\text{Br, [ppm]})\): \(\delta = 45.0\) (s); \textit{elemental analysis} for \(\text{C}_{19}\text{H}_{34}\text{BF}_4\text{P}\): calcd.: C 60.0, H 9.0; found: C 59.9, H 9.1; \textit{ESI MS}: m/z: 293.2391 (calcd. for [M]+: 293.2393).

Synthesis of 1-(diphenylphosphino)-8-(dimethylsilyl)naphthalene 5-5 and 1-(diphenylphosphino)-8-(diphenylsilyl)naphthalene 5-6

These products were prepared by analogous methods and thus a single preparation is detailed. 0.121 g (0.275 mmol, 1.00 equiv.) 1-bromo-8-(diphenylphosphino)naphthalene was dissolved in 2 mL toluene and cooled to \(-35\) °C. 0.11 mL 2.5M \(n\text{-BuLi}\) in \(n\text{-hexanes}\) solution was added dropwise and the mixture was allowed to warm to room temperature for 3h. The resultant light brown slurry was cooled to \(-35\) °C again and a solution of 0.026 g \(\text{Me}_2\text{Si(H)Cl}\) or 0.060 g \(\text{Ph}_2\text{Si(H)Cl}\) (0.275 mmol, 1.00 equiv.) in 0.5 mL toluene cooled to \(-35\) °C was added dropwise. The mixture was allowed to warm to room temperature and stirred for 48 h. It was subsequently filtered and the filtrate concentrated \textit{in vacuo} to a yellow oil. The oil was dissolved in a minimum of DCM, and loaded onto a small silica column. After washing the column with 2 mL n-pentane the yellow product was eluted with 1:1 DCM: n-pentane. The eluted solution was concentrated \textit{in vacuo} and the product was purified by crystallization from the cooled solution at \(-35\) °C, from which x-ray quality crystals were also obtained.
5-5 yield: 56% $^1$H NMR (CDCl$_3$ [ppm]): $\delta = 0.62$ (6H, dd, $^4J_{HH} = 3.9$ Hz, $J_{PH} = 3.4$ Hz, SiH(CH$_3$)), 5.17 (1H, ddsept, $J_{PH} = 21.1$ Hz, $^4J_{HH} = 7.1$ Hz, SiH), 7.23 (4H, m, HAr), 7.30 (6H, m, HAr), 7.42 (1H, dd, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 7.1$ Hz, HAr), 7.48 (2H, m, HAr), 7.90 (1H, m, HAr), 7.98 (1H, dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.4$ Hz $^{13}$C{H} NMR (CDCl$_3$, [ppm]): 1.7 (d, $J_{PC} = 21.5$ Hz, CH$_3$), 125.4 (d, $J_{PC} = 8.3$ Hz, CAr Hz), 128.6 (s, CAr), 128.7 (d, $J_{PC} = 6.3$ Hz, CAr), 131.3 (d, $J_{PC} = 2.3$ Hz, CAr), 132.0 (d, $J_{PC} = 0.7$ Hz, CAr), 133.6 (d, $J_{PC} = 18.0$ Hz, CAr), 134.6 (d, $J_{PC} = 7.4$ Hz, CAr), 135.9 (d, $J_{PC} = 14.7$ Hz, CAr), 136.9 (d, $J_{PC} = 1.4$ Hz, CAr), 137.3 (d, $J_{PC} = 11.4$ Hz, CAr), 138.0 (d, $J_{PC} = 1.7$ Hz, CAr), 138.4 (d, $J_{PC} = 11.4$ Hz, CAr), 142.2 (d, $J_{PC} = 31.8$ Hz, CAr). $^{31}$P{H} NMR (CDCl$_3$, [ppm]): $\delta = -15.1$ (s)

5-6 yield: 61% $^1$H NMR (CDCl$_3$ [ppm]): $\delta = 6.37$ (1H, d(br), $J_{PH} = 21.1$ Hz, SiH), 6.80 (2H, t, $^3J_{HH} = 7.5$ Hz, HAr), 7.16 (4H, t, $^3J_{HH} = 7.4$ Hz, HAr), 7.20–7.46 (12H, m, HAr), 7.50 (4H, m, HAr), 7.96 (1H, m, HAr), $^{31}$P{H} NMR (CDCl$_3$, [ppm]): $\delta = -19.9$ (s)

**Synthesis of 8-Trifluoromethyl-1-bromonaphthalene 5-8**

To an oven-dried 100 mL Schlenk flask was added copper iodide (198 mg, 2.00 mmol, 2.00 equiv). Air in the flask was then evacuated and the flask was re-filled with nitrogen. Under positive pressure of nitrogen, KOtBu (224 mg, 2.00 mmol, 2.00 equiv) and 1,10-phenanthroline (360 mg, 2.00 mmol, 2.00 equiv) were then added, along with 4.0 mL DMF. The Schlenk flask was sealed under nitrogen and the dark red mixture was stirred for 30 minutes. TMSCF$_3$ (0.296 mL, 2.00 mmol, 2.00 equiv) was then added via syringe and the mixture was stirred for a further 60 minutes. The stopper was then removed and under a positive pressure of nitrogen 1-bromo-8-iodonaphthalene was added quickly via powder funnel. The Schlenk flask was then sealed and the mixture was stirred under nitrogen for 18
127 hours at 50 °C. The mixture was then cooled, diluted with 15 mL Et2O, and filtered through Celite. Celite was washed with a further 5 mL Et2O and the combined organic layer was washed sequentially with 10 mL 1M HCl, 10 mL aqueous NaHCO3 solution, and 10 mL brine, and dried over Na2SO4. The yellow solution was then concentrated and placed in a refrigerator at 0 °C overnight, affording brown-tinted yellow, x-ray-quality crystals of 5-8 in 68 % yield. 1H NMR (CDCl3 [ppm]): δ = 7.36 (t, 3JHH = 7.8 Hz, 1H, Ar), 7.53 (t, 3JHH = 7.8 Hz, 1H, Ar), 7.88 (dd, 3JHH = 8.0 Hz, 4JHH = 1.2 Hz, 1H, Ar), 8.03 (dd, 3JHH = 8.3 Hz, 4JHH = 1.3 Hz, 1H, Ar), 8.07 (dd, 3JHH = 7.5 Hz, 4JHH = 1.3 Hz 1H, Ar), 8.12 (dd, 3JHH = 7.4 Hz, 4JHH = 1.2 Hz, 1H, Ar), 8.16 (d, 3JHH = 8.1 Hz, 1H, Ar), 8.21 (d, 3JHH = 8.0 Hz, 1H, Ar), 8.22 (d, 3JHH = 8.0 Hz, 1H, Ar), 8.37 (d, 3JHH = 7.5 Hz, 1H, Ar), 8.42 (d, 3JHH = 7.5 Hz, 1H, Ar).

13C{1H} NMR (CDCl3, [ppm]): 117.4 (s, CAr), 124.8 (s, CAr), 126.5 (s, CAr), 129.0 (q, JFC = 8.0 Hz, CAr), 129.2 (s, CAr), 132.5 (s, CAr), 133.9 (d, JPC = 20.5 Hz, CAr), 135.5 (q, JFC = 1.4 Hz, CAr), 136.2 (d, JPC = 6.4 Hz, CAr), 139.8 (dq, 3JPC = 16.0 Hz, JFC = 2.6 Hz, CAr), 141.4 (d, JPC = 1.4 Hz, CAr).

19F{1H} NMR (CD2Cl2, [ppm]): δ = −51.0 (d, JPF = 110 Hz).

13P{1H} NMR (CD2Cl2, [ppm]): −2.5 (q, JPF = 110 Hz).

Synthesis of 1-diphenylphosphino-8-trifluoromethylnaphthalene 5-9

1-bromo-8-trifluoromethylnaphthalene 5-8 (68.8 mg, 0.250 mmol, 1.00 equiv) was dissolved in 1.5 mL toluene and cooled to -35 °C. 0.100 mL (0.250 mmol, 1.00 equiv.) of a 2.5M solution of nBuLi in hexanes was then added dropwise. The solution was allowed to warm to room temperature over the course of 2h resulting in a brown suspension, which was subsequently cooled to -35 °C. A solution of 0.0552 g Ph2PCl in 0.5 mL toluene was added and the mixture was allowed to stir 24h, resulting in a brown suspension. This suspension was filtered through a glass frit and the filtrate was concentrated in vacuo yielding 57 mg of 5-9 (60 % yield). 1H NMR (CDCl3, [ppm]): δ = 7.22 (4H, m, Ph), 7.29 (6H, m, Ph), 7.43 (1H, dd, 3JHH = 8.0 Hz, 4JHH = 7.2 Hz, Naphth.), 7.56 (1H, ddd, 3JHH = 8.2 Hz, 4JHH = 7.3 Hz, 1H, Ar), 7.94 (dd, 3JHH = 8.1 Hz, 4JHH = 1.5 Hz, 1H, Naphth) 8.06 (dd, 3JHH = 7.5 Hz, 4JHH = 1.5 Hz, 1H, Naphth) 8.10 (d, 3JHH = 8.1 Hz, 1H, Naphth). 13C{1H} NMR (CDCl3, [ppm]): δ = 124.9 (s, CAr), 126.6 (s, CAr), 129.1 (d, 3JPC = 18.5 Hz, CAr), 129.2 (s, CAr), 132.5 (s, CAr), 133.9 (d, JPC = 20.5 Hz, CAr), 135.6 (q, JFC = 1.4 Hz, CAr), 136.2 (d, JPC = 6.4 Hz, CAr), 139.8 (dq, 3JPC = 16.0 Hz, JFC = 2.6 Hz, CAr), 141.4 (d, JPC = 1.4 Hz, CAr) 19F{1H} NMR (CD2Cl2, [ppm]): δ = −51.0 (d, JPF = 110 Hz).
Synthesis of (8-Trifluoromethylnaphthyl)bis(pentafluorophenyl)fluorophosphine 5-10

A solution of 5-8 (68.8 mg, 0.25 mmol) in toluene was cooled to −35 °C. 0.10 mL (0.25 mmol) of a 2.5 M solution of nBuLi in hexanes was added dropwise. Allowing the mixture to warm to room temperature over 2 hours resulted in a brown suspension. The brown suspension was cooled to −35 °C and a cooled solution of (C₆F₅)₂PBr (111.0 mg) in 0.5 mL toluene was added dropwise, resulting in change of the colour of the suspension to dull red. This suspension was allowed to warm to room temperature over the course of 20 hours. Volatiles were then removed in vacuo and the product extracted with 2 mL pentane, which was loaded onto a small silica column. Washing the column with pentane until the yellow colour had reached the bottom of the silica resulted in removal of impurities, and the product was eluted from the column with DCM. This procedure was repeated a second time, affording 5-10 as a sticky white solid in 54% yield. ¹H NMR (CD₂Cl₂, [ppm]): 7.51 (dd, 1H, H Ar, ³JHH = 8.3 Hz, ³JHH = 7.8 Hz, Ar), 7.62 (dd, 1H, HAr, ³JHH = 8.3 Hz), 8.03 (2H, m, HAr), 8.13 (2H, dd, ³JHH = 7.7 Hz, ³JHH = 3.4 Hz ). ¹³C{¹H} NMR (CD₂Cl₂, [ppm]): δ = 119.7 (m, C, CF₃), 126.1 (d, 1C, CAr, ¹JPC = 114 Hz), 130.1 (q, 1C, CAr, ⁴JFC = 7.3 Hz), 132.9 (d, ²JFC = 37 Hz, CAr) 134.3 (s, 1C, CAr), 136.1 (m, 1C, CAr), 136.3 (d, 1C, CAr, ⁴JFC = 8.4 Hz), 141.2 (q, 1C, Car, ¹JFC = 2.0 Hz), 138.7 (d of m, 2C, m-C₆F₅, ¹JFC = 255 Hz), 143.0 (d of m, 1C, C, p-C₆F₅, ¹JFC = 255 Hz), 148.1 (d of m, 2C, o-C₆F₅ ¹JFC = 248 Hz). Resonances for ipso-carbon atoms on phenyl moieties were not observed. ¹⁹F{¹H} NMR (CD₂Cl₂, [ppm]): −52.1 (d, 3F, CF₃, ¹JPF = 120 Hz), −131.1 (t, 4F, o-C₆F₅, ³JFF = 29 Hz), −151.5 (t, 2F, p-C₆F₅, ³JFF = 21 Hz), −161.4 (td, 4F, m-C₆F₅, ³JFF = 29 Hz, ³JFF = 21 Hz). ³¹P{¹H} NMR (CD₂Cl₂, [ppm]): −34.7 (m) Elemental Analysis for C₂₂H₁₉F₂P: calcd.: C 64.7, H 4.7, found: C 63.1, H 4.9; DART MS: m/z 561.00821 (calcd. for MH⁺: 561.00778)

Synthesis of (8-Trifluoromethylnaphthyl)bis(pentafluorophenyl)difluorophosphorane 5-11

To a solution of 5-10 (54 mg, 0.096 mmol) in DCM was added a DCM solution containing 16mg (1.0 equiv.) XeF₂. The solution was allowed to stir for 2 h. Volatiles were then removed in vacuo and the resultant solid washed with 1 mL n-pentane, affording 5-11 as a white solid in 86 %
yield. $^{19}$F$^1$H NMR (CD$_2$Cl$_2$, [ppm]): −53.6 (s, CF$_3$), −133.1 (4F, m(br)), −149.9 (2F, t, p-C$_6$F$_5$, $^3$J$_{FF}$ = 21 Hz), −161.3 (4F, m, m-C$_6$F$_5$). $^{31}$P$^1$H NMR (CD$_2$Cl$_2$, [ppm]): −53.0 (t, $^1$J$_{PF}$ = 736 Hz)

**Synthesis of (8-Trifluoromethyl)naphthyl)bis(pentafluorophenyl)fluorophosphonium salt 5-12**

![Chemical Structure](image)

To a vial containing 5-11 (54 mg, 0.90 mmol) was added 76 mg [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$] (0.86 mmol, 0.95 equiv.) in several portions, with shaking after each addition. Immediately a dark, oily precipitate formed on the bottom of the vial. The vial was left to stand for 4h then the supernatant was decanted from the oily precipitate and the precipitate was washed with toluene (2 x 0.5 mL) and n-pentane (2 x 0.5 mL) and dried in vacuo yielding 70 mg of solid 5-13 (65 % yield). X-ray quality crystals were obtained by slow diffusion of n-pentane into a saturated solution of 5-13 in DCM cooled to −35 °C. $^1$H NMR (CD$_2$Cl$_2$, [ppm]): 7.96 (1H, td, $^3$J$_{HH}$ = 8.0 Hz, $^4$J$_{HH}$ = 3.1 Hz, HAr), 8.01 (1H, ddd, $^3$J$_{HH}$ = 8.3 Hz, $^3$J$_{HH}$ = 7.5 Hz, $^4$J$_{HH}$ = 1.0 Hz), 8.25 (1H, dd, $^3$J$_{HH}$ = 7.6 Hz, $^4$J$_{HH}$ = 1.3 Hz, HAr), 8.52 (2H, m, HAr), 8.73 (1H, d, $^3$J$_{HH}$ = 8.3 Hz). $^{13}$C$^1$H NMR (CD$_2$Cl$_2$, [ppm]): δ = 127.7 (d, $^J_{PC}$ = 18 Hz, CAr), 129.5 (s, CAr), 134.6 (q, $^4$J$_{FC}$ = 5.4 Hz, CAr), 136.2 (d, $^J_{PC}$ = 13.5 Hz, CAr) 138.0 (s, CAr), 138.4 (m, CAr), 138.7 (dm, m-C$_6$F$_5$), 139.6 (dm, $^1$J$_{FC}$ = 262 Hz, C$_6$F$_5$), 141.8 (m, CAr), 144.5 (d, CAr, $^J_{PC}$ = 3.6 Hz), 148.6 (dm, C$_6$F$_5$), 148.9 (dm, $^1$J$_{FC}$ = 242 Hz, C$_6$F$_5$), 150.2 (dm, C$_6$F$_5$ $^1$J$_{PC}$ = 270 Hz). Resonances for ipso-carbon atoms on C$_6$F$_5$, phenyl moieties, CF$_3$ were not observed. $^{19}$F$^1$H NMR (CD$_2$Cl$_2$, [ppm]): −53.1 (3F, d, CF$_3$, $^J_{PF}$ = 27 Hz), −125.3 (4F, m, o-P(C$_6$F$_5$)$_2$), −127.7 (2F, m, p-P(C$_6$F$_5$)$_2$), −133.3 (8F, m, o-B(C$_6$F$_5$)$_4$), −152.2 (4F, tm, $^3$J$_{FF}$ = 19 Hz, m-P(C$_6$F$_5$)$_2$), −163.7 (4F, td, $^3$J$_{FF}$ = 21 Hz p-B(C$_6$F$_5$)$_4$), −167.6 (8F, m, m-B(C$_6$F$_5$)$_4$). Resonance for P-F $^{19}$F nucleus was observed at −100.4 ppm at −80 °C but not observed at room temperature. $^{31}$P$^1$H NMR (CD$_2$Cl$_2$, [ppm]): 70.3 (d, $^1$J$_{PF}$ = 1010 Hz).
Synthesis of 8-
[bis(pentafluorophenyl)naphthylfluorophosphonium]bis(triphenylphosphine)palladium Iodide 5-
15

\[
\begin{array}{c}
\text{(C}_6\text{F}_5)_2\text{PF} \\
\text{Pd(l)(PPh}_3)_2 \\
\text{[OTf]} \\
\end{array}
\]

To a solution of 92 mg (0.072 mmol) 5-14 in toluene was added 13 µL (16 mg, 1.0 equiv.) of trimethylsilyl trifluoromethylsulfonate dropwise at room temperature. A yellow solid formed immediately. The supernatant was decanted and the solid was washed with toluene (3 x 1 mL) and dried \textit{in vacuo}, resulting in 5-15 in 65% yield. X-ray quality crystals were grown by slow diffusion of \textit{n}-pentane into a saturated CH\textsubscript{2}Cl\textsubscript{2} solution. \textsuperscript{1}H (NMR (CD\textsubscript{2}Cl\textsubscript{2}, [ppm]): \(\delta = 6.77\) (t, \(J = 7.6\) Hz, 1H); 7.03 (dd, \(J = 13.9, 7.8\) Hz, 4H); 7.21 (s, 22H); 7.41 (d, \(J = 7.9\) Hz, 7H); 7.55 (h, \(J = 7.8, 4.2\) Hz, 4H); 7.68 (s, 1H); 7.89 (t, \(J = 7.7\) Hz, 2H); 8.09 (d, \(J = 7.7\) Hz, 1H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (CD\textsubscript{2}Cl\textsubscript{2}, [ppm]): \(\delta = 121.3\) (d, \(J_{PC} = 15\) Hz); 123.2 (d, \(J_{PC} = 21\) Hz); 127.3 (d, \(J_{PC} = 86\) Hz); 128.7 (d, \(J_{PC} = 5\)Hz); 131.1 (s); 131.2 (s); 131.3 (s); 131.8 (t, \(J_{PC} = 23\) Hz); 134.0 (d, \(J_{PC} = 12\)Hz); 135.6 (t, \(J_{PC} = 6\)Hz); 138.0 (s); 141.9 (d, \(J_{PC} = 21\) Hz); 143.3 (d, \(J_{PC} = 4\) Hz). Signals for some quaternary carbon atoms not observed. \textsuperscript{19}F (NMR (CH\textsubscript{2}Cl\textsubscript{2}, [ppm]): \(\delta = -111.43\) (dt, \(J_{PF} = 10, 2J_{PF} = 38.8\) Hz) \textsuperscript{31}P{\textsuperscript{1}H} (NMR (CH\textsubscript{2}Cl\textsubscript{2}, [ppm]): \(\delta = 18.6\) (d, \(2J_{PF} = 39\) Hz), 96.4 (d, \(1J_{PF} = 1040\) Hz).

Elemental Analysis for C\textsubscript{10}H\textsubscript{46}Pd\textsubscript{3}F\textsubscript{4}SO\textsubscript{3}: calcd.: C: 57.3; H: 3.8, found: C: 57.0; H: 3.6.
Table 5.1 Crystallographic data and details of the structure refinement of compounds 5-2, 5-5, 5-6, 5-7

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Table 5.2 Crystallographic data and details of the structure refinement of compounds 5-8, 5-12, and 5-15

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(60) Sheldrick, G.M. SHELXTL-97, Program for Crystal Structure Determination, Gottingen, Germany, 1997
Chapter 6

Silylium Cation-Phosphine FLPs in the Generation and Interception of Difluorocarbenium Cations From Aryl Trifluoromethyl Compounds

6.1 Introduction

6.1.1 Trifluoromethyl Groups in Synthesis

Trifluoromethyl functional groups are an increasingly common component of pharmaceutical agents, including such blockbuster drugs as Prozac and Celebrex. They are also found in fluorocarbons used as refrigerants and in non-stick coating materials. Fluorinated fragments in pharmaceuticals are often used as bioisosteric units which are chemically resistant to metabolic oxidation. The significant research emphasis on developing efficient trifluoromethylation protocols is highlighted by recent reviews summarizing photo-induced trifluoromethylation methods,\textsuperscript{1} C-H activation strategies,\textsuperscript{2} and the use of cuprate reagents.\textsuperscript{3} Recent developments using phosphonium cations as trifluoromethylation or difluoroalkylation agents have also been summarized.\textsuperscript{4}

Despite the existence of some difluoroalkylation protocols, the inclusion of CF\textsubscript{2} units is much less common than that of CF\textsubscript{3} units, largely a result of the paucity of reagents and synthetic methodologies\textsuperscript{5} that allow the incorporation of such fragments. Converting CF\textsubscript{3} units to CF\textsubscript{2}X would provide a derivatization route that would have significant synthetic utility. However, the strong nature of C-F bonds (ca. 105 kcal/mol)\textsuperscript{6} makes C-F activation challenging and accounts for the long environmental lifetimes of molecules containing CF\textsubscript{3} fragments.\textsuperscript{6,7} Furthermore, studies have shown that after removal of one fluoride ion from a CF\textsubscript{3} group, activation of the subsequent C-F bonds is less thermodynamically challenging,\textsuperscript{8} rendering it extremely difficult to selectively remove a single fluoride ion from a CF\textsubscript{3} group and trap the resulting difluorocarbenium cation before further C-F activations occur. End-of-lifecycle disposal of CF\textsubscript{3}-containing fluorocarbons is mostly limited to remediation via conversion to more benign, less persistent hydrocarbons through
complete hydrodefluorination processes. Derivatization via selective activation of a single C-F bond would provide potential alternative uses for trifluoromethylated compounds.

Activation of aliphatic C-F bonds requires strongly fluorophilic Lewis acids. While C-F bond activations using transition metal species have been studied by the groups of Milstein, Jones, Grushin, Oestreich and others, these systems effect stoichiometric activations of aryl or monofluoroalkyl C–F bonds. More recently, fluoride abstraction by B(C₆F₅)₃ from a hexafluoropropylene-palladium complex was shown to generate a cationic perfluoroallylpalladium complex.

Non-metal approaches to C-F bond activation have also been explored. In 1964 Olah et al. first reported Friedel–Crafts alkylation of alkyl monofluorides using BF₃. More recently, avenues to functionalization of CF₃ units have been realized using strong Lewis acids. The alkylation of CF₃ species via stoichiometric reactions of alkyl aluminum species was reported by Terao in 2007. In 2008, Ozerov described the hydrodefluorination of C-F bonds catalyzed by silylium cations in the presence of silane while Müller and coworkers subsequently described the use of disilyl-cations in related hydrodefluorination of C-F bonds. Ozerov’s group also described the combination of an aluminum cation and AlMe₃ to alkylate C-F bonds. In 2011, polyaromatic species were formed by Friedel-Crafts reactions of polyaromatic monofluoroarenes initiated by protons or silylium cations, while Kemnitz and coworkers described alkylation of benzene with fluoromethanes using aluminum chlorofluoride as a heterogeneous catalyst.

The utility of main-group Lewis acids for C-F bond activation has been recently reviewed by Oestreich. In our own efforts, we described hydrodefluorinations of fluoroalkanes using B(C₆F₅)₃ in 2012 and in the subsequent years described the use of electrophilic phosphonium cation (EPC) salts (e.g. [(C₆F₅)₃PF][B(C₆F₅)₄]) in similar hydrodefluorinations. We have also utilized EPCs as catalysts to promote concurrent hydrodefluorination and Friedel-Crafts couplings, transforming Aryl-CF₃ fragments to diarylmethanes. In a similar vein, Paquin et al. have described the acid-mediated Friedel-Crafts arylation of benzyl fluorides. The Friedel-Crafts reactions of CF₃ units are proposed to proceed via the generation of a difluorocarbocation. Nonetheless, efforts to intercept the difluorocarbocations were precluded by the accelerated defluorination of these transient difluoro-species. Treatment of trifluoromethyl compounds with hydrodefluorinating
agents results in removal of all three fluorine atoms and conversion of RCF₃ to RCH₃. In cases where sources of hydride such as silanes are used in 1:1 stoichiometric ratios with CF₃-containing substrates, full hydrodefluorination of one-third of an equivalent of substrates occurs while the remaining two-thirds have their CF₃ groups intact. Although an extremely limited number of examples of arresting defluorination of RCF₃ groups after abstraction of a single fluoride ion have been reported, the options for functionalization of these RCF₂X species are limited.

6.1.2 Precedents for Removal of a Single Fluoride Ion from Trifluoromethyl Groups

The dearth of examples of single C-F bond activations from CF₃ groups and interception of a difluorinated carbocation is a testament to the difficulties outlined above. Reductive, selective defluorinations have been reported using electrochemical methods or superstoichiometric amounts of metals. For example, the electrochemical reduction of α,α,α-trifluorotoluene derivatives and subsequent trapping of the transient difluoroanionic fragment with carbonyl electrophiles has been described. The reductive removal of a single fluorine atom from fluoroalkyl groups α to a carbonyl functionality using excess magnesium or zinc has been reported. In 2010, Hilmersson demonstrated that in the case of CF₃ groups α to ester or amide functionalities selective mono- or bis-hydrodefluorination can be effected using a six-to-eight-fold excess of SmI at -78 °C (Scheme 1A).

Based on thorough searches of the chemical literature, it seems that only two previous examples exist of the oxidative removal of a single fluoride ion from CF₃ groups. Twenty years ago, a report by Lectka described an intramolecular reaction of an aryl-CF₃ fragment with an adjacent diazonium cation, generating twenty percent of a product containing a CF₂ linkage between the two arene rings (Scheme 1B). This presumably occurred by C–F activation of the aryl cation followed by Friedel-Crafts-type attack on the resultant difluorocarbenium cation to form the five-membered ring. It was not until 2016 that the first report of a generalized, methodical and high-yielding protocol for the single-fluoride abstraction from a CF₃ moiety was published by Hosoya and co-workers. In their elegant report, they described the rare production of CF₂-moieties by abstraction of a single fluoride ion from an aryl CF₃-group (Scheme 6.1C). Their procedure
featured in situ generation a silylium cation ortho to the CF₃ group of the arene to remove the fluoride ion. Addition of a range of mildly nucleophilic agents permitted subsequent C-X bond formation by trapping the difluorocarbenium cation intermediate, perhaps most interestingly in the case of allylic compounds acting as nucleophiles to form C-C bonds.⁴⁹ Standard protocols are then possible to eliminate the silyl group, effecting net addition of CF₂Ar to the nucleophilic compound. The intramolecular proximity of the CF₃ group to the silylium centre capable of accepting a single fluoride ion undoubtedly facilitated this single-fluoride abstraction and precluded further activation of C-F bonds intermolecularly. Both the examples of Lectka and Hosoya activated C–F bonds of aryl-CF₃ groups, permitting resonance stabilization of the resultant cation.

Scheme 6.1 Examples of activation of a single C–F bond from ArCF₃ by reductive (A) and fluoride abstraction (B,C) methods.

6.2.1 FLP Generation and Capture of an Aryl Difluorocarbenium Cation Within a 1,8-Disubstituted Naphthyl Framework

The generation and capture a difluorocarbenium cation by Hosoya et. al. suggested possibilities for this type of reactivity within a FLP context. Their strategy of generating a fluorophilic silylium
cation *in situ*, capable of abstracting only a single fluoride ion from an aryl-CF$_3$ moiety indicated that controlling stoichiometry was a key factor facilitating single-fluoride ion abstraction. Their reactions also required a very specific solvent combination of 1:1 DCM:1,1,1,3,3,3-hexafluoroisopropanol (HFIP) to achieve optimal reactivity. While both of these solvents could be expected to react readily with free silylium cations, the effect of steric protection and the proximity of the CF$_3$ functional group undoubtedly helped favour fluoride ion abstraction. It was postulated that generating a difluorocarbenium cation from an aryl-CF$_3$ group might be possible by reaction with the common, stable silylium cation [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$] in benign solvent if an intramolecular electron donor was in close proximity to kinetically favour bonding to the difluorocarbenium cation over reaction with solvent. Activation of CF$_3$ functional groups with catalytic C-F bond activators such as electrophilic phosphonium cation (EPC) catalysts or the silylium catalysts of Ozerov has demonstrated that transiently generated difluorocarbenium cations will react readily with coordinating solvents or by Friedel-Crafts-type mechanisms with aromatic solvents, or react with reactive anions. A strategy was adopted to preclude these reactions by choosing solvents unreactive toward silylium cations, by using stoichiometric amounts of this fluorophilic silylium cation, and by incorporating an electron donor in close proximity to the CF$_3$ functionality.

Compounds (8-trifluoromethylnaphthyl)diphenylphosphine and (8-trifluoromethylnaphthyl)-bis(pentafluorophenyl)phosphine reported in Chapter 5 of this thesis, and in this chapter numbered 6-1 and 6-2, respectively, feature a phosphine and an aryl-CF$_3$ functional group held in close proximity by the rigid naphthyl framework. We postulated that reaction with [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$] might result in abstraction of a single fluoride ion. Compound 6-1 resonates as a quartet at -1.7 ppm in the $^{31}$P NMR spectrum with a P-F coupling constant of 110 Hz, presumed to be through-space coupling. The corresponding signal for the CF$_3$ $^{19}$F nuclei resonates as a doublet at -50.7 ppm in the $^{19}$F NMR spectrum. Upon treatment with 0.95 equivalents of [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$] in bromobenzene (Scheme 6.2), a single major product is observed with a quartet resonance at 5.0 ppm in the $^{31}$P NMR spectrum with a P-F coupling constant of 29 Hz and the CF$_3$ resonance in the $^{19}$F NMR spectrum shifted slightly upfield to -53.9 Hz (Figure 6.1). The quartet in the $^{31}$P NMR spectrum and integration against the $^{19}$F resonances for the [B(C$_6$F$_5$)$_4$] anion confirmed that the CF$_3$ group remained intact. Solid 6-3 was isolated from the reaction mixture by decanting the bromobenzene supernatant and washing with
bromobenzene and n-pentane. The isolated solid exhibited $^1$H and $^{13}$C NMR resonances corresponding to the ethyl substituents of the P-bound Et$_3$Si and the signals in the $^1$H NMR spectrum integrated in the expected ratio of 9:6:16 for the CH$_3$:CH$_2$: combined aromatic protons of the naphthyl and phenyl moieties, confirming that the resulting product was 6-3, the phosphine adduct of the silylium cation. Heating this product to 110 °C did not result in further reaction.

**Figure 6.1** $^{31}$P (top) and $^{19}$F (bottom) NMR spectra of 6-3 in CD$_2$Cl$_2$ with P-F coupling shown to the $^{31}$P nucleus (top, inset) and $^{19}$F nuclei of the CF$_3$ moiety at –53.9 ppm (bottom, inset)
Scheme 6.2 Reaction of trifluoromethylnaphthylphosphines 6-1 and 6-2 with [Et₃Si(tol)][B(C₆F₅)₄].

Naphthylphosphine 6-2 was also treated with 0.95 equivalents of [Et₃Si(tol)][B(C₆F₅)₄] in bromobenzene (Scheme 6.2). It was postulated that an adduct, if formed, would be significantly weaker than that of 6-3 due to the reduced basicity of the phosphine, potentially favouring C–F bond activation. As discussed in Chapter 5 of this thesis, phosphine 6-2 exhibits a complex multiplet at −34.7 in the ³¹P¹H NMR spectrum which can be deconvoluted as a quartet of quintets arising from coupling of the CF₃ fluorine atoms with a coupling constant of 120 Hz and coupling to the four ortho-fluorine atoms of the C₆F₅ substituents with a ³JPF coupling constant of approximately 35 Hz.

Addition of [Et₃Si(tol)][B(C₆F₅)₄] to 6-2 dissolved in bromobenzene resulted in precipitation of a microcrystalline solid from the reaction mixture. Isolation of this solid permitted NMR spectroscopic analysis in DCM and confirmed that 6-2 exhibited different reactivity with [Et₃Si(tol)][B(C₆F₅)₄] than 6-1. The product 6-4, obtained in 91% yield, resonated as a triplet in the ³¹P¹H NMR spectrum at 11.5 ppm with a typical ²JPF coupling constant of 108 Hz (Figure 6-3). The corresponding ¹⁹F resonance was the expected doublet of quintets at −84.7 ppm, with ⁵JFF coupling to the four ortho-fluorine atoms of 7 Hz. These data support the formulation of 6-4 as [C₁₀H₈(1-P(C₆F₅)₂)(8-CF₂)] [B(C₆F₅)₄], in which the phosphorus is bound to the CF₂ fragment generated by fluoride ion abstraction by the silylium cation. ¹⁹F¹H NMR spectroscopic analysis of the initial reaction mixture confirmed the formation of Et₃SiF, with an observed resonance at −175.0 ppm in the ¹⁹F NMR spectrum of the reaction mixture.
Figure 6.2 $^{31}\text{P}$ (top) and $^{19}\text{F}$ (bottom) NMR spectra of 6-3 in CD$_2$Cl$_2$ with P-F coupling shown to the $^{31}\text{P}$ nucleus (top, inset) and $^{19}\text{F}$ nuclei of the CF$_3$ moiety (bottom, inset).

The structure of 6-4 was confirmed crystallographically (Figure 6.3). The solid-state structure shows an unusually long P-C$_{\text{CF}_2}$ bond of 1.915(2) Å to the difluoro-substituted carbon atom, significantly longer than the P-C bonds to the fluorarene rings (1.788(2) and 1.797(2) Å). The corresponding C-F bonds are on the short end of the spectrum for aliphatic C-F bonds (av. 1.358 (3) Å). This geometry is consistent with the poor donor ability of the phosphorus centre, suggesting that the carbon atom might be considerably electrophilic.
The isolation of 6-4 represents a FLP trapping of a difluoro-carbocation generated by fluoride abstraction from CF$_3$. When contrasted with the reactivity of 6-1 with [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$], it is apparent that a critical feature permitting the fluoride abstraction is the poorly electron donating phosphine, which facilitates the generation of a FLP in the presence of the silylium cation. 6-4 appears to be the first case in which a phosphine donor intercepts a difluoro-carbocation affording a CF$_2$-P linkage, and an extremely rare example of oxidative removal of a single fluoride ion from a CF$_3$ functional group.

The mechanism of this unusual C-F activation was investigated by DFT calculations, and geometry optimization calculations were carried out at the TPSS-D3/def2-TZVP level of theory by Professor Stefan Grimme and Dr. Hui Zhu at the Mulliken Center for Theoretical Chemistry at the University of Bonn, Germany. The solvation energy has been included in total energy $E$ using the model DCOSMO-RS for CHCl$_3$ ($\varepsilon = 4.81$) as this is similar to the experimental solvent C$_6$H$_5$Br ($\varepsilon = 5.17$). Frequency analysis was used to confirm the nature of stationary points and to calculate thermal free energy corrections $G_c$. Single-point energies were computed at the PW6B95-D3/def2-QZVP level of theory and using a solvation free energy ($G_{sol}$) based on the COSMO-RS (C$_6$H$_5$Br),
BP_TZVP_C30_1301.ctd parameter file. In this fashion, two energetically similar pathways for the formation of 6-4 were computed (Figure 6.4). Beginning with silylium ion complexes interacting with toluene via either the ortho- or para-carbon atom, each were shown to undergo Si-F bond formations with subsequent ring-closure via P-C bond formation affording the products in overall exergonic reactions. The free energy barriers were computed to be 19.7 and 19.2 kcal/mol, respectively. While the silylium-ortho-toluene complex is computed to be slightly less stable, it was also computed to have a lower barrier to F-abstraction. Interactions of the silylium ion via the ortho- or para-fluorine atoms of the borate anion were also considered and shown to be less stable than the silylium-toluene adducts. These species were shown to have comparable barriers to C–F activation of approximately 20 kcal/mol. Both computed pathways show initial abstraction of a fluoride ion by [Et₃Si]⁺ before the phosphorus lone pair forms a ring-closing bond with the carbon atom, indicating that this FLP activation is step-wise, rather than concerted. Neither pathway supports initial formation of a silylium-phosphine adduct.

Figure 6.4A Reaction pathway for abstraction of fluoride ion.
6.2.2 Attempted Activation of PhCF$_3$ with Intermolecular Phosphine-Silylium Cation FLPs

The demonstration by Hosoya et. al. combined with the above results illustrated that it was possible to generate and capture a difluorocarbenium cation with either an intramolecular fluorophilic silylium cation proximal to the CF$_3$ group, or an intermolecular silylium cation and intramolecular electron donor proximal to the CF$_3$ group. These results suggested that it might be possible to generate difluorocarbenium cations from simpler molecules and capture them with the combination of a silylium cation with a weak base as a FLP. This would greatly broaden the scope of potential CF$_3$-containing substrates which could be functionalized to CF$_2$X.

Initial efforts examined mixtures of [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$] with the weakly Lewis basic phosphines P(C$_6$F$_5$)$_3$ and PhP(C$_6$F$_5$)$_2$ (Scheme 6.3), close direct analogues to the FLP combination of 6-2 and [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$]. In the case of PhP(C$_6$F$_5$)$_2$ (Scheme 6.3A), a modest change in the $^{31}$P NMR chemical shift from -45.2 ppm to -32.9 ppm was observed, indicating a weak interaction between the phosphine and silylium cation (Figure 6.5). With the very weakly basic P(C$_6$F$_5$)$_3$, no change in the $^{31}$P NMR chemical shift was observed in solution (Scheme 6.3B, Figure
6.5), indicating that a FLP had indeed been formed. Noting that resonance stabilization of the transient difluorocarbenium cations was available from an aryl substituent in both the examples reported by Lectka and Hosoya, as well as in the formation of 6-4, it was hypothesized that the compounds most likely to form stable difluorocarbenium cations would be stabilized by resonance, and feature no Lewis basic substituents which might bind to the silylium cation and preclude reactivity. Thus PhCF₃ was added to the FLP mixtures shown in Scheme 6.3. However, no change in the ³¹P or ¹⁹F NMR spectra were observed after twenty-four hours, even upon heating to 110 °C.

\[
\begin{align*}
A & \quad [Et_3Si(tol)][B(C_6F_5)_4] + PhP(C_6F_5)_2 \rightarrow \text{FLP} \quad \text{no reaction} \\
B & \quad [Et_3Si(tol)][B(C_6F_5)_4] + P(C_6F_5)_3 \rightarrow \text{weak interaction} \quad \text{PhCF}_3 \rightarrow \text{no reaction}
\end{align*}
\]

**Scheme 6.3** Reaction of intermolecular Si/P FLPs with PhCF₃

**Figure 6.5** ³¹P NMR spectra of reaction mixtures of Scheme 6.1 A (top) and B (bottom)
As the \([\text{Et}_3\text{Si(tol)}]\) cation has previously been shown to activate aliphatic C-F bonds in hydrodefluorination reactions,\(^{47}\) therefore it was apparent that the lack of reactivity was not due to inadequate fluorophilicity of this Lewis acid. It was hypothesized that in the case of the \([\text{Et}_3\text{Si(tol)}][\text{B(C}_6\text{F}_5)_4]/\text{PhP(C}_6\text{F}_5)_2\) combination, the silylium cation was sufficiently quenched as to preclude activation of the C-F bonds, while in the case of the \([\text{Et}_3\text{Si(tol)}][\text{B(C}_6\text{F}_5)_4]/\text{P(C}_6\text{F}_5)_3\) combination, the lack of interaction prevented the formation of the type of FLP encounter complex predicted computationally for \(\text{H}_2\) activation mechanisms.\(^{57}\) In the absence of a FLP encounter complex, either an entropically-challenging termolecular reaction would be required to generate and capture \([\text{PhCF}_2]^+\) by a concerted mechanism, or this species would have to be sufficiently stable to persist as an intermediate until encountering the phosphine donor. Given the computed mechanism of the formation of \(\text{6-4}\), the latter pathway was more likely but nonetheless did not occur.

6.2.3 Generation and Capture of \([\text{PhCF}_2]^+\) from \(\text{PhCF}_3\) by an Intramolecular Silylium Cation-Phosphine FLP

If this type of reaction is indeed viewed as having three components — a \(\text{CF}_3\) moiety, a Lewis acidic fluoride acceptor, and an electron donor — the logical conclusion was to synthesize an intramolecular FLP for the activation of \(\text{CF}_3\)-containing molecules. To this end, the intramolecular FLP containing a phosphorus donor and a silylium cation \(\text{6-6}\) was prepared from the known species \(\text{C}_6\text{H}_4(1-\text{PPh}_2)(2-\text{SiHPh}_2)\) \(\text{6-5}\) via reaction with \([\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]\). This FLP had initially been synthesized in the Stephan laboratory by post-doctoral fellow Dr. Adam Ruddy for the attempted activation of \(\text{CO}_2\). The formation of salt \([\text{C}_6\text{H}_4(1-\text{PPh}_2)(2-\text{SiPh}_2)][\text{B(C}_6\text{F}_5)_4]\) \(\text{6-6}\) was evident as reaction caused a shift in the \(31\text{P}\) NMR resonance from \(-10.4\) ppm in \(\text{6-5}\) to \(+11.6\) ppm in \(\text{6-6}\) in bromobenzene (Figure 6.6). This downfield shift of \(+22.0\) ppm was also indicative of an intramolecular interaction between the phosphorus lone pair and the silylium centre. The \(29\text{Si}\) NMR resonance was identified at \(+12.8\) ppm by a \(29\text{Si}^1\text{H}\) HMBC NMR experiment. Despite this apparent dative interaction in \(\text{6-6}\) indicated by the significant shift in the \(31\text{P}\) NMR signal compared to precursor \(\text{6-5}\), the strain of the four-membered ring is thought to provide access to the open form of the FLP for reactivity. Indeed, the now classic Erker FLP system, \(\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B(C}_6\text{F}_5)_2\)\(^{59}\) is known to access the open-FLP as a result of similar ring strain. Alternately, the interaction was
thought to be simply weak enough that the silylium cation would be sufficiently reactive to activate C-F bonds. This species showed signs of degradation within hours and was not isolated in sufficient purity for full characterization.

**Figure 6.6** Top: $^{29}$Si-$^{1}$H HMBC spectrum of FLP 6-6 Bottom: $^{31}$P NMR spectra of precursor 6-5 (left) and silylium cation-phosphine FLP 6-6 (right)

Using either freshly prepared 6-6 from toluene or generating 6-6 *in situ* in fluorobenzene, a solution of PhCF$_3$ in fluorobenzene was added to the FLP and allowed to stir at room temperature for 24h, resulting in 6-7 in moderate yield (Scheme 6.4). Rigour in drying solvents and in maintaining a
dry glove box atmosphere were key to permitting reliable reactivity. Even under these conditions, significant impurities were formed in the reaction mixture. This reaction was also observed to occur in pentane despite limited solubility of 6-6, though conducting the reaction in this solvent resulted in lower yields of 6-7. 6-7 exhibited a diagnostic triplet of doublets in the $^{31}$P{$^1$H} NMR spectrum of the isolated solid at 23.8 ppm with a $^2$J$_{P-F}$ coupling constant of 104 Hz and $^4$J$_{P-F}$ coupling of 5 Hz to the fluorine nucleus bonded to the silicon atom (Figure 6.7). The corresponding doublets were seen at −94.7 ppm for the CF$_2$ functionality and at −148.4 ppm for the silicon-bound fluorine atom in the $^{19}$F NMR spectrum (Figure 6.7). This unprecedented intermolecular abstraction of a single fluoride ion from a CF$_3$ group and capture of the resultant [PhCF$_2$]$_2$ with a Lewis base represents evidence that single C-F bond activation of CF$_3$-containing molecules without appended functionalities is attainable.

**Scheme 6.4 Synthesis of 6-7**

![Scheme 6.4 Synthesis of 6-7](image)

**Figure 6.7A** $^{31}$P NMR spectrum showing coupling to $^{19}$F nuclei of CF$_2$ functionality (inset).
Figure 6.7B $^{19}$F NMR spectrum of 6-7 showing coupling to $^{31}$P nucleus and $^{19}$F nuclei of CF$_2$ functionality (inset).

NMR spectroscopic yields are reported for 6-7, attained by the quantitative $^{31}$P NMR spectrum of the reaction mixture and supported by integration of the $^{19}$F NMR signal of 6-7 versus remaining PhCF$_3$ starting material. Isolation of 6-7 was challenging due to the presence of significant impurities including presumed salts in the reaction mixture. Pure 6-7 was attained by silica gel column chromatography, precipitation of major impurities, and further silica gel column chromatography. Nonetheless, due to low yields after the isolation process, conversion in situ to a more readily-isolable product was desired.

6.2.4 Completing Reduction of PhCF$_3$ to PhCF$_2$H: Base-Mediated P-C Bond Cleavage

The ability to break phosphorus-carbon bonds has been a useful tool in organic synthesis since the discovery of the Wittig reaction in 1954.\textsuperscript{60,61} Wittig reactions result in P-C bond cleavage from a phosphonium ylide. The mechanism of phosphorus-element bond cleavage from tetravalent phosphonium cations is not believed to proceed through the classical substitution and elimination mechanisms by which carbon-element bonds are broken from tetracoordinate carbon centres. Instead, the capacity of phosphonium cations to form neutral trigonal bipyramidal pentacoordinate phosphorane complexes by accepting electron density from an anionic nucleophile into a $\sigma^*$ orbital defines much of their chemistry. Formation of phosphoranes renders substituents geometrically and electronically inequivalent, with bonds to the axial substituents more labile than bonds to equatorial substituents. The lowest-energy $\sigma^*$ orbital on phosphonium cations is oriented opposite
the most electronegative substituent and bond formation by donation by a nucleophile into this low-energy antibonding orbital generally results in the donor and the electronegative substituent in apical positions of the resultant phosphorane. The tendency of a substituent to occupy the apical position of a trigonal bipyramidal molecule, termed apicophilicity, was first investigated by Earl Muetterties in 1963\textsuperscript{62} who defined it as the difference in energy between two isomers in which the substituent occupies an apical or an equatorial position. Steric considerations also influence apicophilicity. Using phosphonium salts as trifluoromethylation or difluoroalkylation agents is well-established, as fluoroalkyl substituents tend to be apicophilic and therefore prone to elimination. This methodology has been recently reviewed by Zhang\textsuperscript{4} and has also been increasingly exploited in the formation of carbon-carbon bonds.\textsuperscript{63,64}

It has been established that treatment of phosphonium salts with Brønsted bases permits facile cleavage of P-C bonds. This proceeds via attack of hydroxide, generating a phosphorane intermediate\textsuperscript{65-67} leading to protodephosphorylation and liberation of the most apicophilic substituent, resulting in the generation of the phosphine oxide. Previous experimental studies have demonstrated the apicophilicity of electron-withdrawing groups and also of the relative apicophilicity of benzyl substituents over phenyl substituents.\textsuperscript{65-67} It was postulated that a facile isolation of PhCF\textsubscript{2}H, a synthetically useful product derived from 6-7, could proceed through base-promoted protodephosphorylation. This product would formally be the result of hydrodefluorination of a single C-F functionality, a transformation which had been previously targeted by EPC catalysts without success.

6-7 was treated with a 0.40 M solution of KOH in 1:1 H\textsubscript{2}O/THF. \textsuperscript{19}F NMR spectroscopic characterization of the reaction mixture after extraction with pentane confirmed that the only significant fluorine-containing product apart from the intact [B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] counterion was C\textsubscript{6}H\textsubscript{5}CF\textsubscript{2}H, presumably accessed by elimination of phosphine oxide (Scheme 6.5). The \textsuperscript{1}H-coupled \textsuperscript{19}F NMR spectrum exhibited a doublet at \textasciitilde \text{-}111.5 ppm with coupling of 57 Hz to the aliphatic proton, consistent with reported literature values (Figure 6.8).\textsuperscript{68} C\textsubscript{6}H\textsubscript{5}CF\textsubscript{2}H 6-8 was isolated by flash column chromatography using pentane as the eluent. The conversion of PhCF\textsubscript{3} to PhCF\textsubscript{2}H represents the first example of a hydrodefluorination process in which a single fluoride ion was abstracted from RCF\textsubscript{3} and substituted with a formal equivalent of hydride.
Scheme 6.5 Liberation of PhCF$_2$H 6-8 by treatment of 6-7 with aqueous base.

Figure 6.8 $^{19}$F NMR spectrum of PhCF$_2$H 6-8 with $^2J_{FH}$ coupling shown (inset).

Analogously, 6-6 was treated with PhCF$_2$H in fluorobenzene (Scheme 6.6) and after twenty-four hours a doublet at +21.1 ppm in the $^{31}$P NMR spectrum with a coupling constant of 81 Hz was observed, with a doublet of doublets at $-$184.9 ppm in the corresponding $^{19}$F NMR spectrum showed $^2J_{PF}$ coupling of 81 Hz and a $^2J_{FH}$ coupling of 43 Hz, indicating formation of species 6-9 (Scheme 6.7). However, the NMR yield of 6-9 was only 18%, with large amounts of other products observed in the $^{31}$P NMR spectrum and the remaining 82% PhCF$_2$H left unreacted by $^{19}$F NMR analysis. Nonetheless, subsequent treatment of the reaction mixture with a 0.40M solution of KOH in 1:1 H$_2$O:THF permitted isolation of PhCH$_2$F 6-10 by flash column chromatography. This demonstrates the first controlled, stepwise hydrodefluorination of trifluoromethyl groups from CF$_3$ to CF$_2$H to CH$_2$F.

Scheme 6.6 Synthesis of 6-9 and conversion to PhCH$_2$F 6-10
Conversely, when 6-6 was reacted with Ph₂CF₂ in PhF product 6-11 was obtained in 81% yield (Scheme 6.7) as determined by the quantitative ³¹P NMR spectrum and integration of the C-F ¹⁹F NMR resonance. 6-11 exhibited a doublet at 23.1 ppm in the ³¹P NMR spectrum and a doublet at 185.0 ppm in the ¹⁹F NMR spectrum corresponding to the C-F fluorine nucleus and a singlet at –147.8 ppm corresponding to the Si-F fluorine nucleus. 6-11 was then treated with a 0.40M aqueous solution of KOH in 1:1 H₂O:THF to yield the corresponding mono-hydrodefluorination product 6-12.⁶⁹,⁷⁰

The improved yield of 6-11 from the reaction of Ph₂CF with 6-6 compared to 6-9 from the reaction of PhCF₂H with 6-6 can be attributed to the enhanced stability of the transient carbocation [Ph₂CF]⁺ and/or the transition state imparted by resonance stabilization from the addition phenyl group. Carbocation [PhCF₂]⁺ and the corresponding transition state structure could be expected to have intermediate stability by comparison. The π-donation from two fluoride atoms and one phenyl group is superior to the stabilization of [PhCFH]⁺ imparted by one phenyl group, one fluoride atom and one hydrogen atom but inferior to the stabilization offered by two phenyl substituents and one fluoride atom. This trend correlates with the observed yields of the products of fluoride abstraction: Ph₂CF₂ > PhCF₃ > PhCF₂H.

Scheme 6.7 Synthesis of 6-11 and conversion to Ph₂CHF 6-12

6.3 Conclusions

The selective activation of one C-F bond from aryl-CF₃ groups by silylium cation-phosphine FLPs has been demonstrated using two different systems. The formation of 6-4 was achieved using a very weakly basic phosphine and a trifluoromethyl group at the 1- and 8-positions of a naphthalene scaffold, respectively, which permitted capture of the [ArCF₂]⁺ cation generated by abstraction of fluoride ion by an equivalent of [Et₃Si(tol)][B(C₆F₅)₄]. The formation of 6-7, 6-9 and 6-11 was
achieved using an intramolecular silylium cation-phosphine FLP permitting mono-defluorination of PhCF₃, PhCF₂ and Ph₂CF₂, respectively. These species could then be treated with base to liberate the products of step-wise arrested hydrodefluorination, PhCF₂H, PhCH₂F and Ph₂CFH. Efforts to achieve similar reactivity with intermolecular FLP systems and PhCF₃ were unsuccessful.

These FLP transformations consisted of three components: a fluorophilic Lewis acid, a Lewis basic electron donor, and an organic substrate featuring a CF₃ functionality. Key factors permitting this reactivity were the incorporation of two of these three components within the same molecule, the use of rigorously dry, inert arene solvent PhF, and aryl groups bound to the CF₃ carbon atom to permit resonance stabilization of the [ArCF₂]⁺ intermediate.

6.4 Experimental Details

6.4.1 General

All preparations and manipulations were carried out under an anhydrous N₂ atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercially-available reagents such as 1,8-dibromonaphthalene, (2-bromophenyl)diphenylphosphine, (C₆F₅)₂PPh, (C₆F₅)₃P, PhCF₃, and PhCF₂H were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise. [Et₃Si(tol)][B(C₆F₅)₄]⁷¹ and C₆H₄(1-PPh₂)(2-SiHPH₂) 6-5² were prepared following procedures described in literature. (8-Trifluoromethylnaphthyl)diphenylphosphine 6-1 and (8-trifluoromethylnaphthyl)bis(pentafluorophenyl)fluorophosphine 6-2 were prepared as described in Chapter 5 of this thesis. CH₂Cl₂, n-pentane, and toluene were dried using an Innovative Technologies solvent purification system. C₆H₅F and CD₂Cl₂ (Aldrich) were degassed, distilled over CaH₂, then stored over 4 Å molecular sieves before use. C₆D₅Br (Aldrich) was degassed and stored over activated 4 Å molecular sieves before use. Reactions were monitored using multinuclear NMR spectroscopy. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian Agilent DD 2 500 MHz spectrometer, and Varian Agilent DD 2 600 MHz spectrometer. Data for ¹H NMR spectroscopy is reported as follows: chemical shift (δ ppm),
integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, dm = doublet of multiplets, b = broad), coupling constant (Hz). Data for $^{13}$C NMR is reported in terms of chemical shift ($\delta$ / ppm). High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (El), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART). Mass spectroscopy experiments were run for isolated products and reaction mixtures, however in some cases the high fragmentation of compounds or volatility did not allow for mass peak identification.

**X-ray Diffraction Studies.** Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) Data reduction was performed using the Bruker SMART$^{72}$ software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). Structure solutions were found with the SHELXS-97 package using the direct method and were refined with SHELXL-97$^{73}$ against $F^2$ using first isotropic and anisotropic thermal parameters for all non-hydrogen atoms.

**6.4.2 Syntheses of Compounds 6-3, 6-4, 6-7, 6-9, 6-10, 6-11, 6-12**

(8-difluoromethylnaphthyl)bis(pentafluorophenyl)triethylsilylphosphonium tetrakis(pentafluorophenyl)borate 6-2

To a solution of 6-1 (56.0 mg, 0.10 mmol) in bromobenzene (1 mL) 79.7 mg (0.90 equiv.) [Et$_3$Si(tol)][B(C$_6$F$_5$)$_4$] was added in several portions, with gentle shaking after each addition. Allowing the mixture to stand for several hours resulted in the formation of colourless crystals from the dark solution. The supernatant was decanted, and the crystals were washed with bromobenzene (1 x 0.5 mL) and pentane (2 x 0.5 mL) and dried in vacuo resulting in 6-4 in 88 % yield. $^1$H NMR (CD$_2$Cl$_2$, [ppm]): 0.90 (9H, t, CH$_2$CH$_3$, $^3$J$_{HH} = 7.1$ Hz ), 1.31 (6H, q, CH$_2$CH$_3$, $^3$J$_{HH} = 7.1$ Hz), 8.32 (1H, dt, HA, $^3$J$_{HH} = 7.4$ Hz, $^4$J$_{HH} = 2.1$ Hz), 8.33 (2H, d, HA, $^3$J$_{HH} = 7.6$ Hz), 8.40 (2H, m, HA), 8.52 (2H, m, HA), 9.56 (1H, s, Ar). $^{19}$F$[^1$H$]$ NMR
$^{13}$C{¹H} NMR (CD$_2$Cl$_2$, [ppm]): 89.2 (dt, CAr, $^2$J$_{PC}$ = 94 Hz, $^3$J$_{FC}$ = 18 Hz), 106.0 (d, CAr, $^1$J$_{FC}$ = 94 Hz), 127.8 (s, CAr), 128.1 (d, CAr, $^1$J$_{FC}$ = 9 Hz), 130.9 (d, $^1$J$_{PC}$ = 15 Hz, CAr), 130.9 (s, CAr), 132.3 (s, CAr) 134.5 (d, $^1$J$_{PC}$ = 2.0 Hz, CAr), 137.1 (overlapping dm, C$_6$F$_5$, $^1$J$_{FC}$ = 240 Hz), 137.3 (m, CAr), 139.0 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 244 Hz), 139.3 (d, $^1$J$_{PC}$ = 4 Hz, CAr), 140.0 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 264 Hz), 148.9 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 244 Hz), 149.8 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 263 Hz). Resonances for phosphorus- and boron-bound quaternary carbon atoms not observed. $^{19}$F{¹H} NMR (CD$_2$Cl$_2$, [ppm]): −84.7 (2F, dquin, $^2$J$_{FF}$ = 108 Hz, $^3$J$_{FF}$ = 7 Hz, C$F_2$), −124.0 (4F, m, o-F, P(C$_6$F$_5$)$_2$), −129.2 (2F, m, p-F, P(C$_6$F$_5$)$_2$), −133.5 (8F, m, o-F, B(C$_6$F$_5$)$_4$), −152.5 (4F, m, m-F, P(C$_6$F$_5$)$_2$), −164.0 (4F, m, p-F, B(C$_6$F$_5$)$_4$), −168.0 (8F, m, m-F, B(C$_6$F$_5$)$_4$) $^{31}$P{¹H} NMR (CD$_2$Cl$_2$, [ppm]): 11.5 (t, $^2$J$_{PF}$ = 108 Hz); Elemental Analysis for C$_{47}$H$_6$BF$_8$P: calcd.: C 46.3, H 0.5, found: C 46.0, H 0.5; DART MS: m/z 541.00106 for C$_{20}$H$_3$F$_3$Si cation (calcd.: 495.1879)

(8-difluoromethynaphthyl)bis(pentafluorophenyl)phosphonium
tetrakis(pentafluorophenyl)borate 6-4

To a solution of 6-2 (56.0 mg, 0.10 mmol) in bromobenzene (1 mL) 79.7 mg (0.90 equiv.) [SiEt$_3$(tol)][B(C$_6$F$_5$)$_4$] was added in several portions, with gentle shaking after each portion. Allowing the mixture to stand for several hours resulted in the formation of colourless crystals from the dark solution. The supernatant was decanted, and the crystals were washed with bromobenzene (1 x 0.5 mL) and pentane (2 x 0.5 mL) and dried in vacuo resulting in pure 6-4 in 91 % yield. X-ray-quality crystals were obtained from slow diffusion of pentane into a saturated solution of CH$_2$Cl$_2$ at −35 °C: $^1$H NMR (CD$_2$Cl$_2$, [ppm]): 8.09 (2H, m, H$_{Ar}$), 8.32 (1H, dt, H$_{Ar}$, $^3$J$_{HH}$ = 7.4 Hz, $^4$J$_{HH}$ = 2.1 Hz), 8.48 (1H, dm, H$_{Ar}$, $^3$J$_{HH}$ = 8.4 Hz), 8.54 (1H, ddd, H$_{Ar}$, $^3$J$_{PH}$ = 14.3 Hz, $^3$J$_{HH}$ = 7.6 Hz, $^4$J$_{HH}$ = 1.6 Hz), 8.68 (1H, ddd, H$_{Ar}$, $^3$J$_{HH}$ = 8.4 Hz, $^4$J$_{HH}$ = 2.3 Hz, $^4$J$_{HH}$ = 0.8 Hz). $^{13}$C{¹H} NMR (CD$_2$Cl$_2$, [ppm]): 89.2 (dt, CAr, $^2$J$_{PC}$ = 94 Hz, $^3$J$_{PC}$ = 18 Hz), 106.0 (d, CAr, $^1$J$_{FC}$ = 94 Hz), 127.8 (s, CAr), 128.1 (d, CAr, $^1$J$_{FC}$ = 9 Hz), 130.9 (d, $^1$J$_{PC}$ = 15 Hz, CAr), 130.9 (s, CAr), 132.3 (s, CAr) 134.5 (d, $^1$J$_{PC}$ = 2.0 Hz, CAr), 137.1 (overlapping dm, C$_6$F$_5$, $^1$J$_{FC}$ = 240 Hz), 137.3 (m, CAr), 139.0 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 244 Hz), 139.3 (d, $^1$J$_{PC}$ = 4 Hz, CAr), 140.0 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 264 Hz), 148.9 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 244 Hz), 149.8 (dm, C$_6$F$_5$, $^1$J$_{FC}$ = 263 Hz). Resonances for phosphorus- and boron-bound quaternary carbon atoms not observed. $^{19}$F{¹H} NMR (CD$_2$Cl$_2$, [ppm]): −84.7 (2F, dquin, $^2$J$_{FF}$ = 108 Hz, $^3$J$_{FF}$ = 7 Hz, C$F_2$), −124.0 (4F, m, o-F, P(C$_6$F$_5$)$_2$), −129.2 (2F, m, p-F, P(C$_6$F$_5$)$_2$), −133.5 (8F, m, o-F, B(C$_6$F$_5$)$_4$), −152.5 (4F, m, m-F, P(C$_6$F$_5$)$_2$), −164.0 (4F, m, p-F, B(C$_6$F$_5$)$_4$), −168.0 (8F, m, m-F, B(C$_6$F$_5$)$_4$) $^{31}$P{¹H} NMR (CD$_2$Cl$_2$, [ppm]): 11.5 (t, $^2$J$_{PF}$ = 108 Hz); Elemental Analysis for C$_{53}$H$_3$BF$_{23}$Si: calcd.: C 54.2, H 2.7, found: C 54.5, H 3.0; DART MS: m/z for C$_{20}$H$_3$F$_3$Si cation: (calcd.: 495.1879)
(2-(diphenylphosphino)diphenylsilyl)trimetontrakis(pentafluorophenyl)borate 6-6

\[
\begin{array}{c}
\text{Ph}_2\text{SiPh}_2 \\
\text{B(C}_6\text{F}_5)_4
\end{array}
\]

44.4 mg (0.10 mmol) 6-5 was dissolved in 1 mL toluene. 64.5 mg (0.070 mmol, 0.70 equiv.) [Ph$_3$C][B(C$_6$F$_5$)$_4$] was added portion-wise, with shaking, forming a yellow oil. The colourless supernatant was decanted from the yellow oil and the oil was washed with n-pentane (3 x 1 mL) and dried for one minute in vacuo, yielding 60.2 mg 6-6 as a colourless solid with slight impurities. $^1$H NMR (CD$_2$Cl$_2$, [ppm]): 6.99 (4H, m, Ph), 7.03 (4H, m, Ph), 7.15 (4H, dd, Ph, $^3$J$_{HH}$ = 7.5 Hz, $^3$J$_{HH}$ = 7.1 Hz), 7.20 (2H, dd, Ph, $^3$J$_{HH}$ = 8.3 Hz, $^3$J$_{HH}$ = 7.3 Hz), 7.30 (2H, dd, Ph, $^3$J$_{HH}$ = 8.3 Hz, $^3$J$_{HH}$ = 7.5 Hz), 7.36 (4H, d, Ph, $^3$J$_{HH}$ = 7.5 Hz) 7.44 (1H, dd, Ar, $^3$J$_{PH}$ = 9.3 Hz, $^3$J$_{HH}$ = 7.1 Hz); 7.50 (1H, ddd, Ar, $^3$J$_{HH}$ = 7.7 Hz, $^4$J$_{PH}$ = 4.1 Hz, $^4$J$_{HH}$ = 1.2 Hz); 7.56 (1H, ddd, Ar, $^3$J$_{HH}$ = 7.7 Hz, $^4$J$_{PH}$ = 4.1 Hz, $^4$J$_{HH}$ = 1.2 Hz), 7.63 (1H, d, Ar, $^3$J$_{HH}$ = 7.5 Hz). $^{19}$F($^1$H) NMR (CD$_2$Cl$_2$, [ppm]): -133.2 (8F, m, o-C$_6$F$_5$), -148.4 (1F, d, SiF, $^4$J$_{PF}$ = 5 Hz ), -163.9 (4F, m, p-C$_6$F$_5$), -168.0 (8F, m, m-C$_6$F$_5$). $^{29}$Si NMR (CD$_2$Cl$_2$): 13.0 $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, [ppm]): 11.5, s. $^{13}$C NMR data not reported as the presence of impurities precluded definitive peak assignments.

(2-(diphenylfluorosilyl)phenyl)diphenyl(difluorophenyl)phosphonium tetrakis(pentafluorophenyl)borate 6-7

\[
\begin{array}{c}
\text{Ph}_2\text{P} \\
\text{SiFPh}_2 \\
\text{B(C}_6\text{F}_5)_4
\end{array}
\]

To 112.2 mg (0.10 mmol) 6-6 was added a solution of 0.0146 mg (0.10 mmol) PhCF$_3$ in PhF (1.5 mL). The yellow solution was stirred for 24 hours. Analysis of the reaction mixture by quantitative $^{31}$P NMR revealed 52% conversion to 6-7. Volatiles were then removed and the solid mixture was then redissolved in THF for treatment with aqueous KOH for conversion to 6-8. Alternately, to isolate 6-7, the reaction mixture was loaded onto a small silica column and after washing with n-pentane and 1:1 DCM/n-pentane the product was eluted with reduced impurities with 80/20 DCM/n-pentane. This procedure was repeated twice, allowing for the isolation of 6-7 in 2% yield after removal of volatiles in vacuo. $^1$H NMR (CD$_2$Cl$_2$, [ppm]):
6.66 (1H, d, Ph, $^3J_{HH} = 7.9$ Hz); 6.84 (1H, dm, Ph, $^3J_{HH} = 8.1$ Hz); 6.91 (1H, dm, Ph, $^3J_{HH} = 7.7$ Hz); 6.99 (2H, dm, Ph, $^3J_{HH} = 7.1$ Hz); 7.20 (1H, t, Ph, $^3J_{HH} = 7.3$ Hz); 7.25 (3H, t, Ph, $^3J_{HH} = 7.7$ Hz); 7.31 (3H, t, Ph, $^3J_{HH} = 7.7$ Hz); 7.43-7.48 (7H, m, Ph); 7.61 (1H, t, Ph, $^3J_{HH} = 7.7$ Hz); 7.20 (1H, t, Ph, $^3J_{HH} = 7.3$ Hz); 7.70 (2H, m, Ph); 7.90 (1H, m, Ph); 7.99 (1H, tdd, Ph, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 2.4$ Hz, $^4J_{HH} = 1.2$ Hz); 8.05 (1H, tdd, Ph, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 3.5$ Hz, $^4J_{HH} = 1.6$ Hz); 8.88 (1H, dd, Ph, $^3J_{HH} = 12.7$ Hz, $^3J_{HH} = 7.8$ Hz). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, [ppm]): 129.1 (s, Ph); 129.6 (d, Ph, $^3J_{PC} = 2$ Hz); 130.4 (d, Ph, $^3J_{PC} = 16$ Hz); 130.7 (d, Ph, $^3J_{PC} = 13$ Hz); 132.5 (s, Ph); 135.0 (d, Ph, $^3J_{PC} = 1.5$ Hz); 135.6 (d, Ph, $^3J_{PC} = 10$ Hz); 137.4 (d, Ph, $J = 1.7$ Hz). Due to the low isolated yield a partial $^{13}$C($^1$H) NMR spectrum is reported. $^{19}$F($^1$H) NMR (CD$_2$Cl$_2$, [ppm]): –94.2 (2F, d, CF$_2$ $^2J_{PF} = 104$ Hz); –133.2 (8F, m, o-C$_6$F$_5$), –148.4 (1F, d, SiF, $^4J_{PF} = 5$ Hz), –163.9 (4F, m, p-C$_6$F$_5$), –168.0 (8F, m, m-C$_6$F$_5$). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, [ppm]): 23.8 (td, $^2J_{PF} = 104$ Hz, $^4J_{PF} = 5$ Hz). DART MS: m/z 589.1723 for C$_{37}$H$_{29}$F$_3$PS$^+$ cation (calcd.: 589.1723)

**α,α-difluoromethylbenzene 6-8**

![α,α-difluoromethylbenzene 6-8](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.69$ (1H, t, CF$_2$H, $^2J_{FH} = 56$ Hz); 7.21 (2H, m, Ph); 7.46-7.56 (3H, m, Ph). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta = 115.1$ (t, CF$_2$H, $^1J_{FC} = 239$ Hz); 125.9 (t, Ph, $^4J_{FC} = 6$ Hz); 129.0 (t, Ph, $^2J_{FC} = 51$ Hz); 130.1 (t, Ph, $^4J_{FC} = 2$ Hz); 134.7 (t, Ph, $^3J_{FC} = 22$ Hz). $^{19}$F NMR (400 MHz, CDCl$_3$): –110.6 (d, $^2J_{FH} = 56$ Hz)

**fluoromethylbenzene 6-10**

![fluoromethylbenzene 6-10](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.32$ (2H, d, CH$_2$F, $^2J_{FH} = 49$ Hz); 7.20-7.37 (5H, m, Ph). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta = 84.5$ (d, CH$_2$F, $^1J_{FC} = 165$ Hz); 127.7 (d, Ph, $^3J_{FC} = 5$ Hz); 128.5 (s, Ph); 128.8 (d, Ph, $^4J_{CF} = 4$ Hz); 135.5 (d, Ph, $^2J_{CF} = 17$ Hz). $^{19}$F NMR (400 MHz, CDCl$_3$): –204.1 (t, $^2J_{FH} = 49$ Hz)
diphenylfluoromethane 6-12

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta = 6.50 (1\text{H, d, Ph}_2\text{CHF, }^2J_{\text{FH}} = 49 \text{ Hz}); 7.25-7.35 \\
(5\text{H, m, Ph}). & \text{ 13C NMR (126 MHz, CD}_2\text{Cl}_2\text{): } \delta = 84.5 (\text{d, CH}_2\text{F, }^1J_{\text{FC}} = 165 \text{ Hz}); 127.7 (\text{d, Ph, }^3J_{\text{FC}} = 5 \text{ Hz}); 128.5 (\text{s, Ph}); 128.8 (\text{d, Ph, }^4J_{\text{CF}} = 4 \text{ Hz}); 135.5 (\text{d, Ph, }^2J_{\text{CF}} = 17 \text{ Hz}). \\
\text{19F NMR (400 MHz, CDCl}_3\text{): } & -168.0 (\text{d, }^2J_{\text{FH}} = 48 \text{ Hz})
\end{align*}
\]
Table 6.1 Crystallographic data and details of the structure refinement of compounds 6-4

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References


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Chapter 7

Conclusions and Future Work

7.1 Thesis Summary

The work presented in the preceding chapters detailed the synthesis of both main group Lewis acids and frustrated Lewis pair complexes. Activations of C=O and C-F bonds were the primary targets of these Lewis acids and FLP systems. In the course of this research, boron, silicon and phosphorus Lewis acids were explored. In FLP contexts, the boron and silicon Lewis acids were combined with nitrogen and phosphorus Lewis bases, respectively.

While the initial investigations of phosphinimine- and phosphine-amine-ligated P-N-B-type boron Lewis acids did not prove active in FLP bond activations, analysis of spectroscopic and solid-state parameters indicated that tailoring substituents at the boron, phosphorus and nitrogen atoms did fine-tune the electronic environment at the boron atom. Generally, FLP activations utilizing boron Lewis acids require strongly electrophilic boranes featuring either formal positive charges or strongly electron-withdrawing substituents. P-N-B frameworks incorporating positive charges were synthesized but still did not react with small molecules such as CO2 or H2, indicating that π-donation from the adjacent nitrogen atom quenched the Lewis acidity of the boron centre sufficiently to preclude challenging bond activations. Research carried out concurrently in the Stephan group demonstrated that weak Lewis bases such as Et2O could effect H2 activation in combination with the strong Lewis acid B(C6F5)3,\(^1\) while research in the Krempner group has demonstrated that the inverse is possible,\(^2\) with very strong Lewis bases in combination with weakly Lewis acidic boranes such as BPh3 capable of H2 activation.

Investigations of new electrophilic phosphonium cation (EPC) frameworks resulted in two new types of EPC, reported in chapters 3 and 4 of this thesis. As initial cationic and dicationic EPCs featured a P-F bond, it was desired to explore the utility of EPC catalysts without P-F bonds. This required new routes of oxidation of P(III) to P(V). It was demonstrated in chapter 3 that SO2Cl2 is a suitable oxidizing agent for conversion of phosphonium cations [Ph2P(SIMes)] to the
corresponding dichlorophosphorane and subsequently to EPC dication [Ph₂PCl(SIMes)]. The bis-
[B(C₆F₅)₄] salt of this dication proved capable of carrying out catalysis with similar effectiveness
to its fluorophosphonium analogue [Ph₂PF(SIMes)][B(C₆F₅)₄]. Subsequent EPCs featuring
chloride, bromide, phenoxy and siloxy substituents instead of fluoride have since been synthesized.
The derivation of EPCs from commercially-available ferrocenylphosphine ligands, presented in
chapter 4, presented another avenue of diversification of EPC architectures. Though these
fluorophosphonium derivatives were competent catalysts, they were less active than the optimal
cationic and dicationic EPCs.

An interest in the mechanistic aspects of EPC catalysis led to the targeting of 1,8-disubstituted
naphthyl compounds in which a cationic phosphonium centre was in close proximity to a silane or
trifluoromethyl functionality. The use of the “turbo-Grignard” reagent iPrMgCl*LiCl permitted
selective C-Br or C-I monosubstitution of 1,8-dihalonaphthalene compounds, allowing
asymmetrically-substituted naphthalenes to be accessed in good yields. However, the Si-H bonds
of the silyl functionalities proved intolerant of XeF₂ used in the oxidation of the phosphine centre
to the difluorophosphorane, resulting in silyl fluoride. Accessing phosphonium cations via the use
of electrophilic fluorine sources also proved unsuccessful. Installation of a CF₃ functionality
through protocols developed by Hartwig³ permitted the synthesis of a naphthyl CF₃-substituted
phosphonium cation. Natural Bond Order (NBO) calculations and analysis using the Quantum
Theory of Atoms in Molecules (QTAIM) corroborated indications in the solid-state structure and
solution NMR spectroscopic analysis suggesting an interaction between a fluorine atom on the CF₃
unit and the phosphonium centre. This compound presents a unique example of a modelled
intermediate along a phosphonium cation-mediated C-F bond activation.

In chapter 6 it was demonstrated that silylium cation-phosphine FLPs could selectively activate a
single C-F bond in aryl-CF₃ compounds. In the case of abstraction of fluoride ion from PhCF₃ by
an intramolecular silylium cation-phosphine FLP, the P-C bond resulting from trapping of PhCF₂⁺
cation by the phosphine Lewis base could be cleaved under aqueous Bronsted basic conditions,
completing a formal mono-hydrodefluorination process of PhCF₃ to PhCF₂H. Lower yields of the
corresponding conversion of PhCF₂H to PhCH₂F were obtained, demonstrating a step-wise
hydrodefluorination process.
### 7.2 Future Work

The selective removal of a single fluoride ion from a CF₃ functionality is a very rare transformation. Although reductive processes of fluorine atom substitution using superstoichiometric amounts of metal reagents are known to convert CF₃ functionalities to CF₂, these occur in specific cases where the CF₃ group is adjacent to π-accepting groups. Only very recently was a report of reasonably efficient single-fluoride ion abstraction from CF₃ published.⁴ In that case, aryl-CF₃ molecules were converted to aryl-CF₂-arenes.

Because an abundance of pharmaceutical active ingredients bear CF₃ functionalities, the ability to selectively functionalize these C-F bonds could be of significant utility. Given the proliferation of isolable silylium cations described over the past two decades, including those capable of activating aliphatic C-F bonds, it seems achievable to design a stable silylium cation with a fluorophilicity great enough to activate C-F bonds with a proximal Lewis basic donor to capture a transient [R-CF₂]⁺ cation before reaction with solvent or other reagents.

Using phosphines as the Lewis base donor to capture [R-CF₂]⁺ has two significant advantages: the P-CF₂R functionality presents unambiguous evidence of its formation in ³¹P and ¹⁹F NMR spectra, and generally P-CF₂ bonds can be expected to have high apicophilicity,⁵,⁶ and thus can be readily cleaved to permit further functionalization. Continued efforts in this area should also be directed towards C-CF₂ bond formation, rather than simply hydrodefluorination. This type of C-C bond formation has already been demonstrated, and could be attempted using the protocols described by Zhang.⁷ Nonetheless, using different Lewis base donors such as nitrogen or group 16 atoms such as oxygen and sulfur is also an area worthy of investigation. Formation of N-CF₂, O-CF₂ or S-CF₂ bonds would broaden the range of RCF₃ functionalizations and permit investigation of methods to cleave these types of bonds as well.

In addition to silylium cations, EPCs have been demonstrated to activate aliphatic C-F bonds, suggesting that strongly fluorophilic phosphonium cations could also be used as Lewis acids in selective C-F bond activations. Incorporation of an electrophilic phosphonium cationic centre in close proximity to a phosphine Lewis base to form a phosphonium cation-phosphine FLP, in analogy to the silylium cation-phosphine FLP developed in chapter 6, could be investigated (Scheme 7.1). It also seems conceivable that selective C-F bond activations of CF₃ functionalities
will be achieved catalytically, although it is not apparent to the author of this thesis how this might be achieved.

Scheme 7.1 Potential C-F bond activation by a phosphonium cation-phosphine FLP.

In studying the mechanisms of EPC-mediated catalytic C=O and C-F bond activations, further avenues toward the elusive Si-H-P-type adducts of phosphonium cations are possible. Targeting a phosphonium cation without a P-F functionality would preclude the need for XeF$_2$ as an oxidation agent, avoiding the conversion of Si-H to thermodynamically inert Si-F species. In addition, isolation of phosphoranes of type R$_4$PH or R$_3$PHX and studying their stability and stoichiometric reactivity would allow researchers to study more precisely how these species react during catalysis. While targeting EPCs of type R$_3$PHX has thus far been unsuccessful, a wide range of potential substituents of these type of compounds has not been investigated. Calculations and further synthetic investigations can be undertaken to discern why such phosphoranes are often unstable and to assist in ascertaining which phosphoranes would be stable enough to be isolated and reactive enough to study as models of catalytic intermediates.
References


