Electrophilic Phosphenium and Phosphonium Cations: Synthesis and Reactivity of Perfluoro- & Perchloroaryl Phosphorus Systems

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
Department of Chemistry
University of Toronto

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Abstract
Electrophilic phosphonium cations (EPCs) have shown great promise in Lewis acid catalysis typically only mediated by transition metals. The application of EPCs as catalysts has been limited by their air and moisture intolerance, leading to catalyst degradation. Bulkier perchlorinated-aryl substituents (C₆Cl₅) have been previously incorporated into electrophilic boranes yielding compounds with increased stability to air and moisture as compared with their perfluorinated-aryl (C₆F₅) substituted counterparts. In this work, the synthesis of C₆Cl₅-substituted EPCs is described and the Lewis acidity and air stability of these compounds is tested, demonstrating that C₆Cl₅ incorporation is a viable approach to air-stability. Moreover, the capacity of some of these EPCs to act as frustrated Lewis pairs (FLPs) with weak or strong Lewis bases towards the activation of H₂ or CO₂ is probed. The development of a highly electrophilic N-heterocyclic carbene (NHC)-stabilized phosphenium cation and its performance as a Lewis acid catalyst is also described.
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# Table of Contents

Abstract ........................................................................................................................... ii
Acknowledgments ........................................................................................................... iii
Table of Contents ............................................................................................................. v
List of Figures ................................................................................................................... vii
List of Schemes ................................................................................................................. ix
List of Tables ..................................................................................................................... x
List of Symbols and Abbreviations ................................................................................... xi

Chapter 1 Introduction ....................................................................................................... 1

1.1 Frustrated Lewis Pair (FLP) Chemistry ................................................................. 1
  1.1.1 Discovery of Frustrated Lewis Pairs ................................................................. 1
  1.1.2 Reactivity of Frustrated Lewis Pairs ................................................................. 2

1.2 Electrophilic Phosphonium Cation (EPC) Chemistry ............................................. 5
  1.2.1 Reactivity of Phosphonium Cations ................................................................. 5
  1.2.2 Reactivity of EPCs ......................................................................................... 5

1.3 Scope of Thesis .......................................................................................................... 12

Chapter 2 Perchlorinated Phosphonium Cations .......................................................... 13

2.1 Introduction .............................................................................................................. 13

2.2 Results and Discussion ........................................................................................... 16
  2.2.1 Synthesis of Pentachlorophenyl-Substituted Phosphines - Observations and
       Trends .................................................................................................................... 16
  2.2.2 Synthesis of Pentachlorophenyl-Substituted Phosphoranes ......................... 23
  2.2.3 Synthesis of Pentachlorophenyl-Substituted Phosphonium Cations ............ 27
  2.2.4 Lewis Acidity Testing and Catalytic Reactivity ............................................. 32
2.2.5 Reactivity towards Small Molecules .......................................................... 38

2.3 Conclusions .................................................................................................. 40

2.4 Experimental Section .................................................................................. 41
    2.4.1 General considerations ........................................................................... 41
    2.4.2 Synthesis of Compounds ...................................................................... 42
    2.4.3 Reactions of Pentachlorophenyl-Substituted Phosphonium Cations ........ 57
    2.4.4 Collection, Reduction, Solution, and Refinement of X-Ray Data .......... 59

Chapter 3 Phosphonium Cations ......................................................................... 62
    3.1 Introduction .................................................................................................. 62
    3.2 Results and Discussion .............................................................................. 64
        3.2.1 Synthesis of Electrophilic Phosphonium Cations ............................... 64
        3.2.2 Reactivity of Phosphonium Cations .................................................. 70
    3.3 Conclusions ................................................................................................ 75

Chapter 4 Conclusions ....................................................................................... 85
    4.1 Thesis Summary .......................................................................................... 85
    4.2 Future Work ................................................................................................ 87

References ............................................................................................................ 88
List of Figures

**Figure 1.1.1.** Frontier molecular orbital depictions of a) classical Lewis acid-base adduct and b) frustrated Lewis acid-base pair ................................................................. 2

**Figure 1.2.1.** Examples of electrophilic phosphonium cations ........................................ 6

**Figure 2.1.1.** Representation of the Gutmann Beckett (left) and Child’s (right) methods of measuring Lewis acidity ................................................................................................ 14

**Figure 2.2.1.** POV-ray depiction of 2-1; C: black, P: orange, Cl: green, H-atoms omitted for clarity .................................................................................................................. 17

**Figure 2.2.2.** POV-ray depiction of decachlorobiphenyl; C: black, Cl: green ................. 18

**Figure 2.2.3.** POV-ray depiction of 1,1,2,2-tetrakis(perchlorophenyl)diphosphine; C: black, P: orange, Cl: green ................................................................................. 18

**Figure 2.2.4** POV-Ray depiction of 2-4. P: orange, Cl: green, C: black, F: pink .............. 20

**Figure 2.2.5** POV-Ray depiction of 2-5. P: orange, Cl: green, C: black, F: pink ............ 20

**Figure 2.2.6.** Stacked $^3^1$P{$^1$H} NMR spectra of various aryl-substituted phosphines in CH$_2$Cl$_2$ 22

**Figure 2.2.7** POV-Ray depiction of 2-6. P: orange, Cl: green, C: black, F: pink, H-atoms omitted for clarity .......................................................... 24

**Figure 2.2.8** POV-Ray depiction of 2-9. P: orange, Cl: green, C: black, F: pink .............. 26

**Figure 2.2.9.** VT $^{19}$F NMR studies on compound 2-9 .................................................. 27

**Figure 2.2.10** POV-Ray depiction of 2-11. P: orange, Cl: green, C: black, F: pink, [B(C$_6$F$_5$)$_4$]$^-$ counter-anion omitted for clarity ................................................................................. 28

**Figure 2.2.11.** VT $^{19}$F NMR studies on compound 2-12 .................................................. 29

**Figure 2.2.12.** $^{19}$F-$^{19}$F COSY NMR spectrum of compound 2-12 .............................. 30
Figure 2.2.13  POV–Ray depiction of 2-13. P: orange, Cl: green, C: black, F: pink, [B(C₆F₅)₄] counter-anion omitted for clarity ................................................................. 31

Figure 2.2.14 – Phosphonium Lewis acid catalysts 2-10 – 2-13 ................................................................. 33

Figure 2.2.15 – stacked ³¹P{¹H} spectra showcasing the onset of hydrolysis for 2-10 .................. 38

Figure 3.1.1. Representation of phosphonium cation 3p orbitals and lone pair (left and middle) and singlet state carbene 2p orbitals and lone pair (right) ................................................................. 62

Figure 3.1.2 Representation of N-heterocyclic phosphonium cations (NHPs) and N-heterocyclic carbenes (NHCs) ........................................................................................................... 63

Figure 3.2.1.  POV-ray depictions of 3-1; C: black, P: orange, F: pink, N: blue, Br: red, H-atoms omitted for clarity .................................................................................................................. 65

Figure 3.2.2. VT ¹⁹F{¹H} NMR studies on compound 3-1 ................................................................. 66

Figure 3.2.3. VT ³¹P{¹H} NMR studies on compound 3-1 ................................................................. 67

Figure 3.2.4. VT ¹⁹F{¹H} NMR studies on compound 3-2 ................................................................. 69

Figure 3.2.5. VT ¹H NMR studies on compound 3-2 ................................................................. 70

Figure 3.2.6. Representation of the HOMO of 3-2 ............................................................................. 73

Figure 3.2.7. Representation of the LUMO of 3-2 ............................................................................. 74

Figure 3.2.8. Representation of the LUMO + 1 of 3-2 ............................................................................. 74
## List of Schemes

| Scheme 1.1.1. | Reactivity of 2,6-lutidine with BF$_3$ or BMe$_3$ | 2 |
| Scheme 1.1.2. | The first reversible H$_2$ activation by an FLP | 3 |
| Scheme 1.1.3. | Examples of small molecule activation by FLPs composed of bulky phosphines and Lewis acidic boranes | 4 |
| Scheme 1.2.1. | Synthesis of halophosphonium cations | 6 |
| Scheme 1.2.2. | Hydrosilylation and hydrodeoxygenation reaction mechanisms | 8 |
| Scheme 1.2.3. | Hydrodefluorination reaction mechanism | 9 |
| Scheme 1.2.4. | Dehydrocoupling and transfer hydrogenation reaction mechanisms | 10 |
| Scheme 1.2.5. | Friedel-Crafts reactivity mechanisms | 11 |
| Scheme 2.1.1. | Reversible coordination of H$_2$O to B(C$_6$Cl$_5$)(C$_6$F$_5$)$_2$ | 14 |
| Scheme 2.1.2. | Splitting of H$_2$ by B(C$_6$Cl$_5$)(C$_6$F$_5$)$_2$ and TMP | 15 |
| Scheme 2.1.3. | Reversible H$_2$ activation by B(C$_6$Cl$_5$)(C$_6$F$_5$)$_2$ in THF | 15 |
| Scheme 2.2.1. | General synthetic approach to yield phosphonium cations with the C$_6$Cl$_5$ group | 16 |
| Scheme 2.2.2. | Syntheses of C$_6$Cl$_5$ containing phosphines, phosphoranes, and phosphonium cations | 23 |
| Scheme 3.2.1 | Synthesis of SIMes-stabilized phosphenium cation | 65 |
| Scheme 3.2.2 | Synthesis of IDipp-stabilized phosphenium cation 3-1 | 65 |
| Scheme 3.2.3 | Counter-anion exchange reaction affording 3-2 | 68 |
List of Tables

Table 2.2.1: Sum of angles around P of selected compounds .......................................................... 21

Table 2.2.2: Summary of select bond lengths and angles of interest .............................................. 32

Table 2.2.3: Summary of Catalytic Activity ................................................................................... 37

Table 2.4.1: Crystallographic data for compounds 2-1, 2-4, 2-5, and 2-6 ........................................ 60

Table 2.4.2: Crystallographic data for compounds, 2-9, 2-11, Perchlorobiphenyl, and 1,1,2,2-tetrakis(perchlorophenyl)diphosphine .......................................................... 61

Table 3.2.1: Summary of Catalytic Activity ................................................................................... 72

Table 3.4.1: Crystallographic Data for Compound 3-1 .................................................................. 84
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
</tr>
</thead>
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<tr>
<td>Å</td>
<td>ångstrom, $10^{10}$ m</td>
</tr>
<tr>
<td>Anal.</td>
<td>analysis</td>
</tr>
<tr>
<td>Atm.</td>
<td>atmosphere</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>Calcd.</td>
<td>calculated</td>
</tr>
<tr>
<td>COSY</td>
<td>correlational spectroscopy</td>
</tr>
<tr>
<td>Cryst.</td>
<td>crystal</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
<tr>
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<td>degrees</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>DART</td>
<td>direct analysis in real time</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>dd</td>
<td>doublet of doublets</td>
</tr>
<tr>
<td>Dipp</td>
<td>diisopropylphenyl</td>
</tr>
<tr>
<td>dt</td>
<td>doublet of triplets</td>
</tr>
<tr>
<td>eq.</td>
<td>equivalent(s)</td>
</tr>
<tr>
<td>EPC</td>
<td>electrophilic phosphonium cation</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>et al.</td>
<td><em>et alia</em> (and others)</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>F. C.</td>
<td>Friedel-Crafts</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>FLP</td>
<td>frustrated Lewis pair</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>GOOF</td>
<td>goodness of fit</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>HMBC</td>
<td>heteronuclear multiple bond correlation</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectroscopy</td>
</tr>
<tr>
<td>HSQC</td>
<td>heteronuclear single quantum correlation</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>IDipp</td>
<td>1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene</td>
</tr>
<tr>
<td>$^nJ_{xy}$</td>
<td>n-scalar coupling constant between X and Y atoms (Hz)</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>meta</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>M</td>
<td>molar concentration</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Mes</td>
<td>mesityl, 2,4,6-trimethylphenyl</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>$\mu$L</td>
<td>microliter</td>
</tr>
<tr>
<td>$\mu$mol</td>
<td>micromole</td>
</tr>
<tr>
<td>mg</td>
<td>milligram</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>mL</td>
<td>milliliter</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole</td>
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</tbody>
</table>
MS  mass spectroscopy
M.S.  molecular sieves
NHC  \emph{N}-heterocyclic carbene
NHP  \emph{N}-heterocyclic phosphenium
NMR  nuclear magnetic resonance
\( o \)  \emph{ortho}
OTf  trifluoromethanesulfonate; triflate = [CF\(_3\)SO\(_3\)]\(^-\)
\( \pi \)  \emph{pi}
\( p \)  \emph{para}
POV-Ray  Persistence of Vision Raytracer
Ph  phenyl
ppm  parts per million, \( 10^6 \)
\( \{^1\text{H}\} \)  proton decoupled
q  quartet
quint  quintet
r.t.  room temperature
\( \sigma \)  \emph{sigma}
\( \sigma^* \)  \emph{sigma antibonding (orbital)}
s  singlet
SIMes  1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene
syst.  system
t  triplet
\('t\)Bu  \emph{tert}-butyl
THF  tetrahydrofuran
TMP  2,2,6,6-tetramethylpiperidine
TMS  trimethylsilyl
tol  toluene
VT  variable temperature
Wt.  weight
Chapter 1
Introduction

1.1 Frustrated Lewis Pair (FLP) Chemistry

1.1.1 Discovery of Frustrated Lewis Pairs

One hundred years ago, Gilbert Lewis published his seminal work entitled ‘The Atom and the Molecule’. Therein he described the dative bond as a sharing of electrons between one atom that can donate a pair of electrons and one atom that can accept the pair, later defined as Lewis bases and acids, respectively.\(^1\,^2\) Generally, the combination of Lewis acids and bases generates what is known as a classical Lewis acid-base adduct. Ammonia borane \(\text{H}_3\text{N-BH}_3\) serves as a prototypical example of such an adduct, with ammonia’s lone pair of electrons residing in the highest occupied molecular orbital (HOMO) being donated to the borane’s lowest unoccupied molecular orbital (LUMO) – the vacant p-orbital – creating the bond. Formation of the adduct serves to quench the reactivity of the Lewis acid and base, and forms a more stable complex with a lower energy HOMO (Figure 1.1.1a).\(^3\)

The first reported exception to Lewis’ classical model came in 1942 from H. C. Brown \(et\ al\), when the reaction between 2,6-lutidine and \(\text{BMe}_3\) did not yield the expected adduct.\(^4\) However, when the less sterically-hindered Lewis acid \(\text{BF}_3\) was tested in the same reaction with 2,6-lutidine, a donor-acceptor adduct did form (Scheme 1.1.1). The preclusion of adduct formation was attributed to the steric hindrance the methyl substituents imparted on the boron and nitrogen centres. A few other isolated examples of exceptions to Lewis’ concept were observed and reported throughout the 20\(^{th}\) century.\(^5\,^6\) Since the early 21\(^{st}\) century, these exceptions have been investigated more carefully, culminating in the articulation of these phenomena as frustrated Lewis pair (FLP) chemistry by Stephan and coworkers.\(^7\,^9\) These were so named due to the antagonistic nature of the unquenched basic and acidic components of the pair, a result of the steric demands which prohibit classical adduct formation. The unquenched HOMO and LUMO of these Lewis bases and acids, respectively (Figure 1.1.1b), can be exploited for non-classical reactivity discussed in Section 1.1.2.
1.1.2 Reactivity of Frustrated Lewis Pairs

The breakthrough in the field of FLPs came in 2006 when Stephan and coworkers reported the heterolytic cleavage of H₂ by the linked phosphino-borane species Mes₂P(C₆F₄)B(C₆F₅)₂, affording the zwitterionic salt Mes₂PH(C₆F₄)BH(C₆F₅)₂ as the product.¹⁰ This salt was shown to effect the release of hydrogen gas at temperatures above 100 °C, representing the first example of metal-free reversible hydrogen activation. (Scheme 1.1.2). More FLP systems capable of activating H₂ have since been developed, notably intramolecular variants employing B(C₆F₅)₃ with sterically-encumbered phosphines.⁸,⁹,¹¹-¹³
Two proposed mechanisms for this dihydrogen activation come from the theoretical studies performed by Pápai\textsuperscript{14-16} and Grimme\textsuperscript{17} on the FLP system comprising of $^t$Bu$_3$P and B(C$_6$F$_5$)$_3$ as the Lewis base and acid, respectively. Both groups suggest that the H$_2$ molecule is initially polarized in an ‘encounter complex’ which entails the generation of a cavity between the proximal P and B central atoms that are sterically-precluded from forming an adduct. In the case of the electron transfer model proposed by Pápai,\textsuperscript{18} the donation of electron density from the H$_2$ $\sigma$ bond into a vacant orbital of the Lewis acid occurs in conjunction with electron donation from the Lewis base into the $\sigma$H$_2^*$ resulting in H$_2$ bond cleavage. This is contrasted with Grimme’s proposed electric field model in which H$_2$ is activated through the action of a sufficiently strong electrical field formed by the FLP encounter complex. Interpretation of Grimme’s model is somewhat challenging due to lack of consideration of orbitals or electron transfer. Indeed these models are not limited solely to the activation of dihydrogen, but encompass other small molecules that FLPs have been reported to activate. FLPs have proven themselves very versatile in both form and function, and have been reported to activate small molecules such as CO$_2$,\textsuperscript{19-24} SO$_2$,\textsuperscript{25} N$_2$O,\textsuperscript{26} NO,\textsuperscript{27} CO,\textsuperscript{28, 29} alkenes,\textsuperscript{30-32} disulfides,\textsuperscript{33, 34} and alkynes\textsuperscript{35-38} (Scheme 1.1.3)

Notably, the ability of FLPs to activate H$_2$ prompted the research of catalytic and stoichiometric hydrogenation reactions of a myriad of organic substrates with a wide range of functional groups.\textsuperscript{39-41} In 2012, our group has also demonstrated that tunable NHC-stabilized borenium salts were able to affect the hydrogenation of imines, circumventing the need to employ the highly electrophilic C$_6$F$_5$ groups and boron Lewis acids such as B(C$_6$F$_5$)$_3$.\textsuperscript{42}

It is worth noting that some reported examples demonstrate that reversible weak Lewis acid-base adducts can behave similarly to FLPs upon dissociation of the acid-base adduct.\textsuperscript{36, 43} As well, some systems that activate H$_2$ in the enzyme family of hydrogenases have been described as FLP-like,\textsuperscript{44} demonstrating that strict preclusion of adduct formation is not a necessity for FLP reactivity.
Scheme 1.1.3. Examples of small molecule activation by FLPs composed of bulky phosphines and Lewis acidic boranes
1.2 Electrophilic Phosphonium Cation (EPC) Chemistry

1.2.1 Reactivity of Phosphonium Cations

Expansion of FLP chemistry to also include group 15-based Lewis acids is of recent interest in our group. Phosphonium salts are cationic tetracoordinate P(V) species that can exhibit Lewis acidic properties when possessing electrophilic substituents. Unlike in the case of electronically unsaturated boranes which derive their Lewis acidity from a vacant p-orbital, phosphonium cations are electronically saturated and derive their Lewis acidity from a low lying σ* orbital oriented opposite an electron-withdrawing group.\(^45\)

In the past, such phosphonium cations have found use as cocatalysts in Diels-Alder reactions\(^46\) by increasing the reactivity of the dienophile through coordination, have aided in various additions to polar unsaturated compounds,\(^47\) and are the key component in the classic alkene-forming Wittig reaction with aldehydes or ketones.\(^48\) Another catalytic example is the cyanosilylation of aldehydes\(^49\) and ketones\(^50\) reported by the Plumet and Tian groups, respectively.

1.2.2 Reactivity of EPCs

In 2013, our group published the synthesis of the highly electrophilic fluorophosphonium salt \([\text{FP(C}_6\text{F}_5)_3][\text{B(C}_6\text{F}_5)_4]\), and demonstrated its facile hydrodefluorination of fluoroalkanes.\(^51\) Since then, other EPC architectures have been developed (\textbf{Figure 1.2.1}), exploiting either highly electron withdrawing substituents or additional positively charged centres to lower the σ* orbital and enhance Lewis acidity.\(^51\)-\(^57\)

A noteworthy example is the extremely reactive SIMes-based dication seen in the bottom left of \textbf{Figure 1.2.1} which served as motivation for the development of other NHC-stabilized phosphonium and phosphonium cations discussed in \textbf{Chapter 3}.\(^51\)-\(^57\)
Figure 1.2.1. Examples of electrophilic phosphonium cations

The syntheses of the halophosphonium salts \([X \text{P(C}_6\text{F}_5)_3][\text{B(C}_6\text{F}_5)_4]\), \(X = \text{F, Cl, Br}\) proceeds via oxidation of the commercially available phosphine \(\text{P(C}_6\text{F}_5)_3\) with \(\text{XeF}_2\), \(\text{SO}_2\text{Cl}_2\), or \(\text{Br}_2\), and is followed by halide abstraction with \([\text{Et}_3\text{Si}][\text{B(C}_6\text{F}_5)_4]\) to yield the corresponding fluoro-, chloro-, or bromophosphonium cation (Scheme 1.2.1).

Scheme 1.2.1. Synthesis of halophosphonium cations

A report from our lab in 2015 has shown that the reactivity trend based on rates of catalysis in the hydrosilylation of ketones, imines, nitriles, and olefins using these halophosphonium cation catalysts is the following: \([\text{FP(C}_6\text{F}_5)_3]^+ > [\text{BrP(C}_6\text{F}_5)_3]^+ > [\text{ClP(C}_6\text{F}_5)_3]^+\), with the bromo and chlorophosphonium salts requiring higher temperatures and longer conversion times.\(^{57}\) Computational studies suggest that despite the higher electronegativity of Cl, \([\text{BrP(C}_6\text{F}_5)_3]^+\) has
the higher hydride affinity. It was postulated that this is due to electron back-donation along the shorter P-Cl bond into the 3d orbitals of the P centre, resulting in a less Lewis acidic system,\textsuperscript{57} although the role of putative d-orbitals on phosphorus is disputed. This result suggested that fluoride is the superior halide of choice for the formation of highly reactive Lewis acidic EPCs, and is prominent in much of EPC architecture (Figure 1.2.1). The computed mechanism for the hydrosilylation reaction involves activation of the Si-H bond through a cooperative ‘FLP’ type interaction between the substrate and the catalyst, and the silane and the catalyst, both interactions dissociating freely at room temperature.\textsuperscript{57} This generates a hypervalent silicon species alongside a transient carbocation followed by simultaneous transfer of hydride to the P centre, and carbonyl binding to the Si centre, forming a fluorophosphorane and another carbocation. This carbocation then abstracts the hydride from the phosphorane to afford the hydrosilylated product and regenerate the catalyst (Scheme 1.2.2).\textsuperscript{57} Hydrosilylation of alkynes has also been reported previously by our group.\textsuperscript{58}

This hydrosilylation mechanism is thought to be analogous to that proposed for B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} by Oestreich and coworkers\textsuperscript{59} who elucidated the mechanism building on prior work done by Piers \textit{et al.}\textsuperscript{60}

The highly electrophilic phosphonium salt [FP(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}], has found use as a catalyst in a variety of other reactions. Hydrodeoxygenation of ketones to form silyl ethers and alkanes is also reported with the catalyst. As in the case of hydrosilylation, the Si-H bond of the silane is once again activated to generate a hypervalent silicon species and a phosphorane, with substrate binding to generate a carbocation that can react with a second equivalent of silane. This species then abstracts the hydride from the phosphorane to regenerate the hydrodeoxygenated product. An alternative pathway suggests an S\textsubscript{N}2-like nucleophilic attack by the transiently generated [(Et\textsubscript{3}Si)OCPhMe]+ species prior to hydride abstraction and catalyst regeneration. It would appear that variations of substrate, catalyst, or silane could affect which mechanistic pathway is employed by the reaction (Scheme 1.2.2).\textsuperscript{52} These systems are competent catalysts in a number of transformations effected by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} including hydrodeoxygenation of cyclic and silyl ethers.\textsuperscript{61}
Hydrodefluorination reactions proceed with initial C-F bond activation and cleavage, generating a carbocation and a difluorophosphorane. The former reacts with silane to form the hydrodefluorinated product, while the generated silylium cation abstracts a fluoride from the phosphorane to regenerate the catalyst (Scheme 1.2.3). Control experiments with octafluorotoluene suggest preferential activation by the fluorophosphonium cation in the presence of [Et₃Si][B(C₆F₅)₄], suggesting the Lewis acidic EPC is the catalyst.⁵¹
Another type of reaction that the fluorophosphonium catalyst has been reported to facilitate is the dehydrocoupling reaction of silanes with amines and other functional groups such as thiols, phenols, and carboxylic acids.\textsuperscript{62} In the presence of an olefin, transfer hydrogenation reactivity can also be observed. The mechanism for the dehydrocoupling is similar to the hydrosilylation one in that the Si-H bond is once again activated by the catalyst, prior to backside attack of the silicon species by the Lewis basic substrate, generating a transient hypervalent silicon species. This species contains protic and hydridic hydrogens, prompting loss of H\textsubscript{2} to regenerate the catalyst and yield the dehydrocoupled product. If an alkene is present, H\textsubscript{2} can be added across it instead, which disrupts the completion of the dehydrocoupling pathway. Rather than H\textsubscript{2} elimination, protonation of the olefin occurs by the generated [Ar\textsubscript{2}NHSiEt\textsubscript{3}]\textsuperscript{+} species, forming a carbocation that abstracts a hydride from the fluorophosphorane to regenerate the catalyst and produce the alkane product. (Scheme 1.2.4)
In a very recent example that highlights the versatility of the catalyst, \([\text{FP(C}_6\text{F}_3)_3]^+\) has been found to catalyze the Friedel-Crafts reactivity of various CF₃ containing molecules, effecting benzylation or alkylation of the compounds followed by hydrodefluorination to result in transformation of the CF₃ groups into CH₂-aryl fragments.⁶³

Activation of the trifluoromethyl group by the catalyst forms a difluorophosphorane and a transient carbocation that undergoes electrophilic aromatic substitution. Reaction of silane with the liberated proton eliminates H₂ to afford a silylum cation that abstracts the fluoride from the difluorophosphorane to regenerate the catalyst. Two additional equivalents of silane aid in the rapid hydrodefluorination of the incipient difluorobenzyl product to afford the final product (Scheme 1.2.5).
The EPC $[FP(C_6F_5)_3]^+$ has also been reported to catalyze olefin isomerization,\textsuperscript{58} amide reduction,\textsuperscript{64} and hydroarylation and hydrothiolation of olefins.\textsuperscript{65} The principle limitation of this reactive and versatile catalyst is its observed air and moisture intolerance, leading to degradation of the catalyst. It would be of immense benefit to find a similarly reactive EPC catalyst able to perform under bench top conditions, namely being manipulated in air without decomposition for a sufficiently long time.
1.3 Scope of Thesis

In light of electrophilic air and moisture stable C₆Cl₅-substituted boranes, it was of interest to see if development of C₆Cl₅-substituted EPCs would offer similar advantages while retaining comparable reactivity and Lewis acidity. The objective of this work was to expand the scope of air stable EPCs via incorporation of C₆Cl₅ groups as electron-withdrawing groups in place of C₆F₅ substituents. The capacity of these newly developed EPCs to catalyze a host of reactions is explored, as well as potential FLP reactivity is probed.

Furthermore, the methodology to develop a highly electrophilic NHC-stabilized phosphonium cation is developed and described, and the capacity of the phosphonium cation to perform in Lewis acidic catalysis is examined.

Compounds 2-1, 2-2, 2-3, 2-6, 2-7, 2-10, and 2-11 (See Scheme 2.2.2) have been synthesized collaboratively with Shawn Postle. The experimental details of their synthesis appear in the publication resulting from this project and will also be detailed in his Ph.D thesis. The syntheses of the remaining compounds will be detailed herein. Furthermore, the reactivity and catalytic experiments with the compound 2-11 were also performed by Shawn Postle. Moreover, the syntheses of compounds 2-5, 2-9, and 2-13, as well as the reactivity of compound 2-13 remain unpublished.

Portions of chapters that have been published or drafted at the time of writing:

**Chapter 1:** Postle S.; Podgorny V.; and Stephan D. W. “Electrophilic phosphonium cations (EPCs) with perchlorinated-aryl substituents: towards air-stable phosphorus-based Lewis acid catalysts.” *Dalton Transactions*, 2016, DOI: 10.1039/c6dt01339b. ‡ = equal contribution.
Chapter 2
Perchlorinated Phosphonium Cations

2.1 Introduction

The highly Lewis acidic electrophilic phosphonium cation (EPC) [FP(C₆F₅)₃]⁺ has proven to be an exceptional Lewis acid catalyst capable of catalyzing many useful organic transformations at low catalyst loadings, as described in Chapter 1, Section 1.2.2. However, no catalyst is without its drawbacks. [FP(C₆F₅)₃]⁺ is prone to hydrolysis in the presence of water, akin to the widely used hygroscopic Lewis acid B(C₆F₅)₃.⁶⁷ Other decomposition pathways of the catalyst include cleavage of the P-F bond, and in the case of Lewis basic substrates the possibility of coordination or of nucleophilic aromatic substitution at the para-fluorine positions of the perfluorinated rings, in a similar fashion to B(C₆F₅)₃.⁶⁸,⁶⁹ Thus, work with [FP(C₆F₅)₃][B(C₆F₅)₄] necessitates strictly air and moisture-free conditions. This catalyst was also found to have poor solubility in most organic solvents with the exception of DCM, and bromobenzene to a lesser degree. It would therefore be advantageous to develop a catalyst with comparable Lewis acidity but enhanced tolerance towards moisture and increased solubility in common organic solvents.

In 2011, Ashley and coworkers synthesized the step-wise substituted electron-deficient boranes of the formula B(C₆Cl₅)ₙ(C₆F₅)₃⁻ₙ (n = 1-3) and have shown that replacing even one of the perfluorinated aryl rings of B(C₆F₅)₃ for a perchlorinated aryl ring results in a more sterically-protected compound that is stable to oxygen and able to release a water molecule once it binds (Scheme 2.1.1).⁷⁰ A C₆Cl₅ group was rationalized to be more electron withdrawing than a C₆F₅ group as a result of Cl’s weaker (3p-2p) π-overlap with the aromatic carbon atom, which overshadows the reduced electronegativity and thus inductive withdrawal via the σ-bond capacity of Cl as compared with F. Thus, they also note that their spectroscopic characterization, electrochemical testing, and their computational work (at the B3LYP/TZVP basis set level) suggest the boron centre becomes more electron-deficient as n increases. The natural charge on B steadily increases with each replacement of a C₆F₅ moiety by a C₆Cl₅ one, correlating with increased Lewis acidity in principle. However, Ashley and coworkers seek to point out the differences between electrophilicity and Lewis acidity. Although the electrophilicity of the system is increased with each replacement of a C₆F₅ group for the more electron withdrawing C₆Cl₅ one, the Lewis acidity, or the ability to behave as a Lewis acid, decreases as n increases, primarily due
to increased steric crowding. This was probed using the Gutmann Becket method \((n = 0-2)\), and the Child’s method \((n = 0, 1)\), two commonly employed tests for measuring Lewis acidity (Figure 2.1.1). It was also noted that presumably due to its sheer bulk, the fully chlorinated species \(\text{B(C}_6\text{Cl}_5)_3\) would not bind to either Lewis base. Nevertheless, although Lewis acidity is somewhat impacted, the presence of the pentachlorophenyl group provides additional steric protection to the boron centre yielding a significant stability towards water.

![Scheme 2.1.1. Reversible coordination of H₂O to B(C₆Cl₅)(C₆F₅)₂](image)

The groups of Ashley and O’Hare have subsequently shown that the compound \(\text{B(C}_6\text{Cl}_5)(\text{C}_6\text{F}_5)_2\) is able to activate dihydrogen with 2,2,6,6-tetramethylpiperidine (TMP) (Scheme 2.1.2) or THF (Scheme 2.1.3) and further act as a competent hydrogenation catalyst in tandem with THF. In the case of TMP, this became the first structurally characterized example of a geometrically unconstrained dihydrogen bond within a hydrogenated FLP system,\(^7\) and in the case of THF this represented the first case of metal-free hydrogenation of furan heterocycles with no polymerization of the donor-solvent.\(^7\) A further study of aryl-substituted boranes including the effects of the pentachlorophenyl moiety on Lewis acidity and cleavage of dihydrogen as part of an FLP was very recently authored by Wildgoose et al.\(^7\)
With such great success in both the reactivity and air stability of these pentachlorophenyl-substituted boranes, it was therefore of interest to see if C₆Cl₅ substituents could also impart increased air stability and solubility in common organic solvents for phosphorus Lewis acids, while maintaining their reactivity.
2.2 Results and Discussion

2.2.1 Synthesis of Pentachlorophenyl-Substituted Phosphines - Observations and Trends

In 1966, Gordon et al. successfully synthesized \((\text{C}_6\text{Cl}_5)\text{PPh}_2\) by initially studying and reporting the first ever synthesis of \(\text{C}_6\text{Cl}_5\text{Li}\), which they subsequently reacted with \(\text{Ph}_2\text{PCl}\). This is the more reliable and higher yielding approach to the synthesis of pentachlorophenyl-substituted phosphines over the corresponding \(\text{C}_6\text{Cl}_5\text{MgBr}\) Grignard reagent. The first synthetic report of all three phosphines of the form \((\text{C}_6\text{Cl}_5)_n\text{PPh}_3-n (n = 1-3)\) came from Gilman and coworkers in 1970 where both the Grignard and the \(\text{C}_6\text{Cl}_5\text{Li}\) species were utilized in the syntheses. However, in all cases the phosphines were characterized by either IR, UV-vis, or EA analyses, with no NMR parameters reported, and were often isolated by either chromatography on a column of silica gel in \(\text{CCl}_4\), or recrystallized from hot benzene; both undesirable solvents. The first NMR data reported for any phosphine in this family, \((\text{C}_6\text{Cl}_5)\text{PPh}_2\), was in 2009.

The general synthetic approach to generate pentachlorophenyl-substituted phosphines, and ultimately phosphonium cations, is shown in Scheme 2.2.1. Formation of the \(\text{C}_6\text{Cl}_5\text{Li}\) species via a lithium-halogen exchange reaction from the cheap and readily available \(\text{C}_6\text{Cl}_6\) is followed by a substitution reaction with a halophosphine to yield the pentachlorophenyl-substituted phosphine of interest. This phosphine is then oxidized to a dihalophosphorane with the desired oxidizing agent before a halide abstracting agent is utilized to arrive at the halophosphonium salt of choice.

Scheme 2.2.1. General synthetic approach to yield phosphonium cations with the \(\text{C}_6\text{Cl}_5\) group

One equivalent of \(\text{C}_6\text{Cl}_6\) in a diethyl ether solution was reacted with \(n\)-BuLi at -15 °C under an atmosphere of \(\text{N}_2\) to form the \(\text{C}_6\text{Cl}_5\text{Li}\) species in situ, before being chilled to -78 °C. A solution of \(\text{PPh}_2\text{Cl}\) in diethyl ether was added dropwise and the solution was allowed to react overnight. After filtering in DCM through a Celite plug and recrystallizing at -35 °C, a white solid was obtained in
70% yield. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displayed a singlet at 10.7 ppm in C$_6$D$_6$ matching the reported literature value of (C$_6$Cl$_5$)PPh$_2$. The $^1$H NMR spectrum displayed the expected aromatic resonances. Suitable single crystals of the solid for X-ray diffraction were grown by vapour diffusion of $n$-pentane into a solution of the compound in DCM, and confirm the identity, unambiguously as 2-1, (C$_6$Cl$_5$)PPh$_2$ (Scheme 2.2.2) (Figure 2.2.1).

![Figure 2.2.1. POV-ray depiction of 2-1; C: black, P: orange, Cl: green, H-atoms omitted for clarity](image)

In a similar fashion, two equivalents of C$_6$Cl$_5$Li were reacted with one equivalent of PPhCl$_2$ to yield 2-2, (C$_6$Cl$_5$)$_2$PPh, as a pale yellow solid in 36% yield after similar workup. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibited a singlet at 15.1 ppm in C$_6$D$_6$.

Attempts to synthesize P(C$_6$Cl$_5$)$_3$ by reaction of three equivalents of C$_6$Cl$_5$Li with PCl$_3$ consistently resulted in the formation of mixtures of multiple phosphorus-containing species. A single product could not be obtained despite varying reaction conditions such as temperature, solvents, and stoichiometry. $^{31}$P NMR spectroscopy revealed two resonances, one at 19.1 ppm as a singlet, and the major one at 10.1 ppm as a singlet in C$_6$D$_6$. By cooling a DCM solution of the reaction filtrate, two separate X-ray suitable crystals could be grown. The first has been attributed to decachlorobiphenyl (Figure 2.2.2), and the other to a symmetric diphosphine with two pentachlorophenyl rings on each of the P atoms (Figure 2.2.3). A possible weak $\pi$-stacking interaction may exist in the solid-state between two of the aromatic rings - one ring on each P atom - as noted by the distance between the ipso-carbons of 3.030 Å. This diphosphine has also been confirmed by mass spectrometry. The formation of these species suggests that the oxidation proceeds via a radical mechanism at least to some degree, as the decachlorobiphenyl is likely

† Molecular structure obtained by Shawn Postle
generated from the radical coupling of two \((\text{C}_6\text{Cl}_5)\) radicals. Some precedence is given by Ang and Miller, who observed decomposition to the analogous perfluorinated species in reactions employing \((\text{C}_6\text{F}_5)_2\text{PBr}\) or \((\text{C}_6\text{F}_5)_2\text{PCl}\).\(^77\)

![Figure 2.2.2.](image)

**Figure 2.2.2.** POV-ray depiction of decachlorobiphenyl; C: black, Cl: green

![Figure 2.2.3.](image)

**Figure 2.2.3.** POV-ray depiction of 1,1,2,2-tetrakis(perchlorophenyl)diphosphine; C: black, P: orange, Cl: green

Addition of stoichiometric amounts of CuI to the reaction increased the formation of the species corresponding to the 19.1 ppm singlet in the \(^{31}\text{P}\) NMR spectrum. This was presumably due to formation of the more selective cuprate reagent, though a method of purifying the desired product was still not realized.
Attempts to use a reactive Grignard reagent known as the ‘Turbo Grignard’ (an isopropylmagnesium chloride lithium chloride complex) with an equivalent of PCl₃ were unsuccessful as the major products were isopropyl-substituted phosphines as determined by ³¹P and ¹H NMR spectroscopies. The selectivity was increased by switching the solvent from diethyl ether to THF, but the approach was ultimately abandoned.

Due to the increased lability of the P-Br bond over the P-Cl bond, PBr₃ was selected as the next halophosphine of choice. Reacting three equivalents of C₆Cl₅Li with one equivalent of PBr₃ cleanly generated a product containing only the 19.1 ppm peak by ³¹P NMR, and the compound 2-3, P(C₆Cl₅)₃, was confirmed by mass spectrometry and isolated as a white solid in 21% yield upon similar workup to 2-1 and 2-2. Compound 2-3 is not very soluble in common organic solvents.

Analogous to Ashley’s electrophilic boranes, it was also of interest to develop more electron-deficient phosphines of the form (C₆Cl₅)ₙP(C₆F₅)₃₋ₙ (n = 1, 2), especially to see if replacement of the C₆F₅ moiety with C₆Cl₅ would increase steric bulk sufficiently to greatly enhance the air and moisture stability of the corresponding phosphonium cation. The halophosphines (C₆F₅)₂PBr and (C₆F₅)PBr₂ were distilled from the reaction between the Grignard C₆F₅MgBr and PBr₃. Extra caution must be used when reacting (C₆F₅)PBr₂ as P(C₆F₅)₃ is a common impurity even upon redistillation. If left undisturbed, it is possible to form the highly Lewis acidic [FP(C₆F₅)₃]⁺ cation upon treatment with the oxidizing and halide abstracting agents, which even in a very small concentration is known to be a competent Lewis acidic catalyst in all reactions of interest.

Two equivalents of the C₆Cl₅Li species were generated as previously described and chilled to -78 °C. A solution containing one equivalent of (C₆F₅)PBr₂ in diethyl ether was added and allowed to react overnight. Upon filtering in DCM through Celite and recrystallization at -35 °C, a white powder was obtained in 42% yield. The ³¹P{¹H} NMR spectrum shows a triplet centred at -17.8 ppm in C₆D₆ with ³JPF = 40 Hz. Suitable single crystals of the solid for X-ray diffraction were grown by vapour diffusion of n-pentane into a DCM solution of the compound, confirming the molecular structure of 2-4 as (C₆Cl₅)₂P(C₆F₅) (Figure 2.2.4).
Analogously, one equivalent of C₆Cl₅Li was reacted with an equivalent of (C₆F₅)₂PBr in diethyl ether. After filtration in DCM through Celite and threefold recrystallization at -35 °C, a white fluffy powder was obtained in 20% yield. The $^{31}$P{$^1$H} NMR spectrum showed a quintet centred at -40.8 ppm in C₆D₆ with $^3J_{PF} = 32$ Hz. Suitable single crystals of the solid for X-ray diffraction were grown by vapour diffusion of n-pentane into a DCM solution of the compound, unambiguously confirming the molecular structure of 2-5 as (C₆Cl₅)P(C₆F₅)₂ (Figure 2.2.5).

It is interesting to note the chemical shift trend in the $^{31}$P{$^1$H} NMR of these phosphines 2-1 – 2-5 and the analogous P(C₆F₅)ₙPPh₃₋ₙ ($n = 0$-3) phosphines (Figure 2.2.6). With each substitution of a Ph or C₆Cl₅ group for a C₆F₅ one in the series P(C₆F₅)ₙPPh₃₋ₙ ($n = 0$-3) or (C₆Cl₅)ₙP(C₆F₅)₃₋ₙ ($n = 1, 2$), the $^{31}$P{$^1$H} NMR signal shifts upfield. This is in direct contrast to substituting a Ph or C₆F₅ group for a C₆Cl₅ moiety in the same series which shifts the signal downfield. A possible explanation centers around the increased steric bulk that the ortho-chlorine atoms impart onto the
phosphorus coordination sphere which distorts it towards planarity. The sum of the angles around the stepwise C₆Cl₅-substituted phosphines of the form (C₆Cl₅)ₙP(C₆F₅)₃₋ₙ (n = 1-3) is displayed in Table 2.2.1. The sum of angles about the P atom of P(C₆F₅)₃ has been found⁸⁰ to be 310.0 (0.3)° while that of compounds 2-5 and 2-4, the mono and bis C₆Cl₅-substituted phosphines has been determined to be 311.51 (0.21)° and 317.76 (0.35)°, respectively. The sum of angles about P of compound 2-3 has been calculated† to be 323°, and all structures appear pseudo trigonal pyramidal. The increased planarity about P with each substitution of a C₆F₅ for a C₆Cl₅ substituent is consistent with the incremental deshielding about such pentachlorophenyl-substituted phosphines.

Table 2.2.1: Sum of angles around P of selected compounds

<table>
<thead>
<tr>
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<th>Σ∠P</th>
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<tbody>
<tr>
<td>2-5</td>
<td>310.0 (0.3)°</td>
</tr>
<tr>
<td>2-4</td>
<td>311.51 (0.21)°</td>
</tr>
<tr>
<td>2-3</td>
<td>317.76 (0.35)°</td>
</tr>
<tr>
<td></td>
<td>323°</td>
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† Calculation results obtained by Levy Cao.
Figure 2.2.6. Stacked $^{31}\text{P}^{1}\text{H}^1$ NMR spectra of various aryl-substituted phosphines in CH$_2$Cl$_2$
Scheme 2.2.2. Syntheses of C₆Cl₅ containing phosphines, phosphoranes, and phosphonium cations

2.2.2 Synthesis of Pentachlorophenyl-Substituted Phosphoranes

One equivalent of 2-1 in a DCM solution was treated with equimolar amount of XeF₂, generating a white powder upon workup with n-pentane in 83% yield. The $^{31}$P{$^1$H} NMR spectrum exhibited a triplet centred at -50.7 ppm in C₆D₆ with a $^1$J$_{PF}$ = 716 Hz, and a doublet in the $^{19}$F{$^1$H} NMR spectrum at -41.8 ppm bearing the same coupling constant, consistent with the $^{31}$P NMR data. The NMR data for 2-6 are consistent with other difluorophosphoranes synthesized by our group, which
typically exhibit $J$ coupling constants ranging from 680 – 790 Hz. Single crystals of 2-6 suitable for X-ray diffraction were grown from vapour diffusion of $n$-pentane into a solution of the solid in DCM, and confirm the identity of the compound 2-6 in the solid-state as (C$_6$Cl$_5$)PF$_2$Ph$_2$ (Figure 2.2.7).

![Figure 2.2.7](image.png)

**Figure 2.2.7** POV-Ray depiction of 2-6. P: orange, Cl: green, C: black, F: pink, H-atoms omitted for clarity

Similarly, an equivalent of 2-2 was reacted with XeF$_2$ to yield a yellow solid in 76% yield upon workup. The compound exhibited a triplet centered at -44.9 ppm in C$_6$D$_6$ in the $^{31}$P {$^1$H} NMR spectrum with a $^1J_{PF} = 747$ Hz, and a doublet in the $^{19}$F {$^1$H} NMR spectrum at -28.9 ppm with the same coupling constant. In lieu of a solid-state molecular structure, the analogous NMR parameters to 2-6 give evidence to the formulation of 2-7 as (C$_6$Cl$_5$)$_2$PF$_2$Ph.

In a similar fashion, an equivalent of 2-3 was reacted with XeF$_2$. The $^{31}$P NMR spectrum showed a doublet of triplets, and a triplet centred at -38.7 ppm in C$_6$D$_6$ with a coupling constant of 786 Hz. The doublet of triplets was centered at -26.0 ppm, with coupling constants of 1019 Hz and 895 Hz, respectively. The $^{19}$F NMR spectrum had three major resonances, the first a doublet of doublets centred at -5.5 ppm with a coupling constants of 895 Hz and 59 Hz. The second a doublet centred at -15.5 ppm with a $J$ value of 786 Hz. Lastly, the third was a doublet of triplets centred at -71.1 ppm with a coupling constant of 1019 Hz and 59 Hz, respectively. These data indicate the presence of two fluorophosphorus species: it was reasoned that the 786 Hz coupling belonged to tris(perchlorophenyl)difluorophosphorane (C$_6$Cl$_5$)$_3$PF$_2$, which was consistent with the doublet in the $^{19}$F NMR spectrum and the corresponding triplet in the $^{31}$P NMR spectrum. The doublet of triplets observed by $^{31}$P NMR spectroscopy was attributed to bis(perchlorophenyl)
trifluorophosphorane \((\text{C}_6\text{Cl}_5)_2\text{PF}_3\). The axial fluorine atoms are responsible for the doublet of doublets signal in the \(^{19}\text{F}\) NMR spectrum with the \(^1J_{PF} = 895\) Hz and the \(^2J_{FF} = 59\) Hz, having been split by the P atom and the equatorial F atom, respectively. The equatorial fluorine thus gave rise to the doublet of triplets signal in the \(^{19}\text{F}\) NMR spectrum with \(^1J_{PF} = 1019\) Hz and the \(^2J_{FF} = 59\) Hz, having been split by the P atom and the two chemically equivalent axial F atoms, respectively. The doublet of triplets in the \(^{31}\text{P}\) NMR spectrum is then in support of this, being split by the equatorial F atom and the two axial F atoms, respectively. The molar ratio between the two species was 1:3 for the desired difluorophosphorane over the trifluorophosphorane by \(^{19}\text{F}\) NMR spectroscopy, and all efforts to separate the two species were unsuccessful. Optimization of original reaction conditions, especially with respect to temperature, to attempt to control the distribution of the products was not successful. It is possible that formation of the desired product in an appreciable yield is not possible due to the activation energy for the formation of the two observed species being similar, and due to the incredible steric crowding imparted by three pentachlorophenyl substituents on the phosphorus coordination sphere. It is also likely that this reaction proceeds via a radical mechanism to some degree, consistent with two \(\text{C}_6\text{Cl}_5\) radicals coupling to yield the essentially NMR silent decachlorobiphenyl.

The corresponding analogous \((\text{C}_6\text{F}_5)_2\text{PF}_3\) was similarly first observed as a side product in the reaction between the fluorinating agent \(\text{SbF}_3\) and \((\text{C}_6\text{F}_5)_2\text{PX}\) (X = Cl, Br) by Fild and Schmutzler in 1969.\(^{81}\) However, they also noted the reaction between the mild fluorinating agent \(\text{AsF}_3\) with \((\text{C}_6\text{F}_5)_2\text{PCl}_3\) yields the corresponding trifluorophosphorane selectively.

In a similar fashion to the fluorinating methodology employed earlier, one equivalent of \(2-4\) was reacted with an equimolar amount of \(\text{XeF}_2\) to yield a yellow solution which upon cooling precipitated a white solid in 80% yield upon similar workup. The compound exhibited a triplet centered at -41.2 ppm in \(\text{C}_6\text{D}_5\text{Br}\) in the \(^{31}\text{P}\) NMR spectrum with \(^1J_{PF} = 757\) Hz, and a doublet of multiplets in the \(^{19}\text{F}\) NMR spectrum at -10.9 ppm with the same coupling constant, as well as the expected three signals for the aromatic \(\text{C}_6\text{F}_5\) group. Analogous NMR parameters to \(2-6\) and \(2-7\), give evidence to the formulation of \(2-8\) as \((\text{C}_6\text{Cl}_5)_2\text{PF}_2(\text{C}_6\text{F}_5)\).

One equivalent of \(2-5\) was reacted with an equivalent of \(\text{XeF}_2\) to yield a white solid in 37% yield upon thorough workup. The compound exhibited a triplet centered at -44.6 ppm in CDCl\(_3\) in the
$^{31}\text{P}$ NMR spectrum with a $J_{PF} = 725$ Hz, and a doublet of multiplets by $^{19}\text{F}$ NMR spectroscopy at -6.4 ppm with the same coupling constant. The compound has been characterized by X-ray crystallography from single crystals grown by vapour diffusion, confirming the identity of 2-9 in the solid-state as $(\text{C}_6\text{Cl}_5)\text{PF}_2(\text{C}_6\text{F}_5)_2$ (Figure 2.2.8). Interestingly, in contrast to 2-8 there were four resonances in the aromatic region of the $^{19}\text{F}$ NMR spectrum integrating to 1:1:1:2 (2:2:2:4), suggesting inequivalency of the ortho-fluorine atoms. Indeed, $^{19}\text{F}$ NMR variable temperature (VT) studies (Figure 2.2.9) in C$_6$H$_5$Br display coalescence of the two ortho-fluorine signals at high temperatures before merging to a single sharp peak, indicative of restricted rotation around the P-C bond. This restricted rotation on the NMR time scale arises from the bulk that the C$_6$Cl$_5$ ring introduces, as well as due to the asymmetry inherent in the system. The asymmetry comes about from the C$_6$F$_5$ groups being flanked by a neighbouring C$_6$F$_5$ group on one side, and a C$_6$Cl$_5$ group on the other, resulting in the inequivalency observed in the $^{19}\text{F}$ NMR signals. It is interesting to note that such inequivalency is not observed in the analogous more bulky 2-8, and it is likely that although restricted rotation is present in both systems, it is not manifested in the spectra of 2-8 due to the symmetry present in the compound.

Figure 2.2.8 POV–Ray depiction of 2-9. P: orange, Cl: green, C: black, F: pink
2.2.3 Synthesis of Pentachlorophenyl-Substituted Phosphonium Cations

One equivalent of 2-6 was reacted with 0.95 eq. [Et₃Si][B(C₆F₅)₄], prepared via literature procedure, in toluene affording a dark orange oil after the course of an hour. Upon washing the oil with toluene, trituration with pentane, and removal of the solvent in vacuo, a white fluffy powder was obtained in 80% yield. $^{31}P\{^1H\}$ NMR analysis of the product in C₆D₅Br revealed a change in chemical shift from the triplet centred at -50.7 ppm with $^{1}J_{PF} = 716$ Hz to a doublet centred at the much downfield shifted 89.5 ppm having a $^{1}J_{PF} = 1009$ Hz, indicating complete consumption of the phosphorane starting material. The $^{19}F\{^1H\}$ NMR spectrum displayed a doublet at -116.0 ppm with the same 1010 Hz coupling, and the expected three resonances for the perfluorophenyl groups of the non-coordinating [B(C₆F₅)₄]⁻ counter-anion. The $^{11}B$ NMR spectrum showed a singlet at -16.5 ppm, consistent with the four-coordinate borate salt, while the $^1H$ NMR spectrum displayed the expected aromatic resonances. From the synthesis of such
phosphonium cations in our group, a $J$ coupling constant of about 1000 – 1080 Hz is generally indicative of a fluorophosphonium species. Collectively, this evidence pointed to the formulation of the product 2-10 as $[(C_6Cl_5)PFPh_2][B(C_6F_5)_4]$.

Similarly, one equivalent of 2-7 was reacted with 0.95 eq. $[Et_3Si][B(C_6F_5)_4]$ in toluene affording a dark amber coloured oil. An off-white solid was obtained in 90% yield after an analogous workup. The $^{31}P\{^1H\}$ NMR spectrum in CD$_2$Cl$_2$ showed a doublet centred at 84.4 ppm with a $^1J_{PF} = 1010$ Hz while the $^{19}F\{^1H\}$ NMR spectrum displayed a doublet at -125.6 ppm with the same coupling constant, and the expected three resonances for the $[B(C_6F_5)_4]$ anion. The $^{11}B$ NMR and $^1H$ NMR spectra were consistent as before. The molecular structure of compound 2-11 $[(C_6Cl_5)PFPh][B(C_6F_5)_4]$ was obtained by X-ray crystallography (Figure 2.2.10)† displaying a pseudo-tetrahedral geometry and a P-F bond length of 1.5454(6) Å. For comparison, the analogous $[(C_6F_5)_2PFPh]^+$ cation species has a slightly shortened P-F bond length of 1.533(2) Å, which is also reflected in the slightly larger $J$ coupling constant of 1041 Hz arising from the increased capacity to exchange spin density, presumably due to the less sterically-encumbering substituents – though not to a statistically significant extent. The P-F bond length of the $[(C_6F_5)PFPh_2]^+$ cation in the same series was found to be somewhat larger and is in fact 1.547(2) Å.

![Figure 2.2.10](image_url)

**Figure 2.2.10** POV–Ray depiction of 2-11. P: orange, Cl: green, C: black, F: pink, $[B(C_6F_5)_4]^-$ counter-anion omitted for clarity

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† Molecular structure obtained by Shawn Postle.
Analogously, an equivalent of 2-8 was reacted with 0.95 eq. [Et$_3$Si][B(C$_6$F$_5$)$_4$] in toluene affording a dark amber coloured oil after an hour. An off-white solid was collected in 74% yield after workup. The $^{31}$P NMR spectrum in C$_6$D$_5$Br revealed a doublet centred at -50.7 ppm with $^1J_{PF} = 1031$ Hz consistent with a P-F moiety. The $^{19}$F NMR spectrum displayed a doublet of doublets centred at -117.0 ppm with $^1J_{PF} = 1031$ Hz and $^4J_{FF} = 26$ Hz, three resonances attributable to a [B(C$_6$F$_5$)$_4$] anion, and four resonances attributed to a perfluorophenyl substituent with an integration ratio of 1:1:1:2. Variable temperature $^{19}$F NMR studies (Figure 2.2.11) revealed coalescence of the ortho-fluorine signals and sharpening of the meta-fluorine peaks at higher temperatures suggesting restricted rotation about the P-C bond. The inequivalence of the fluorine atoms of the C$_6$F$_5$ ring is thought to be a result of the enforced pseudo-tetrahedral geometry about the P atom and the steric demands imparted by the C$_6$Cl$_5$ substituents.

**Figure 2.2.11.** VT $^{19}$F NMR studies on compound 2-12
Looking at a $^{19}$F-$^{19}$F COSY 2D NMR spectrum of 2-12 (Figure 2.2.12), it was noted that at room temperature only one of the ortho-fluorine atoms of the C$_6$F$_5$ ring couples to the F atom on P with a $^4J_{FF} = 26$ Hz, giving rise to the doublet of doublets signal observed in the 1D $^{19}$F NMR spectrum, whereas a doublet of triplets was expected. This is likely a result of hindered rotation, where the coupling observed may mostly consist of a through-space dipole interaction, further demonstrating the immense steric bulk that the C$_6$Cl$_5$ groups impart, especially at the pseudo-tetrahedral phosphonium cation stage. Finally, analogous NMR parameters to 2-10 and 2-11, give evidence to the formulation of 2-12 as [(C$_6$Cl$_5$)$_2$PF(C$_6$F$_5$)][B(C$_6$F$_5$)$_4$].

Figure 2.2.12. $^{19}$F-$^{19}$F COSY NMR spectrum of compound 2-12
An equivalent of 2-9 was reacted with 0.95 eq. [Et₃Si][B(C₆F₅)₄] in toluene over three hours affording a brown oil upon settling. A white solid was collected in 98% yield after workup of the brown oil in pentane. The ³¹P NMR spectrum in CDCl₃ exhibited a doublet centred at 66.3 ppm with ¹J_PF = 1043 Hz consistent with a P-F moiety. The ¹⁹F NMR spectrum displayed a broad doublet of multiplets centred at -112.1 ppm with the same coupling, three resonances attributable to a [B(C₆F₅)₄]⁻ counter-anion, and three resonances attributed to the two equivalent pentafluorophenyl substituents. As evidenced by the expected 2:1:2 integration in the ¹⁹F NMR spectrum, it would seem that unlike in the case of the trigonal bipyramidal difluorophosphorane 2-9, one C₆Cl₅ group is insufficient to induce restricted rotation of the C₆F₅ substituents in the distorted tetrahedral fluorophosphonium cation 2-13 at room temperature. Additionally, the molecular structure of 2-13 was obtained by X-ray diffraction (Figure 2.2.13).

![Figure 2.2.13 POV-Ray depiction of 2-13. P: orange, Cl: green, C: black, F: pink, [B(C₆F₅)₄]⁻ counter-anion omitted for clarity](image)

At the time of writing, the molecular structures of compounds 2-5, 2-9, and 2-13 represent the only fully solved series of structures in the series of either (C₆X₅)ₙPPh₃₋ₙ (X = F, Cl; n = 0-3), or (C₆Cl₅)ₙP(C₆F₅)₃₋ₙ (n = 1, 2) and their respective difluorophosphoranes and fluorophosphonium salts. Thus it would be of potential benefit to note angles and bond lengths of interest and these are displayed in Table 2.2.2. In the case of the phosphine 2-5, the sum of the angles around P as
noted before is: 311.51 (0.21)°, and the structure appears pseudo trigonal pyramidal. In the case of the difluorophosphorane 2-9, the average P-F bond length is: 1.6332(2) Å, the F-P-F angle is: 178.23 (0.10)°, with the \( \Sigma \angle P = 359.98 \) (0.23)°, and the structure appears trigonal bipyramidal. The P-F bond length of 1.5432(133) Å in the case of 2-13 is much smaller than that of 2-8, consistent with a much stronger bond between the P and the F atoms. This increased strength is also evidenced by the enhanced ability to exchange spin information between the two nuclei, thus resulting in the much greater \( J_{PF} \) coupling constant (725 Hz vs. 1043 Hz). The structure appears pseudo-tetrahedral with a \( \Sigma \angle P = 339.44 \) (1.53)°. The bond length is likely the closest P-F bond length to that of the as-of-yet crystallographically uncharacterized \([\text{FP(C}_6\text{F}_5)_3]^+\) phosphonium cation due to the similar structural parameters that encompass similar electron-withdrawing aryl groups.

Table 2.2.2: Summary of select bond lengths and angles of interest

<table>
<thead>
<tr>
<th></th>
<th>2-5</th>
<th>2-9</th>
<th>2-13</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma \angle P )</td>
<td>310.0 (0.3)°</td>
<td>359.98 (0.23)°</td>
<td>339.44 (1.53)°</td>
</tr>
<tr>
<td>( \angle F-P-F )</td>
<td>-</td>
<td>178.23 (0.10)°</td>
<td>-</td>
</tr>
<tr>
<td>P-F bond length</td>
<td>-</td>
<td>1.6332(2) Å</td>
<td>1.5432(133) Å</td>
</tr>
</tbody>
</table>

2.2.4 Lewis Acidity Testing and Catalytic Reactivity

With the four phosphonium cations in hand (Figure 2.2.14), the relative Lewis acidity of these species was investigated. One of the most commonly applied methods for measuring Lewis acidity is the Gutmann Beckett method. The technique utilizes Et₃PO as a Lewis basic donor which through its interaction with the Lewis acid, deshields the pendant P atom, modifying the \( ^{31} \text{P} \) NMR

---

Footnote:

*This number must be viewed with some caution. Collection of the diffraction data was interrupted halfway through collection, and thus the \( R_1 = 0.1006 \) value is somewhat high.
chemical shift. This relative chemical shift of the adduct to free Et₃PO is then used to correlate Lewis acidity. This relative distance can also be used to calculate a Lewis acceptor number (AN) by standardizing against the chemical shift of Et₃PO in a strongly Lewis acidic SbCl₅ solution (AN = 100) or the chemical shift of Et₃PO in a hexane solution (AN = 0).

Figure 2.2.14 – Phosphonium Lewis acid catalysts 2-10 – 2-13

Three equivalents of the bulkier 2-11 were combined with one equivalent of Et₃PO in DCM, and no reactivity was noted by $^{31}$P{¹H} NMR. By increasing the amount of Et₃PO until it was 1:1 with 2-11, a minor broad peak was observed at 58.5 ppm as well as several minor sharp peaks scattered upfield of that (free Et₃PO displays a resonance around 50.7 ppm in DCM) at 35.6, 29.2, 27.6, and -44.7 ppm, with the largest resonance being the downfield doublet attributed to unreacted 2-11. From this data it was concluded that preclusion of adduct formation was evident, or formation in minute quantities at best likely due to an unfavourable equilibrium. This result spoke to some of the drawbacks and limitations of employing the Gutmann Beckett method for Lewis acidity testing. The method does not take into account steric factors which may make it more difficult for sterically-encumbered species to form an adduct. Additionally, in the case of more electrophilic systems, fluorine-oxygen exchange may occur, invalidating the method, as observed for the highly electrophilic $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$ dication species when reacted with Et₃PO.$^{54}$

Thus, it was decided that since it would not be possible to corroborate Lewis acidities using the Gutmann Beckett method, especially in the case of the even bulkier 2-12, and 2-13, relative Lewis acidities could be probed by the ability and performance of the species in catalysis mediated by Lewis acids.

The activity of catalysts 2-10 – 2-13 was tested in hydrodefluorination, hydrodeoxygenation, hydrosilylation, dehydrocoupling, and Friedel-Crafts type reactions. As discussed in Chapter 1,
Section 1.2.2. phosphonium cations, including the highly Lewis acidic \([\text{FP(C}_6\text{F}_5)_3][\text{B(C}_6\text{F}_5)_4]\), have been shown to catalyze these reactions with varying rates of success\(^{51,52,57,88-90}\) offering an easy route for comparison. In all catalytic reactivity test reactions, 5 mol\% of the catalyst was employed.

Lewis acids are known to catalyze the cyclodimerization of 1,1-diphenylethylene, and the conversion can be monitored by \(^1\text{H} NMR\) spectroscopy. The summary of the catalytic activity of all four catalysts is summarized in Table 2.2.3. A characteristic sign of reaction completion is the disappearance of the vinylic signal at 5.33 ppm in the \(^1\text{H} NMR\) spectrum, and the appearance of the diastereotopic methylene resonances at 2.94 and 2.61 ppm as a set of two doublets for the dimerized bicyclic product. It can be noted that as expected, replacement of the phenyl group by the more electron withdrawing \(\text{C}_6\text{Cl}_5\) moiety lowers the energy of the \(\sigma^*_{\text{P-F}}\) orbital resulting in a more Lewis acidic system as observed for \(2\text{-10}\) and \(2\text{-11}\) which catalyzed the reaction in 18 and 6 hours, respectively. Replacement of the phenyl group in \(2\text{-11}\) by a \(\text{C}_6\text{F}_5\) group further bolsters Lewis acidity as observed by the reactivity of \(2\text{-12}\) which only took an hour to catalyze the complete conversion to the product. Lastly, replacement of a \(\text{C}_6\text{Cl}_5\) group in \(2\text{-12}\) by a \(\text{C}_6\text{F}_5\) one seems to provide yet increased reactivity as evidenced by the superior catalytic results obtained for catalyst \(2\text{-13}\) of 50 minutes.

The hydrodefluorination reaction of 1-fluoropentane with \(\text{Et}_3\text{SiH}\) has been previously shown to generate carbocationic rearrangement and Friedel-Crafts type products\(^{91}\) In order to avoid the possibility of similar by-products, 1-fluoroadamantane was chosen for the reaction for its more rigid structure. The reaction is very rapid and in most cases complete in 10 minutes or less as seen for \(2\text{-11}, 2\text{-12},\) and \(2\text{-13},\) yielding adamantane and \(\text{Et}_3\text{SiF}\) as may be observed by \(^1\text{H}\) and \(^{19}\text{F}\) NMR spectroscopies. The reaction is complete in 3.5 hours in the case of the Lewis acid \(2\text{-10}\). The reaction is completed when the starting material 1-fluoroadamantane C-F signal at -128.5 ppm in the \(^{19}\text{F}\) NMR spectrum is fully converted to the Si-F resonance attributable to \(\text{Et}_3\text{SiF}\) at -175.8 ppm, and the \(^1\text{H}\) NMR spectrum is compared with an authentic sample.

The hydrodeoxygenation reaction of benzophenone with two equivalents of \(\text{Et}_3\text{SiH}\) was monitored by \(^1\text{H}\) NMR spectroscopy. Most diagnostically, the reaction is complete when the multiplet resonance appearing at 7.64 - 7.68 ppm attributable to benzophenone is fully absent, while the
singlet at 3.77 ppm belonging to the methylene group of diphenylmethane grows in. Most of the phosphonium cations proved to be competent catalysts, with 2-11 completing the reaction in 40 h, 2-12 in 2 h, and 2-13 in 25 min. 2-10 was also successful in affording full conversion to the product, albeit in 17 h at 140 °C, further supporting the reactivity trend as: 2-13 > 2-12 > 2-11 > 2-10.

The dehydrocoupling reaction between phenol and Et₃SiH was monitored by ¹H NMR spectroscopy. The reaction produces visible H₂ bubbling, but more diagnostically the reaction is complete when the doublet resonance at 6.74 ppm and the two triplets centred at 6.88 and 7.17 ppm attributable to phenol have fully disappeared, and in their stead the triplet centred at 7.24 ppm and multiplet appearing at 6.93 - 7.00 ppm attributable to triethyl(phenoxysilane) become visible. 2-13 was able to catalyze the reaction to completion in 30 minutes at room temperature, while the same feat was accomplished in 4 h in the case of 2-12. 2-11 took 72 h to complete at room temperature while 2-10 ultimately afforded full conversion to the product in 24 h at 140 °C. Once again this reactivity supports the previously established trend: 2-13 > 2-12 > 2-11 > 2-10.

The progression of the hydrosilylation reaction of α-methylstyrene with Et₃SiH was monitored by ¹H NMR spectroscopy. The reaction is complete when the vinylic resonances centred at 5.27 and 4.95 ppm attributable to α-methylstyrene are fully consumed, while signals attributable to the methylene group of the silane product at 0.91 - 0.98 ppm grow in. Most of the phosphonium cations required harsher conditions to afford complete transformation, with 2-10 requiring 48 h at 140 °C, 2-11 32 h at 120 °C, and 2-12 30 h in 80 °C. 2-13 was able to successfully catalyze the reaction in 5 hours at room temperature, showcasing the difference the altered aryl groups make with the best performance attributed to the catalyst containing the most C₆F₅ groups in the series. This yields further evidence to the previously established reactivity trend.

Furthermore, Friedel-Crafts type reactivity on 1-bromo-4-(trifluoromethyl)benzene with three equivalents of Et₃SiH was attempted. The reactions were monitored by both ¹⁹F and ¹H NMR spectroscopies. The reactions were deemed complete when the starting material signal at -62.7 ppm in the ¹⁹F NMR spectrum is fully converted to the resonance attributable to Et₃SiF at -175.8 ppm. The catalysts 2-10 and 2-11 were deemed insufficiently Lewis acidic to effect the transformation, even at elevated temperatures in the span of days, and only afforded minimal conversion to the product. The stronger Lewis acid catalysts 2-12 and 2-13 were able to afford
complete conversion to the Friedel-Crafts product in 22 h and 1.5 h at 80 °C, respectively. This represents an important reaction due to the general perceived inertness of the CF₃ moiety, but it is noted that the [FP(C₆F₅)₃]+ cation is able to catalyze this, and all of the aforementioned reactions in a more rapid fashion and in milder conditions. The major downside to this incredible reactivity is its equally incredible air-sensitivity. Thus the air stability of the four catalysts was qualitatively probed. Moreover, all reactivity is presumed to proceed via the analogous mechanisms to [FP(C₆F₅)₃]+ as discussed in Chapter 1, Section 1.2.2.

A sample of each catalyst in a solution of PhBr was transferred to a 5 mm diameter NMR tube. The sample was taken out of the glovebox and opened to air for successively longer intervals. The solution was recapped and shaken between recordings of the NMR spectra in order to avoid issues related to diffusion. The onset of hydrolysis for each Lewis acid was determined by ¹⁹F and ³¹P NMR spectroscopies. A typical sequential NMR spectrum is shown in Figure 2.2.15.

The Lewis acids 2-10 and 2-11 proved to be quite robust to hydrolysis in air. The former showing signs of degradation at 21 h presumably to the phosphine oxide although no attempts were made to isolate the species, while the latter showed no signs of decomposition even after 48 hours of exposure. In fact, solid samples of both catalysts could be manipulated in air, and could afford the complete hydrodefluorination of 1-fluoroadamantane in undried solvent-grade bromobenzene. A solution of 2-12 was found to be less stable than either 2-10 or 2-11, showing minor formation of HC₆F₅ by ¹⁹F NMR spectroscopy after 4 h. Least stable of all, 2-13 showed evidence of decomposition in just 15 minutes. The onset of hydrolysis trend was observed to be – in order of most stable to least stable: 2-11 > 2-10 >> 2-12 >> 2-13, which interestingly is not quite the reverse of the reactivity trend. Although 2-11 is more Lewis acidic than 2-10, and is thus perhaps predicted to be less air stable purely from an electronic point of view, the increased steric protection offered by the two C₆Cl₅ rings offsets the Lewis acidity factor. By comparison, the cation [FP(C₆F₅)₃]+ shows significant decomposition in air within 1 minute. Furthermore, in the case of the poor tolerance of 2-13 to benchtop conditions, it would be more efficient to use the [FP(C₆F₅)₃]+ catalyst in the complete absence of air. These results suggest that C₆Cl₅ moieties do indeed offer increased air stability, presumably due to the shielding of the P-F bond fragment by the ortho-chlorine atoms of the ring. However, reactivity decreases concurrently, except for when the C₆Cl₅ substituent is substituted in place of a phenyl group as in the case of 2-11 over 2-10, which demonstrates both
superior Lewis acidity, and air stability. As a side note, the solubilities of 2-10 – 2-14 in C₆H₅Br were all greater than that of [FP(C₆F₅)₃]⁺ although not by much in the case of 2-13.

Table 2.2.3. Summary of Catalytic Activity

<table>
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<th>Catalyst</th>
<th>Conditions</th>
<th>Time/Temp</th>
</tr>
</thead>
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<tr>
<td>2</td>
<td>cat. 5 mol%</td>
<td>PhBr, r.t.</td>
<td>2-10: 18 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-11: 6 h*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-12: 1 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-13: 50 min</td>
</tr>
<tr>
<td>3</td>
<td>cat. 5 mol%</td>
<td>PhBr, r.t.</td>
<td>2-10: 3.5 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 eq. Et₃SiH</td>
<td>2-11: 10 min*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-12: &lt;10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-13: &lt;10 min</td>
</tr>
<tr>
<td>4</td>
<td>cat. 5 mol%</td>
<td>PhBr, r.t.</td>
<td>2-10: 17 h, 140 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0 eq. Et₃SiH</td>
<td>2-11: 40 h*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-12: 2 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-13: 25 min</td>
</tr>
<tr>
<td>5</td>
<td>cat. 5 mol%</td>
<td>PhBr, r.t.</td>
<td>2-10: 24 h, 140 °C</td>
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<tr>
<td></td>
<td></td>
<td>1.0 eq. Et₃SiH</td>
<td>2-11: 72 h*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-12: 4 h</td>
</tr>
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<td></td>
<td></td>
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<td>2-13: 30 min</td>
</tr>
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<td>PhBr, r.t.</td>
<td>2-10: 48 h, 140 °C</td>
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<tr>
<td></td>
<td></td>
<td>1.0 eq. Et₃SiH</td>
<td>2-11: 32 h, 120 °C*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-12: 30 h, 80 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-13: 5 h</td>
</tr>
<tr>
<td>7</td>
<td>cat. 5 mol%</td>
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<td>3.6 eq. Et₃SiH</td>
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<td></td>
<td>2-12: 22 h, 80 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-13: 1.5 h, 80 °C</td>
</tr>
</tbody>
</table>

* Reactivity performed by Shawn Postle.
2.2.5 Reactivity towards Small Molecules

It was also of interest to see how the increased bulk and perhaps decreased risk of nucleophilic aromatic substitution at the para position of the pentachlorophenyl-substituted phosphonium cations would lend itself to reactivity with Lewis bases. Lack of such nucleophilic attack would make these EPCs more suitable for use as the Lewis acidic partner in an FLP.

There are no examples of an all-phosphorus intermolecular FLP system that has been employed for small molecule activation. To this end 2-10 and 2-11 were combined with bulky, weakly basic PPh$_3$ in DCM in an attempt to explore such systems. Initially the system appeared stable by $^{31}$P{$^1$H} and $^{19}$F{$^1$H} NMR spectroscopies, showing no reaction or adduct formation at 6 h; however, by 13 h the PPh$_3$ had been completely consumed though signals for 2-10 and 2-11 were still present.
Given the slow reaction between 2-10 or 2-11 with PPh₃, both combinations were tested for activation of small molecules, in hopes that FLP reactivity would occur before decomposition. This would represent the first all-phosphorus intermolecular FLP system.

Unfortunately, no reactivity was observed between the FLP of 2-10 or 2-11 with PPh₃, and 4 atm. of H₂ or 1 atm. of CO₂. This is attributable to the weak nature of the Lewis acids, and the weak nature of the Lewis base, which although potentially frustrated, did not possess enough reactivity to split H₂ or trap CO₂. A stronger base such as P(t-Bu)₃ would be a more suitable candidate for such reactivity. Thus P(t-Bu)₃ was reacted in an equimolar fashion with 2-10 and 2-11 in DCM. In both cases, rapid reaction leads to multiple unidentifiable products that were observed by ³¹P NMR, and thus reactivity with small molecules was not tested. It is possible that nucleophilic aromatic substitution at the para position of a C₆Cl₅ ring occurred, followed by disproportionation to yield a complex mixture of phosphoranes and phosphonium cations consistent with doublets and triplets with suitable coupling in the ³¹P NMR spectra but efforts to isolate the by-products were unsuccessful.

Krempner and co-workers have recently explored the FLP activation of small molecules using the very bulky Verkade superbases - a family of proazaphosphatranes - as the Lewis base, and moderate to weak Lewis acidic boranes. Following suit, the triisopropyl derivative of Verkade’s superbase was reacted in an equimolar fashion with both 2-10 and 2-11, but once more in both cases a mixture of products could be observed by ³¹P NMR spectroscopy and the effort was abandoned.

Lastly, efforts to react the catalysts with TMP before attempting activation of H₂ or CO₂ were also unsuccessful, once again speaking to the weakly Lewis acidic nature of the two catalysts employed. No such reactivity was attempted with 2-12 or 2-13 due to concerns over attack at the para position of the C₆F₅ ring.
2.3 Conclusions

A series of pentachlorophenyl-substituted phosphines of the forms \((C_6Cl_5)_nPPh_{3-n}\) \((n = 1-3)\) and \((C_6Cl_5)_nP(C_6F_5)_{3-n}\) \((n = 1, 2)\) as well as their corresponding difluorophosphoranes and fluorophosphonium cations were synthesized and characterized, with the exception of the difluorophosphorane and fluorophosphonium cation of \(P(C_6Cl_5)_3\) which proved to preferentially form a diphosphine by-product during oxidation attempts.

Being too sterically-encumbered to undergo the Gutmann-Beckett test effectively, the Lewis acid capacities of the fluorophosphonium cations were evaluated in a series of standard Lewis acidic catalytic reactions. The Lewis acids were demonstrated to be competent catalysts, uncovering the following reactivity trend: \(2-13 > 2-12 > 2-11 > 2-10\).

Although Ashley and coworkers noted that \(C_6Cl_5\) moieties are more electron withdrawing than \(C_6F_5\) groups, as in the case of increasing electrophilicity in the boron series \(B(C_6Cl_5)_n(C_6F_5)_{3-n}\) \((n = 1-3)\), \(C_6F_5\) groups show enhancement in Lewis acidity and catalytic reactivity as compared with \(C_6Cl_5\) ones in the capacity of fluorophosphonium cations. The observed reactivity strengthens Ashley’s conclusion that electrophilicity does not necessarily translate to Lewis acidity. This is evidenced by \(2-13\) being more reactive than \(2-12\). The steric protection offered by the ortho-chlorine atoms does suggest that protection of the P-F bond is a viable approach to air stability, though this generally comes at a cost of lowered reactivity. The qualitative air stability tests uncovered the onset of hydrolysis trend to be – from most to least stable: \(2-11 > 2-10 > 2-12 > 2-13\). This trend suggests that although a \(C_6Cl_5\) substituent enhances Lewis acidity when compared to a phenyl group, the added steric protection overcompensates for it, leading to an overall increase in the air stability of the species. Thus there is some tunability to the compounds as it pertains to aromatic groups offering steric protection or electron withdrawing capacities.

Lastly, the weak and moderate Lewis acids \(2-10\) and \(2-11\) formed FLPs with the weakly Lewis basic \(PPh_3\) or \(TMP\) in order to activate small molecules such as \(H_2\) or \(CO_2\), but the combination proved to be too weak to afford such reactivity. Using stronger Lewis bases such as \(P(t-Bu)_3\) or triisopropyl proazaphosphatrane yielded a complex mixture in the \(^{31}\text{P}\) NMR spectra, indicative of reactivity that is not compatible with FLPs and small molecule activation.
2.4 Experimental Section

2.4.1 General considerations

All manipulations were performed in a Glove box MB Unilab produced by MBraun (equipped with a -35 °C freezer) or using standard Schlenk techniques under an inert atmosphere of anhydrous N₂. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (CH₂Cl₂, Et₂O, toluene, and n-pentane) were prepared using an Innovative Technologies solvent purification system, degassed, and stored over 4 Å molecular sieves before use. Tetrahydrofuran (Aldrich) was distilled over Na/benzophenone prior to use. CD₂Cl₂ (Aldrich) was deoxygenated, distilled over CaH₂, then stored over 4 Å molecular sieves before use. C₆D₆, CDCl₃ and C₆D₅Br (Aldrich) were deoxygenated and stored over 4 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, Apollo Scientific, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. [Et₃Si][B(C₆F₅)₄]·(C₇H₈), P(C₆F₅)₂Br, and P(C₆F₅)Br₂ were prepared by the reported procedures.⁷₈,⁷₉,⁸₂ NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian NMR system 400 MHz spectrometer, Agilent DD2-500 MHz spectrometer, or Agilent DD2-600 MHz spectrometer. All NMR experiments were conducted at 25 °C unless otherwise stated. ¹H NMR data, referenced to residual solvent resonances relative to external SiMe₄, are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), normalized integrals. ¹³C{¹H} NMR chemical shifts (δ) are referenced to external SiMe₄. Other nuclei are referenced relative to an external standard (¹¹B: (Et₂O)BF₃, ¹⁹F: CFCl₃, ³¹P: 85% H₃PO₄). 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.
2.4.2 Synthesis of Compounds

\[ \text{C}_6\text{Cl}_{16} \text{P} \sim \text{C}_6\text{F}_5 \]

**bis(perchlorophenyl)(perfluorophenyl) phosphine (2-4)**. A 250 mL Schlenk flask was charged with \( \text{C}_6\text{Cl}_{16} \) (513 mg, 1.80 mmol), a large magnetic stir-bar and anhydrous \( \text{Et}_2\text{O} \) (40 mL), generating a white slurry. The reaction flask was cooled to -15 °C using a dry ice/acetone bath. A hexane solution of 2.5 M \( n\)-BuLi (0.72 mL, 1.80 mmol) was added dropwise to the stirring solution under an atmosphere of \( \text{N}_2 \); slowly turning the slurry to a clear light yellow solution. The solution was cooled to -78 °C and a solution of \( \text{P} (\text{C}_6\text{F}_5) \text{Br}_2 \) (323 mg, 0.90 mmol) in anhydrous \( \text{Et}_2\text{O} \) (3 mL) was added dropwise by syringe over 4 minutes. The stirring solution was left to warm to room temperature overnight. The solvent was removed in vacuo and the solid extracted with anhydrous \( \text{CH}_2\text{Cl}_2 \) (6 mL) before being filtered over Celite. The solvent was reduced and the solution cooled to -35 °C to produce a white precipitate, which was collected by filtration. The white filtrate was then washed with \( n\)-pentane (2 x 2 mL) before removing the solvent in vacuo, producing a white solid (261 mg, 42% yield). Vapour diffusion of \( n\)-pentane into a solution of the compound in dichloromethane yielded X-Ray quality crystals. Anal. Calcd. for \( \text{PC}_{18}\text{F}_{10}\text{Cl}_{10} \): C: 31.03. Found: C: 31.19%.

\[^{19}\text{F}\{^1\text{H}\} \text{NMR} \ (376 \text{ MHz, } \text{C}_6\text{D}_6)\]: \( \delta \) -129.2 to -129.6 (m, 2F, \( o\)-\( \text{C}_6\text{F}_5 \)), -147.5 (tt, \( 3^J_{\text{FF}} = 22 \text{ Hz}, 5^J_{\text{FF}} = 5 \text{ Hz}, 1\text{F}, \ p\)-\( \text{C}_6\text{F}_5 \)), -159.6 to -159.9 (m, 2F, \( m\)-\( \text{C}_6\text{F}_5 \)) ppm.

\(^{31}\text{P}\{^1\text{H}\} \text{NMR} \ (162 \text{ MHz, } \text{C}_6\text{D}_6)\): \( \delta \) -17.8 (t, \( 3^J_{\text{PF}} = 40 \text{ Hz} \)) ppm.

\(^{13}\text{C}\{^1\text{H}\} \text{NMR} \ (125 \text{ MHz, } \text{C}_6\text{D}_6)\): \( \delta \) 147.9 (br d, \( 1^J_{\text{FC}} = 245 \text{ Hz}, \ o\)-\( \text{C}_6\text{F}_5 \)), 143.2 (br d, \( 1^J_{\text{FC}} = 258 \text{ Hz}, \ p\)-\( \text{C}_6\text{F}_5 \)), 137.9 (br d, \( 1^J_{\text{FC}} = 248 \text{ Hz}, \ m\)-\( \text{C}_6\text{F}_5 \)), 137.1 (d, \( 2^J_{\text{PC}} = 21 \text{ Hz}, \ o\)-\( \text{C}_6\text{Cl}_5 \)), 136.4 (s, \( p\)-\( \text{C}_6\text{Cl}_5 \)), 133.6 (s, \( m\)-\( \text{C}_6\text{Cl}_5 \)), 132.4 (d, \( 1^J_{\text{PC}} = 34 \text{ Hz}, \ i\)-\( \text{C}_6\text{Cl}_5 \)), 108.6 (br s, \( i\)-\( \text{C}_6\text{F}_5 \)) ppm.

HRMS (DART Ionization) m/z: [M+H]^+ Calcd. for \( \text{C}_{18}\text{F}_5\text{Cl}_{10}\text{P} \): 692.66213, Found: 692.66280.
$^{31}$P-$^1$H-NMR in C$_6$D$_6$

$^{19}$F-$^1$H-NMR in C$_6$D$_6$
$^{13}$C-NMR in C$_6$D$_6$
(perchlorophenyl)bis(perfluorophenyl) phosphine (2-5). A 250 mL Schlenk flask was charged with C$_6$Cl$_6$ (513 mg, 1.80 mmol), a large magnetic stir-bar and anhydrous Et$_2$O (60 mL), generating a white slurry. The reaction flask was cooled to -15 °C using a dry ice/acetone bath. A hexane solution of 2.5 M $n$-BuLi (0.87 mL, 2.19 mmol) was added dropwise to the stirring solution under an atmosphere of N$_2$; slowly turning the slurry to a clear light yellow solution. The solution was cooled to -78 °C and a solution of P(C$_6$F$_5$)$_2$Br (973 mg, 2.19 mmol) in anhydrous Et$_2$O (6 mL) was added dropwise by syringe over 4 minutes. The stirring solution was left to warm to room temperature overnight. The solvent was removed in vacuo and the solid extracted with anhydrous CH$_2$Cl$_2$ (3 x 5 mL) before being filtered over Celite. The solvent was reduced and the solution recrystallized 3 times at -35 °C to yield a white crystalline solid, which was collected by filtration and then washed with $n$-pentane (2 x 2 mL) before removing the solvent in vacuo, producing a white fluffy solid (263 mg, 20% yield). Vapour diffusion of $n$-pentane into a solution of the compound in dichloromethane yielded X-Ray quality crystals. Anal. Calcd. for C$_{18}$F$_{10}$Cl$_5$P: C: 35.19. Found: C: 35.07%.

$^{19}$F{$_1^1$H} NMR (376 MHz, CDCl$_3$): δ -130.0 to -130.3 (m, 2F, o-C$_6$F$_5$), -148.6 (t br t, $^3$J$_{FF}$ = 21 Hz, $^5$J$_{FF}$ = 4 Hz, 1F, p-C$_6$F$_5$), -159.6 to -159.8 (m, 2F, m-C$_6$F$_5$) ppm.

$^{31}$P{$_1^1$H} NMR (243 MHz, CDCl$_3$): δ -40.8 (p, $^3$J$_{PF}$ = 32 Hz) ppm.

$^{13}$C{$_1^1$H} NMR (125 MHz, C$_6$D$_6$): δ 147.5 (br d, $^1$J$_{FC}$ = 250 Hz, o-C$_6$F$_5$), 142.9 (br d, $^1$J$_{FC}$ = 260 Hz, p-C$_6$F$_5$), 137.8 (d br m, $^1$J$_{FC}$ = 256 Hz, m-C$_6$F$_5$), 138.2 (d, $^2$J$_{PC}$ = 21 Hz, o-C$_6$Cl$_5$), 137.3 (s, p-C$_6$Cl$_5$), 133.5 (s, m-C$_6$Cl$_5$), 129.8 (d, $^1$J$_{PC}$ = 31 Hz, i-C$_6$Cl$_5$), 106.4 (br m, i-C$_6$F$_5$) ppm.

HRMS (DART Ionization) m/z: [M+H]$^+$ Calcd. for C$_{18}$F$_{10}$Cl$_5$P: 612.80988, Found: 612.80757.
$^{31}\text{P}^{(1\text{H})}$-NMR in CDCl$_3$

$^{19}\text{F}^{(1\text{H})}$-NMR in CDCl$_3$
\[ \text{C}_6\text{Cl}_6 \xrightarrow{P} \text{C}_6\text{F}_6 \]

\[ ^{13}\text{C-NMR in CDCl}_3 \]
Difluoro bis(perchlorophenyl)(perfluorophenyl) phosphorane (2-8). In a cold well, a 20 mL vial was charged with \((C_6F_5)_2P(C_6Cl_5)_2\) (228 mg, 0.33 mmol), \(CH_2Cl_2\) (5 mL), and a magnetic stir bar, forming a light yellow solution. XeF\(_2\) (56 mg, 0.33 mmol) was quickly added to the stirring solution which gradually lightens as it was left to stir and warm up to room temperature for 2 hours. The solvent was reduced and the solution cooled to -35 °C to produce a white precipitate, which was collected by filtration. The filtrate was then washed with \(n\)-pentane (2 x 3 mL) before removing the solvent \textit{in vacuo}, producing a white solid (192 mg, 80% yield). Anal. Calcd. for PC\(_{18}\)Cl\(_{10}\)F\(_{7}\): C: 29.43. Found: C: 28.52%.

\(^{19}\)F\textsubscript{\textsuperscript{1}H} NMR (376 MHz, C\(_6\)D\(_5\)Br): \(\delta -10.9\) (dm, \(^1J_{PF} = 756\) Hz, PF\(_2\)), -129.2 to -129.6 (m, 2F, \(\alpha\)-C\(_6\)F\(_5\)), -145.9 (t, \(^3J_{PF} = 22\) Hz, 1F, \(p\)-C\(_6\)F\(_5\)), -158.5 to -158.7 (m, 2F, \(m\)-C\(_6\)F\(_5\)) ppm.

\(^{31}\)P\textsubscript{\textsuperscript{1}H} NMR (162 MHz, C\(_6\)D\(_5\)Br): \(\delta -41.2\) (t, \(^1J_{PF} = 757\) Hz) ppm.

\(^{13}\)C\textsubscript{\textsuperscript{1}H} NMR (125 MHz, C\(_6\)D\(_5\)Br): \(\delta 146.5\) (br d, \(^1J_{FC} = 254\) Hz, \(\alpha\)-C\(_6\)F\(_5\)), 143.9 (br d, \(^1J_{FC} = 259\) Hz, \(p\)-C\(_6\)F\(_5\)), 137.9 (br dm, \(^1J_{FC} = 255\) Hz, \(m\)-C\(_6\)F\(_5\)), 136.9 (d, \(^4J_{PC} = 4\) Hz, \(p\)-C\(_6\)Cl\(_5\)), 135.0 (br d, \(^2J_{PC} = 264\) Hz, \(\alpha\)-C\(_6\)Cl\(_5\)), 134.5 (dt, \(^1J_{PC} = 217\) Hz, \(^2J_{PC} = 29\) Hz, \(i\)-C\(_6\)Cl\(_5\)), 134.5 (dm, \(^3J_{PC} = 18\) Hz, \(m\)-C\(_6\)Cl\(_5\)), 113.0 (br dm, \(^1J_{PC} = 201\) Hz, \(i\)-C\(_6\)F\(_5\)) ppm.
$^{19}$F-$^1$H-NMR in C$_6$D$_5$Br

$^{13}$C-NMR in C$_6$D$_5$Br
**Difluoro (perchlorophenyl)bis(perfluorophenyl) phosphorane (2-9).** In a cold well, a 20 mL vial was charged with \((\text{C}_6\text{F}_5)_2\text{P(C}_6\text{Cl}_5)\) (241 mg, 0.39 mmol), \(\text{CH}_2\text{Cl}_2\) (5 mL), and a magnetic stir bar, forming a light grey solution. \(\text{XeF}_2\) (56 mg, 0.33 mmol) was quickly added to the stirring solution which gradually lightened as it was left to stir and warm up to room temperature for 2 hours. The solvent was reduced and the solution cooled to -35 °C to produce clear crystalline needles, which were collected by filtration. The filtrate was then washed with \(n\)-pentane (2 x 3 mL) before removing the solvent in vacuo, producing a white solid (96 mg, 37% yield). Vapour diffusion of \(n\)-pentane into a solution of the compound in dichloromethane yielded X-Ray quality crystals

Analyzed. Calcd. for \(\text{PC}_{18}\text{Cl}_5\text{F}_{12}\): C: 33.14. Found: C: 33.13%.

\(^{19}\text{F}\{^1\text{H}\}\) NMR (564 MHz, CDCl\(_3\)): δ -6.4 (dm, \(\text{J}_{\text{PF}} = 725 \text{ Hz}, \text{PF}_2\)), -128.3 (s, 1F, \(\text{o-C}_6\text{F}_5\)), -132.3 (s, 1F, \(\text{o-C}_6\text{F}_5\)), -146.0 (t, \(\text{J}_{\text{FF}} = 20 \text{ Hz}, 1\text{F}, \text{p-C}_6\text{F}_5\)), -158.9 (d, \(\text{J}_{\text{FF}} = 78 \text{ Hz}, 2\text{F}, \text{m-C}_6\text{F}_5\)) ppm.

\(^{31}\text{P}\{^1\text{H}\}\) NMR (243 MHz, CDCl\(_3\)): δ -44.6 (t, \(\text{J}_{\text{PF}} = 725 \text{ Hz}\)) ppm.

\(^{13}\text{C}\{^1\text{H}\}\) NMR (125 MHz, CDCl\(_3\)): δ 146.6 (br d, \(\text{J}_{\text{FC}} = 254 \text{ Hz}, \text{o-C}_6\text{F}_5\)), 146.0 (br d, \(\text{J}_{\text{FC}} = 256 \text{ Hz}, \text{o-C}_6\text{F}_5\)), 144.1 (br d, \(\text{J}_{\text{FC}} = 258 \text{ Hz}, \text{p-C}_6\text{F}_5\)), 137.9 (br dm, \(\text{J}_{\text{FC}} = 255 \text{ Hz}, \text{m-C}_6\text{F}_5\)), 137.9 (d, \(\text{J}_{\text{PC}} = 4 \text{ Hz}, \text{p-C}_6\text{Cl}_5\)), 134.5 (d, \(\text{J}_{\text{PC}} = 18 \text{ Hz}, \text{o-C}_6\text{Cl}_5\)), 133.9 (br s, \(\text{m-C}_6\text{Cl}_5\)), 133.4 (dt, \(\text{J}_{\text{PC}} = 223 \text{ Hz}, \text{J}_{\text{FC}} = 31 \text{ Hz}, \text{i-C}_6\text{Cl}_5\)), 111.0 (br dm, \(\text{J}_{\text{PC}} = 201 \text{ Hz}, \text{i-C}_6\text{F}_5\)) ppm.
Fluoro bis(perchlorophenyl)(perfluorophenyl)phosphonium tetrakis(perfluorophenyl) borate (2-12). A 20 mL vial was charged with (C₆Cl₅)₂PF₂(C₆F₅) (172 mg, 0.23 mmol), toluene (5 mL), and a magnetic stir bar. To the stirring solution, [Et₃Si][B(C₆F₅)₄] (197 mg, 0.22 mmol) was added as a solid. The clear solution was stirred for an hour, before allowing it to settle. Upon settling, a brown oil collected at the bottom of the vial, leaving a clear supernatant. After decanting the toluene from the oil, additional toluene (2 x 3 mL) was used to wash the oil before being decanted off. The oil was triturated in n-pentane (4 mL) until an off-white solid was formed. The solid was subsequently washed with n-pentane (2 x 4 mL) before removing the solvent in-vacuo resulting in an off-white solid (229 mg, 74% yield). Anal. Calcd. for PC₄₂Cl₁₀F₂₆B: C: 36.17. Found: C: 37.21%

³¹P{¹H} NMR (162 MHz, C₆D₅Br): δ 71.0 (d, JₚF = 1031 Hz) ppm.

¹⁹F{¹H} NMR (377 MHz, C₆D₅Br): δ -117.0 (dd, J⁺F = 1030 Hz, J₋F = 26 Hz, 1F, PF), -123.4 (br s, 1F, P(o-C₆F₅)), -124.7 (m, 1F, P(p-C₆F₅)), -126.8 (br s, 1F, P(o-C₆F₅)), -132.2 (m/br, 8F, B(o-C₆F₅)), -150.4 (br s, 1F, P(m-C₆F₅)), -162.4 (t, J₋F = 21 Hz, 4F, B(p-C₆F₅)), -166.4 (m/br, 8F, B(m-C₆F₅)) ppm.

¹¹B NMR (128 MHz, CD₂Cl₂): -16.6 (s) ppm.

¹³C{¹H} NMR (125 MHz, CDCI₃): δ 150.6 (br d, J_FC = 277 Hz, P(o-C₆F₅)), 148.3 (br d, J_FC = 241 Hz, B(o-C₆F₅)), 147.1 (d, J_FC = 3 Hz, P(p-C₆Cl₅)), 139.4 (br d, J_FC = 269 Hz, P(p-C₆F₅)), 138.3 (br d, J_FC = 241 Hz, B(p-C₆F₅)), 137.7 (d, J_FC = 15 Hz, P(m-C₆Cl₅)), 136.7 (d, J_FC = 6 Hz, P(o-C₆Cl₅)), 136.4 (br d, J_FC = 235 Hz, B(m-C₆F₅)), 134.9 (br d, J_FC = 260 Hz, P(m-C₆F₅)), 124.0 br s, B(i-C₆F₅)), 116.3 (dd, J_FC = 144Hz, J_FC = 10 Hz, P(i-C₆Cl₅)), 95.8 (br d, J_FC = 137 Hz, P(i-C₆F₅)) ppm.

HRMS (DART Ionization) m/z: [M]+ Calcd. for C₁₈F₆Cl₁₀P: 710.65271, Found 710.65339.
$^{31}$P($^1$H)-NMR in C$_6$D$_3$Br

$^{19}$F($^1$H)-NMR in C$_6$D$_3$Br
$^{11}$B-NMR in C$_6$D$_5$Br

$^{13}$C-NMR in CDCl$_3$
Fluoro ( perchlorophenyl) bis(perfluorophenyl) phosphonium tetrakis(perfluorophenyl) borate (2-13). A 20 mL vial was charged with (C₆Cl₅)PF₂(C₆F₅)₂ (96 mg, 0.15 mmol), toluene (2 mL), and a magnetic stir bar. To the stirring solution, [Et₃Si][B(C₆F₅)₄] (124 mg, 0.14 mmol) was added as a solid. The clear solution was stirred for 3 hours, before allowing it to settle. Upon settling, a brown oil collected at the bottom of the vial, leaving a clear supernatant. After decanting the toluene from the oil, additional toluene (2 x 2 mL) was used to wash the oil before being decanted off. The oil was triturated in n-pentane (4 mL) until an off-white solid was formed. The solid was subsequently washed with n-pentane (2 x 2 mL) before removing the solvent in vacuo resulting in a white solid (179 mg, 98% yield). Vapour diffusion of n-pentane into a solution of the compound in dichloromethane yielded X-Ray quality crystals. Anal. Calcd. for PC₄₂Cl₅F₃₁B: C: 38.44 Found: C: 40.04%

³¹P{¹H} NMR (243 MHz, CDCl₃): δ 66.3 (d, J₉F = 1043 Hz) ppm.

¹⁹F{¹H} NMR (564 MHz, CDCl₃): δ -112.1 (br dm, J₉F = 1042, 1F, PF), -123.1 (br m, 2F, P(p-C₆F₅)), -125.3 (br s, 4F, P(o-C₆F₅)), -133.1 (br s, 8F, B(o-C₆F₅)), -149.9 (br m, P(m-C₆F₅)), -163.2 (t, J₉F = 20 Hz, 4F, B(p-C₆F₅)), -166.43 (br t, J₉F = 17 Hz, 8F, B(m-C₆F₅)) ppm.

¹¹B NMR (128 MHz, CDCl₃): -16.7 (s) ppm.

¹³C{¹H} NMR: Inability to obtain due to poor solubility in all common organic NMR solvents.

HRMS (DART Ionization) m/z: [M]+ Calcd. for C₁₈F₁₁Cl₅P: 630.80046, Found 630.80130.
$^{19}$F\( (^{1}H) \)-NMR in CDCl₃

$^{11}$B-NMR in CDCl₃
2.4.3 Reactions of Pentachlorophenyl-Substituted Phosphonium Cations

**Gutmann Beckett test:** The reaction of 2-11 with Et₃PO was meant to gauge the phosphonium cation’s Lewis acidity by way of a shift in the $^{31}$P NMR spectrum, and as such no isolated product was obtained or characterized.

In a 20 mL vial, 2-11 (25 mg, 22 µmol) was dissolved in CH₂Cl₂ (1 mL). Et₃PO (1 mg, 7 µmol) was added to the clear solution. The reaction was monitored by $^{31}$P{¹H} NMR spectroscopy.

**Friedel-Crafts cyclodimerization of 1,1-diphenylethylene reactions:** All F. C. cyclodimerization reactions were performed in an analogous manner and therefore only one reaction is described in detail. In a 20 mL vial, a solution of 1,1-diphenylethylene (13.8 mg, 77 µmol) in C₆D₅Br (0.7 mL) was added onto 5 mol% of the catalyst 2-10 (4.4 mg, 3.9 µmol) at ambient temperature. The sample was transferred to a 5 mm diameter NMR tube and allowed to react for the desired time while being monitored by $¹$H NMR spectroscopy, giving 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene as the product: $¹$H NMR (500 MHz, C₆D₅Br): δ = 6.92 - 7.22 (m, 19H, Ar-H), 3.33 (d, $³$J_HH = 13 Hz, 1H, CH₂), 3.00 (d, $³$J_HH = 13 Hz, 1H, CH₂), 1.48 (s, 3H, CH₃) ppm.

**Hydrodefluorination of 1-fluoroadamantane reactions:** All hydrodefluorination reactions were performed in an analogous manner and therefore only one reaction is described in detail. In a 20 mL vial, a solution of 1-fluoroadamantane (6.6 mg, 43 µmol) and Et₃SiH (6.0 mg, 52 µmol) in C₆D₅Br (0.7 mL) was added onto 5 mol% of the catalyst 2-12 (3.0 mg, 2.2 µmol). The reaction was taken up in a 5 mm diameter NMR tube and monitored by multinuclear NMR spectroscopy at ambient temperature until reaction completion which afforded adamantane as the product: $¹$H NMR (500 MHz, C₆D₅Br): δ = 1.71 (br s, 4H), 1.58 - 1.60 (m, 12H); $¹³$C{¹H} NMR (C₆D₅Br, 125 MHz): δ 37.6, 28.3 ppm.

**Hydrodeoxygenation of benzophenone reactions:** All hydrodeoxygenation reactions were performed in an analogous manner and therefore only one reaction is described in detail. In a 20 mL vial, a solution of benzophenone (9.2 mg, 50 µmol) and Et₃SiH (14.0 mg, 120 µmol) in C₆D₅Br (0.7 mL) was added onto 5 mol% of the catalyst 2-13 (3.3 mg, 2.5 µmol) at ambient temperature. The sample was transferred to a 5 mm diameter NMR tube and allowed to react for the desired time at the desired temperature while being monitored by multi NMR spectroscopy, giving
diphenylmethane as the product: \(^1\text{H NMR}\) (400 MHz, \(\text{C}_6\text{D}_5\text{Br}\)): \(\delta\) 7.12 – 7.18 (m, 4H, \(m\)-\(\text{C}_6\text{H}_5\)), 7.04 – 7.11 (m, 6H, \(o\)-, \(p\)-\(\text{C}_6\text{H}_5\)), 3.81 (s, \(\text{CH}_2\)) ppm; \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (\(\text{C}_6\text{D}_5\text{Br}\), 125 MHz): \(\delta\) 140.9, 128.8, 128.3, 125.9, 41.8 ppm.

### Dehydrocoupling of phenol with \(\text{Et}_3\text{SiH}\) reactions:
All dehydrocoupling reactions were performed in an analogous manner and therefore only one reaction is described in detail. In a 20 mL vial, a solution of phenol (5.0 mg, 53 \(\mu\)mol) and \(\text{Et}_3\text{SiH}\) (6.2 mg, 53 \(\mu\)mol) in \(\text{C}_6\text{D}_5\text{Br}\) (0.7 mL) was added onto 5 mol\% of the catalyst 2-12 (3.7 mg, 2.7 \(\mu\)mol) at ambient temperature. The sample was transferred to a 5 mm diameter NMR tube and allowed to react for the desired time at the desired temperature while being monitored by \(^1\text{H NMR}\) spectroscopy, giving triethyl(phenoxysilane as the product: \(^1\text{H NMR}\) (400 MHz, \(\text{C}_6\text{D}_5\text{Br}\)): \(\delta\) 7.13 – 7.18 ppm (m, 2H; \(o\)-\(\text{C}_6\text{H}_5\)), 6.85 – 6.91 (m, 3H; \(m\)-, \(p\)-\(\text{C}_6\text{H}_5\)), 0.96 (t, \(^3\text{J}_{\text{HH}} = 8\) Hz, 9H; \(\text{CH}_3\)), 0.67 (q, \(^3\text{J}_{\text{HH}} = 8\) Hz, 6H; \(\text{CH}_2\)) ppm.

### Hydrosilylation of \(\alpha\)-methylstyrene reactions:
All hydrosilylation reactions were performed in an analogous manner and therefore only one reaction is described in detail. In a 20 mL vial, a solution of \(\alpha\)-methylstyrene (6.1 mg, 52 \(\mu\)mol) and \(\text{Et}_3\text{SiH}\) (6.0 mg, 52 \(\mu\)mol) in \(\text{C}_6\text{D}_5\text{Br}\) (0.7 mL) was added onto 5 mol\% of the catalyst 2-12 (3.6 mg, 2.6 \(\mu\)mol) at ambient temperature. The sample was transferred to a 5 mm diameter NMR tube and allowed to react for the desired time at the desired temperature while being monitored by \(^1\text{H NMR}\) spectroscopy, giving triethyl(2-phenylpropyl)silane as the product: \(^1\text{H NMR}\) (400 MHz, \(\text{C}_6\text{D}_5\text{Br}\)): \(\delta\) 7.13 – 7.23 (m, 4H; \(o\)-, \(m\)-\(\text{C}_6\text{H}_5\)), 7.06 - 7.12 (m, 1H; \(p\)-\(\text{C}_6\text{H}_5\)), 2.76 – 2.87 (m, 1H; \(\text{CH}\)), 1.23 (d, \(^3\text{J}_{\text{HH}} = 7\) Hz, 3H; \(\text{CH}_3\)), 0.91 – 0.98 (m, 2H; \(\text{CH}_2\)), 0.86 (t, \(^3\text{J}_{\text{HH}} = 8\) Hz, 9H; \(\text{SiCH}_2\text{CH}_3\)), 0.31 – 0.46 (m, 6H; \(\text{SiCH}_2\)) ppm.

### 1-bromo-4-(trifluoromethyl)benzene Friedel Crafts reactions:
All F. C. reactions were performed similarly and therefore only one reaction is described in detail. In a 20 mL vial, a solution of 1-bromo-4-(trifluoromethyl)benzene (7.7 mg, 34 \(\mu\)mol) and \(\text{Et}_3\text{SiH}\) (14.4 mg, 124 \(\mu\)mol) in \(\text{C}_6\text{D}_6\) (0.7 mL) was added onto 5 mol\% of the catalyst 2-12 (2.4 mg, 1.7 \(\mu\)mol) at ambient temperature. The sample was transferred to a 5 mm diameter NMR tube and allowed to react for the desired time at the desired temperature while being monitored by \(^1\text{H NMR}\) spectroscopy, giving 1-(4-bromobenzyl)benzene-2,3,4,5,6-ds as the product: \(^1\text{H NMR}\) (400 MHz, \(\text{C}_6\text{D}_6\)): \(\delta\) = 7.17 – 7.21 (m, 2H, \(m\)-\(\text{C}_6\text{H}_5\)), 6.61 – 6.66 (m, 2H, \(o\)-\(\text{C}_6\text{H}_5\)), 3.52 (s, 2H, \(\text{CH}_2\)) ppm.
2.4.4 Collection, Reduction, Solution, and Refinement of X-Ray Data

Single crystals were coated with Paratone-N oil, and mounted using a glass fibre pin under a cold N\textsubscript{2} stream. Data sets were collected on a Bruker Kappa Apex II CCD X-ray diffractometer using a graphite monochromator with MoK\textsubscript{α} 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 reduction was performed using the Bruker SMART software package and data sets were corrected for absorption effects using the SADABS routine (empirical multi-scan method). The structures were solved by direct methods using XS and refined by full-matrix. Least-squares on F\textsuperscript{2} using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically unless otherwise noted. Hydrogen atoms bonded to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.
Table 2.4.1: Crystallographic data for compounds 2-1, 2-4, 2-5, and 2-6

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<th>2-5</th>
<th>2-6</th>
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<td>C\textsubscript{18}Cl\textsubscript{5}F\textsubscript{10}P</td>
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<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
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Table 2.4.2: Crystallographic data for compounds, 2-9, 2-11, Perchlorobiphenyl, and 1,1,2,2-tetrakis(perchlorophenyldiphosphine

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Chapter 3
Phosphenium Cations

3.1 Introduction

Phosphenium cation chemistry has also garnered much interest over the last few decades. Phosphenium cations can be defined as P(III) species possessing an empty π orbital, a lone pair of electrons, and a localized positive charge on the P atom. One of the initial reports of phosphenium cations came over five decades ago from Dimroth and Hoffmann in 1964, wherein the development of P(III) phosphacyanines was detailed. Several years later both cyclic and acyclic phosphenium cations were developed, all of which possessed a stabilizing donor.

The reactivity of phosphenium cations can be thought of as stemming from two possible representations of the species, one in which the 3p orbital is filled by a pair of electrons from a donor, and the other in which it remains empty – drawing a parallel to the singlet carbene (Figure 3.1.1). Thus, though the species is electrophilic, Lewis basicity can be exhibited by the lone pair on the P atom.

Figure 3.1.1. Representation of phosphenium cation 3p orbitals and lone pair (left and middle) and singlet state carbene 2p orbitals and lone pair (right)

The cyclic phosphenium cations that were developed in the 1970’s from halide abstraction of diaminohalophosphines became known as N-heterocyclic phosphenisium cations (NHPs), and are isovalent with N-heterocyclic carbenes (NHCs) (Figure 3.1.2). Both NHPs and NHCs have been used extensively as ligands for coordination chemistry and it is interesting to note that although isovalent, NHPs have inverse electronic properties to NHCs, with strong π-acceptor and weak σ-donation characters, compared with NHCs’ strong σ-donation and weak π-acceptor capacities, and a multitude of metals have been used for a variety of chemistries. That is to say, NHPs are more Lewis acidic.
Another class of phosphonium compounds have been developed by the Burford and Ragogna groups, wherein ‘phosphine-phosphonium cations’ have been synthesized by cleavage of the halogen-phosphorus bond and ligand exchange reactions.\(^{109,110}\)

![Diagram of N-heterocyclic phosphonium cations (NHPs) and N-heterocyclic carbenes (NHCs)](image)

**Figure 3.1.2** Representation of \(N\)-heterocyclic phosphonium cations (NHPs) and \(N\)-heterocyclic carbenes (NHCs)

Although these types of P(III) phosphonium cations have exhibited some small molecule reactivity with DCM, water, and isopropanol,\(^{111}\) another type of phosphonium cations that has proven to be electrophilic is a class of carbone stabilized phosphonium salts. An example of some mono cationic and dicationic NHC-stabilized phosphonium salts come from the Weigand group.\(^{112}\) Recently Alcarazo and coworkers have also synthesized the first tricationic carbene-stabilized phosphonium salt and used it as a ligand for platinum chemistry demonstrating that the consequent increased \(\pi\)-acidity at Pt can be harnessed to activate alkynes towards nucleophilic attack.\(^{113}\)

NHC-stabilized phosphonium salts have been used by our group as precursors to phosphonium dications of the type \([\text{SIMes}PFR_2]^{2+}\), \(R = \text{Me, Et, Ph}\), via oxidation with \(\text{XeF}_2\) and fluoride ion abstraction with \([\text{Et}_3\text{Si}][\text{B(C}_6\text{F}_5)_4]\). These dicationic salts have been shown to perform as competent Lewis acid catalysts in some of the reactions explored in **Section 2.2.4**, especially \([\text{SIMes}PFPh_2]^{2+}\).\(^{54,114}\) The preceding phosphonium ions were tested and screened as control reactions alongside the phosphonium dications, but could not effect any reactivity, likely due to an inherent lack of Lewis acidity.

It was of interest to see if increasing the Lewis acidity of an NHC-stabilized phosphonium cation, with \(\text{C}_6\text{F}_5\) groups, as observed in **Chapter 2**, would allow for the possibility of Lewis acid catalysis with phosphonium ions. It was also of related interest to subsequently attempt development of a more reactive dicationic phosphonium species, to be isolated and characterized, which could be employed as a superior Lewis acid catalyst to the related dicationic ones currently available.
3.2 Results and Discussion

3.2.1 Synthesis of Electrophilic Phosphenium Cations

Efforts to replicate the synthesis of the cationic [(SIMes)PPh₂]+ species (Scheme 3.2.1) by adding equimolar amounts of 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp) and P(C₆F₅)₂Br (or P(C₆F₅)₂Cl) together in toluene proved challenging. A bright yellow oil forms upon addition, and the reaction proved to be extremely sensitive to factors such as temperature, reaction time, and concentration, with room temperature reactions allowed to react over 12 hours being most selective. Success in solidifying the oil into a powder upon workup varied depending on the conditions chosen. To avoid issues regarding the variability of oil formation, PhBr was chosen as the reaction solvent, and although the solution became homogenous, evidence for the formation of multiple products was evident by ¹⁹F NMR spectroscopy. Gratifyingly, precipitating the ionic product out of solution by adding a solution of the carbene in n-pentane, to a stirring dilute solution of the halophosphine in n-pentane at room temperature over the course of five minutes generated a single product as a white powder in 87% yield upon workup. The ³¹P{¹H} NMR spectrum displayed a quintet at -76.2 ppm with ³JPF = 46 Hz in CDCl₃, and the ¹⁹F{¹H} spectrum displayed three resonances consistent with the C₆F₅ moieties. The ortho-fluorine atoms of the rings appeared as a broad singlet, suggesting restricted rotation. The ¹H NMR spectrum was consistent with an incorporated IDipp group, and indeed, vapour diffusion of n-pentane into a DCM solution of the product yielded X-ray quality crystals, confirming the molecular structure of 3-1 as [(IDipp)P(C₆F₅)₂][Br] (Two views shown in Figure 3.2.1) (Scheme 3.2.2). At the time of writing, this is believed to be the first structurally characterized NHC-stabilized phosphenium cation incorporating C₆F₅ groups into its structure. In the solid-state the compound possesses a pseudo trigonal pyramidal geometry with a sum of angles about the P atom of 310.57 (0.20)° and a bond length of 1.8369(26) Å between the P and the ipso-carbon atom of the imidazolylidene.
Scheme 3.2.1 Synthesis of SIMes-stabilized phosphenium cation

Scheme 3.2.2 Synthesis of IDipp-stabilized phosphenium cation 3-1

Figure 3.2.1. POV-ray depictions of 3-1; C: black, P: orange, F: pink, N: blue, Br: red, H-atoms omitted for clarity
Variable temperature $^{19}\text{F}\{^{1}\text{H}\}$ NMR studies (Figure 3.2.2) were performed in DCM to probe the exhibited restricted rotation of 3-1. The stacked spectra showcase separation of the two resonances for the ortho-fluorine atoms at low temperatures as well as for the two resonances for the meta-fluorine atoms, and coalescence of both at higher temperatures, indicative of restricted rotation around the P-C bond of the pentafluorophenyl rings. This is further supported by the $^{31}\text{P}\{^{1}\text{H}\}$ VT NMR studies (Figure 3.2.3) where a quintet is observed at room temperature and what appears to be a triplet of triplets is noted at -70 °C, but what is more likely a complex splitting of doublet of doublets. This restricted rotation on the NMR time scale arises from the bulk that the IDipp group imparts, leading to an increased energy barrier to rotation of the pentafluorophenyl rings.

![Figure 3.2.2. VT $^{19}\text{F}\{^{1}\text{H}\}$ NMR studies on compound 3-1](image-url)
With the methodology established to synthesize phosphonium cation [(IDipp)P(C₆F₅)₂][Br] cleanly and reproducibly, a more non-coordinating anion was sought to replace the bromide ion before subsequent reactivity could be pursued. This would also circumvent any possibility of Br⁻ acting as a nucleophile. The counter-anion [OTf⁻] is often avoided as it tends to limit catalytic reactivity in EPCs, presumably due to coordination of oxygen to the P centre of the reactive species, and is thus generally replaced by the non-coordinating [B(C₆F₅)₄].

Attempting the counter-anion exchange reaction several times between 3-1 and 0.95 eq. [Et₃Si][B(C₆F₅)₄] in toluene yielded once more an oil whose NMR parameters were not as selective as desired in that a mixture of products was observed. Another [B(C₆F₅)₄]⁻ source was tried, [K][B(C₆F₅)₄], but its reaction with 3-1 in DCM proved messy due to the insolubility of [K][B(C₆F₅)₄] in the solvent. Other solvents proved unsuccessful as well. Another source of the borate counter-anion that has salt elimination as its driving force for counter-anion exchange is [Ag][B(C₆F₅)₄]. Although difficult to handle due to its extreme light sensitivity, reacting an equimolar amount of [Ag][B(C₆F₅)₄] with 3-1 in DCM in the dark overnight yielded a clean
product by $^{19}$F{$^1$H}, $^{31}$P{$^1$H} and $^1$H NMR spectroscopies as an orange solid in 85% yield upon workup. The $^{31}$P{$^1$H} NMR spectrum in CDCl$_3$ displayed a quintet at -76.3 ppm with $^3$J$_{PF}$ = 46 Hz, almost identical to 3-1. The $^{19}$F{$^1$H} NMR spectrum displayed the expected resonances for a borate counter-anion, and the three signals for the two C$_6$F$_5$ substituents on P, in which the resonance for the ortho-fluorine atoms manifested itself as broad singlet as before. $^{31}$P{$^1$H}, $^{19}$F{$^1$H}, and $^1$H VT NMR studies in C$_6$D$_5$Br were conducted to once again demonstrate the restricted rotation exhibited in the system. The stacked $^{19}$F{$^1$H} NMR spectra (Figure 3.2.4) reveal coalescence of the ortho-fluorine peaks and sharpening of the meta-fluorine signals at higher temperatures suggesting restricted rotation around the P-C bond is evident once more. The stacked $^1$H NMR spectra (Figure 3.2.5) demonstrate sharpening of the four methine protons, as well as the two sets of 12 methyl protons at higher temperatures, lending further evidence to this claim. The low-temperature NMR spectra are nearly identical to the low-temperature NMR spectra of 3-1 and are thus not shown. Mass spectrometry and elemental analysis support the NMR data and the formulation of 3-2 as the product [(IDipp)P(C$_6$F$_5$)$_2$][B(C$_6$F$_5$)$_4$] (Scheme 3.2.3).

Scheme 3.2.3 Counter-anion exchange reaction affording 3-2

An attempt to synthesize [(SIMes)P(C$_6$F$_5$)$_2$]$^+$ by analogous methodology proved less successful. A solution of SIMes in n-pentane was treated in the same fashion as IDipp, and reacted in an equimolar fashion with a dilute stirring solution of P(C$_6$F$_5$)$_2$Br in n-pentane, yielding a white powder upon similar workup to 3-1. The major product in the $^{31}$P{$^1$H} NMR spectrum of the compound in CDCl$_3$ displayed a quintet centred at -72.0 ppm with $^3$J$_{PF}$ = 50 Hz. The major product in the $^{19}$F{$^1$H} NMR spectrum had three resonances consistent with the C$_6$F$_5$ moieties analogous
to 3-1 and 3-2 with the ortho-fluorine signals being a very broad singlet likely indicating restricted rotation as well. The $^1$H NMR spectrum was consistent with SIMes being incorporated into the phosphonium cation. The NMR parameters of the major product give evidence towards the formation of [(SIMes)P(C$_6$F$_5$)$_2$][Br] but this reaction proved to be more sensitive than the IDipp analogue, and optimization of conditions to isolate a clean product are still elusive.

![VT $^{19}$F/$^1$H NMR studies on compound 3-2](image)

**Figure 3.2.4.** VT $^{19}$F/$^1$H NMR studies on compound 3-2
3.2.2 Reactivity of Phosphenium Cations

With 3-2 in hand, oxidation to the corresponding difluorophosphorane was then attempted with XeF₂. An equimolar amount XeF₂ was reacted with 3-2 in DCM, yielding a yellow solid upon workup. The major product in the "P{¹H} NMR spectrum displayed a broad doublet centered at 11.3 ppm with a coupling constant of 1064 Hz, more reminiscent of the splitting and coupling constant of a phosphonium cation or phosphine oxide species than a phosphorane. The F{¹H} NMR spectrum displayed a broad doublet of quintets centered at -54.3 ppm with the same coupling constant as well as J_FF = 22 Hz. The rest of the spectrum displayed many more undefined resonances. The major peak in the B NMR spectrum was a sharp singlet at -1.2 ppm instead of the expected borate signal around -17.0 ppm of the counter-anion. Attempts to purify or modify reaction conditions proved unsuccessful. It is possible that initial oxidation with XeF₂ forms a very reactive species which decomposes – possibly due to reaction with glass, consistent with a phosphine oxide – in a short period of time.
However, due to the increased electron-deficiency at the P centre, it was of interest to see if the phosphonium species 3-1 and 3-2 would be capable of performing as Lewis acid catalysts themselves. Thus, the same test reactions in Section 2.2.4 were probed using 5 mol% of 3-1 and 3-2. All reaction conditions are analogous to those employed in Section 2.2.4, and all analyses of spectra are the same. The results are summarized in Table 3.2.1.

The Friedel-Crafts cyclodimerization was attempted using 5 mol% of 3-1 but was unsuccessful even with heating in the span of days, whereas 5 mol% of 3-2 was able to catalyze the reaction to 70% conversion by $^1$H NMR after 48 hours at room temperature. Heating the reaction did not show signs of accelerated conversion. This moderate conversion after two days suggested the species was not a very strong Lewis acid, but subsequent reactivity was still sought out. A stark difference between 3-1 and 3-2 is evident by $^1$H NMR, where the $^1$H signal for the imidazolylidene two backbone protons comes at 8.96 ppm in the case of 3-1 in CDCl$_3$, and 7.66 ppm in the case of 3-2. In the molecular structure of 3-1 the Br-P and Br-H (backbone) bond distances are about 9.71 Å and 8.69 Å. This could suggest that the bromide counter-anion is not as non-coordinating in solution as the solid state structure implies, and that the difference in reactivity between 3-1 and 3-2 is likely due to this stronger coordination of the bromide counter-anion which translates to halted reactivity for 3-1. As such, all subsequent reactivity was performed with 5 mol% of 3-2.

The hydrodefluorination of 1-fluoroadamantane with Et$_3$SiH proceeded cleanly and fully in 10 minutes at room temperature affording adamantane as the product, with loss of Et$_3$SiF. The hydrodeoxygenation of benzophenone with Et$_3$SiH was catalyzed to completion in 13 h at 140 °C affording diphenylmethane.

The dehydrocoupling of phenol with Et$_3$SiH proceeded to 51% conversion in 14 h at 140 °C by $^1$H NMR spectroscopy, whereas the hydrosilylation of $\alpha$-methylstyrene and Friedel-Crafts reactivity of 1-bromo-4-(trifluoromethyl)benzene only showed minimal signs of conversion despite being heated for days at 140 °C by $^1$H NMR analysis. Most of the catalyst remains intact as observed by $^{31}$P, $^{19}$F, and $^1$H NMR spectroscopies throughout the majority of these catalytic runs despite the elevated temperatures.
Table 3.2.1. Summary of Catalytic Activity

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Conditions</th>
<th>Products</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 phenyl-1,1-diphenylethene</td>
<td>cat. 5 mol%</td>
<td>PhBr, r.t.</td>
<td></td>
<td></td>
<td>3-2: 70% 48 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CDCl₃, r.t.</td>
<td>1.0 eq. Et₃SiH</td>
<td></td>
<td>3-1: No reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3-2: 10 min</td>
</tr>
<tr>
<td>2 cyclohexene</td>
<td>cat. 5 mol%</td>
<td></td>
<td></td>
<td></td>
<td>3-2: 13 h, 140 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3-2: 51% in 14 h, 140 °C</td>
</tr>
<tr>
<td>2 benzyl alcohol</td>
<td>cat. 5 mol%</td>
<td>PhBr, r.t.</td>
<td>1.0 eq. Et₃SiH</td>
<td></td>
<td>3-2: No reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3-2: No reaction</td>
</tr>
</tbody>
</table>

To further glean insight into this reactivity, calculations* were performed to visualize the HOMO, LUMO, and LUMO + 1 orbitals of the phosphenium cation at the B3LYP/6-311G(d,p) basis set level.

*Calculations performed by Levy Cao
It can be seen from Figure 3.2.6 that the HOMO is primarily localized on the central phosphorus atom, and is filled with the lone pair of electrons on the P. The LUMO seen in Figure 3.2.7 appears to be delocalized over the N-C atoms of the imidazolylidene backbone, whereas the LUMO + 1 observed in Figure 3.2.8 appears to be somewhat centred on the ipso-carbon of the backbone. It is difficult to say how much physical significance these molecular orbital representations hold for this species but are suggestive of the P atom not being the site of Lewis acidity in the phosphonium cation as it is in the case of the phosphonium cation. Rather it would seem that the ‘site’ of Lewis acidity is delocalized about the imidazolylidene ring. Nevertheless, the results of the catalysis indicate considerable Lewis acidity on the P atom.

Figure 3.2.6. Representation of the HOMO of 3-2
Figure 3.2.7. Representation of the LUMO of 3-2

Figure 3.2.8. Representation of the LUMO + 1 of 3-2
Without further mechanistic and computational studies it is difficult to say what and how the catalysis proceeds. It is possible that \([\text{Et}_3\text{Si}]^+\) is generated during the course of the reaction, especially at elevated temperatures, and this species is known to behave as a Lewis acid and catalyze similar reactivity.\(^9\)

Lastly, analogous to the air stability tests of Section 2.2.4, a sample of \(3-2\) in a solution of PhBr was transferred to a 5 mm diameter NMR tube. The sample was taken out of the glovebox and opened to air for successively longer intervals. The solution was recapped and shaken between recordings of the NMR spectra in order to avoid issues related to diffusion. The sample was monitored by \(^{19}\text{F}\{^1\text{H}\} \) and \(^1\text{H}\) NMR spectroscopies for signs of hydrolysis. After four days of such testing, no signs of degradation were evident.

### 3.3 Conclusions

Two IDipp-stabilized pentafluorophenyl-substituted phosphonium cations with [Br\(^-\)] and [B(C\(_6\)F\(_5\))\(_4\)]\(^-\) as the counter-anions were synthesized and characterized.

Not oxidizing cleanly with XeF\(_2\), the Lewis acid capacity of the phosphonium cations was examined in a series of prototypical Lewis acid catalyzed reactions at 5 mol\% catalyst loading. Due to the possible complications with the bromide counter-anion in \(3-1\), only \(3-2\) was used for the full catalytic scope. \(3-2\) was shown to have some capacity to perform as a Lewis acid, especially as seen from the hydrodefluorination of 1-fluoroadamantane, though further studies and controls are needed to discern how the catalysis proceeds. Calculations on the HOMO, LUMO, and LUMO + 1 molecular orbitals suggest that the site of Lewis acidity is not localized around the P atom of the phosphonium cation as is the case for the phosphonium cation, but rather more delocalized about the imidazolylidene ring.

The phosphonium cation \(3-2\) has also qualitatively been shown to be air stable in a solution of PhBr over the course of four days.
3.4 Experimental Section

3.4.1 General considerations

All manipulations were performed in a Glove box MB Unilab produced by MBraun (equipped with a -35 °C freezer). All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (CH$_2$Cl$_2$, Et$_2$O, toluene, and n-pentane) were dried using an Innovative Technologies solvent purification system, degassed, and stored over 4 Å molecular sieves before use. C$_6$D$_6$, CDCl$_3$ and C$_6$D$_5$Br (Aldrich) were deoxygenated and stored over 4 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, Apollo Scientific, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. [Ag][B(C$_6$F$_5$)$_4$]·(C$_7$H$_8$)$_3$ was prepared either via the reported procedure$^{115}$ or by reaction of [Et$_3$Si][B(C$_6$F$_5$)$_4$]·(C$_7$H$_8$) with [Ag][OTf] in toluene in the dark followed by removal of excess toluene and [Et$_3$Si][OTf] in vacuo. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian NMR system 400 MHz spectrometer, Agilent DD2-500 MHz spectrometer, or Agilent DD2-600 MHz spectrometer. All NMR experiments were conducted at a temperature of 25 °C unless otherwise stated. $^1$H NMR data, referenced to residual solvent resonances relative to external SiMe$_4$, are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), normalized integrals. $^{13}$C{$^1$H} NMR chemical shifts (δ) are referenced to external SiMe$_4$. Other nuclei are referenced relative to an external standard ($^{11}$B: (Et$_2$O)BF$_3$, $^{19}$F: CFCl$_3$, $^{31}$P: 85% H$_3$PO$_4$). 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.
3.4.2 Synthesis of Compounds

\[
\begin{align*}
\text{[IDipp]P(C}_6\text{F}_5)_2[\text{Br}] \quad \text{(3-1). A 20 mL vial was charged with P(C}_6\text{F}_5)_2\text{Br} \\
(59 \text{ mg, 133 } \mu\text{mol}), \text{ a magnetic stir-bar and anhydrous } n\text{-pentane (5 mL). In} \\
\text{a separate vial 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp) } \quad \text{(52 mg, 133 } \mu\text{mol) was fully dissolved in} \\
n\text{-pentane (7 mL) and added} \\
dropwise over 5 minutes to the stirring clear solution generating a white slurry. After an additional 5 minutes the mixture was put on a fine glass frit and washed with benzene (3 x 1 mL) and } n\text{-pentane (5 x 1 mL). The solid imidazolylidene stabilized phosphonium salt product was collected as a white powder (96 mg, 87\% yield). Vapour diffusion of } n\text{-pentane into a solution of the compound in dichloromethane yielded X-Ray quality crystals. Anal. Calcd. for C}_{39}\text{H}_{36}\text{BrF}_{10}\text{N}_2\text{P: C: 56.19, H: 4.35, N: 3.36 Found: C: 57.35\%, H: 4.74\%, N: 3.06\%.}
\end{align*}
\]

\(^1\text{H NMR (500 MHz, CDCl_3): } \delta 8.96 (d, ^4J_{PH} = 1 \text{ Hz, 2H, } N\text{-CH}), 7.49 (t, ^3J_{HH} = 8 \text{ Hz, 2H, } p\text{-Dipp}), \quad \text{7.22 (d, } ^3J_{HH} = 8 \text{ Hz, 4H, } m\text{-Dipp}), \quad 2.48 (\text{sept, } ^3J_{HH} = 7 \text{ Hz, 4H, CH}), \quad 1.24 (d, ^3J_{HH} = 7 \text{ Hz, 12H, CH}_3), \quad 1.23 (d, ^3J_{HH} = 7 \text{ Hz, 12H, CH}_3) \text{ ppm.}
\]

\(^{19}\text{F}'{^1}\text{H}} \text{ NMR (376 MHz, CDCl}_3\text{): } \delta -124.2 (\text{br s, } 4\text{F, } o\text{-C}_6\text{F}_5), \quad -141.8 (t, ^3J_{FF} = 20 \text{ Hz, 2F, } p\text{-C}_6\text{F}_5), \quad -156.6 \text{ to } -156.8 (\text{m, } 4\text{F, } m\text{-C}_6\text{F}_5) \text{ ppm.}
\]

\(^{31}\text{P}'{^1}\text{H}} \text{ NMR (162 MHz, CDCl}_3\text{): } \delta -76.2 (\text{quin, } ^3J_{PF} = 46 \text{ Hz}) \text{ ppm.}
\]

\(^{13}\text{C}'{^1}\text{H}} \text{ NMR (125 MHz, CDCl}_3\text{): } \delta 147.7 (\text{br d, } ^1J_{FC} = 253 \text{ Hz, } o\text{-C}_6\text{F}_5), \quad 145.7 (\text{s, } o\text{-Dipp}), \quad 144.5 (\text{br d, } ^1J_{FC} = 264 \text{ Hz, } p\text{-C}_6\text{F}_5), \quad 137.8 (\text{br d, } ^1J_{FC} = 257 \text{ Hz, } m\text{-C}_6\text{F}_5), \quad 139.9 (\text{br d, } ^1J_{FC} = 48 \text{ Hz, PCN}), \quad 133.3 (\text{s, } p\text{-Dipp}), \quad 132.9 (\text{s, } m\text{-Dipp}), \quad 130.0 (\text{s, } i\text{-Dipp}), \quad 124.9 (\text{s, } NCH), \quad 100.5 (\text{br s, } i\text{-C}_6\text{F}_5), \quad 29.8 (\text{s, } \text{CH}), \quad 27.1 (\text{s, } \text{CH}_3), \quad 21.6 (\text{s, } \text{CH}_3) \text{ ppm.}
\]

HRMS (ESI+ Ionization) m/z: [M]^+ Calcd. for C_{39}H_{36}F_{10}N_2P: 753.2451, Found: 753.2453.
$\text{Dipp} \quad \text{Br} \quad \text{Dipp}$

$\text{C}_6\text{F}_5$

$\text{C}_6\text{F}_5$

$^1\text{H-NMR in CDCl}_3$

$\text{f1 (ppm)}$

$1.27 \quad 1.26 \quad 1.25 \quad 1.24 \quad 1.23 \quad 1.22 \quad 1.21 \quad 1.20$

$8.98 \quad 8.97 \quad 8.96 \quad 8.95 \quad 8.94 \quad 8.93$

$\text{f1 (ppm)}$

$2.00 \quad 2.02 \quad 4.03 \quad 4.06 \quad 11.63 \quad 11.66$

$\text{f1 (ppm)}$

$-156.2 \quad -156.6 \quad -157.0 \quad -157.4$

$\text{f1 (ppm)}$

$3.32 \quad 2.00 \quad 3.74$
$^{31}$P$\left(^1\text{H}\right)$-NMR in CDCl$_3$

$^{13}$C$\left(^1\text{H}\right)$-NMR in CDCl$_3$
[(Dipp)P(C₆F₅)₂][B(C₆F₅)₄] (3-2). [Ag][B(C₆F₅)₄]·(C₇H₈)₃ (43 mg, 40 µmol) was dissolved in DCM (1 mL) with the aid of a magnetic stir bar in a 20 mL vial wrapped in tinfoil in the dark. To it, a solution of 3-1 (34 mg, 41 µmol) in DCM (2 mL) was added rapidly. The reaction was allowed to proceed overnight. The yellow solution was then filtered over a Celite plug, solvent was removed in vacuo resulting in an orange oil which was subsequently washed with n-pentane (3 x 4 mL). The solvent was removed in vacuo yielding the imidazolylidene stabilized phosphonium salt product as an orange solid (49 mg, 85% yield). Anal. Calcd. for C₆₃H₆₆BF₃₀N₂P: C: 52.81, H: 2.53, N: 1.96 Found: C: 53.14%, H: 2.58%, N: 1.61%.

¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, ⁴JₚH = 1 Hz, 2H, N-CH), 7.56 (t, ³JₜH = 8 Hz, 2H, p-Dipp), 7.28 (d, ³JₜH = 8 Hz, 4H, m-Dipp), 2.44 (sept, ³JₜH = 7 Hz, 4H, CH), 1.28 (d, ³JₜH = 7 Hz, 12H, CH₃), 1.11 (d, ³JₜH = 7 Hz, 12H, CH₃) ppm.

¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -124.0 (br s, 4F, P(o-C₆F₅)), -132.7 (m/br, 8F, B(o-C₆F₅)), -140.3 (t, ³JₚF = 20 Hz, 2F, P(p-C₆F₅)), -155.8 to -156.0 (m, 4F, P(m-C₆F₅)), -163.0 (t, ³JₚF = 21 Hz, 4F, B(p-C₆F₅)), -166.9 (m/br, 8F, B(m-C₆F₅)) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ -76.3 (quin, ³JₚF = 46 Hz) ppm.

¹¹B NMR (128 MHz, CDCl₃): δ -16.7 (s) ppm.

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 148.2 (br d, ¹J.FC = 242 Hz, B(o-C₆F₅)), 147.7 (br d, ¹J.FC = 252 Hz, P(o-C₆F₅)), 145.4 (s, o-Dipp), 144.9 (br d, ¹J.FC = 266 Hz, P(p-C₆F₅)), 138.2 (br d, ¹J.FC = 231 Hz, P(m-C₆F₅)), 137.1 (br d, ¹J.FC = 48 Hz, PCN), 136.3 (br d, ¹J.FC = 242 Hz, B(p-C₆F₅)), 133.6 (s, p-Dipp), 129.4 (s, i-Dipp), 129.3 (s, m-Dipp), 125.3 (s, NCH), 123.9 (br s, B(i-C₆F₅)), 99.8 (br s, P(i-C₆F₅)), 29.8 (s, CH), 26.5 (s, CH₃), 21.4 (s, CH₃) ppm.

HRMS (DART Ionization) m/z: [M]+ Calcd. for C₃₀H₃₆F₁₀N₂P: 753.24564, Found: 753.24523.
$^{1}H$-NMR in CDCl$_3$

$^{19}F$($^{1}H$)-NMR in CDCl$_3$
$^{31}P\left(^1H\right)$-NMR in CDCl$_3$

$^{11}B$-NMR in CDCl$_3$
$^1$H-NMR in CDCl$_3$
3.4.3 Collection, Reduction, Solution, and Refinement of X-Ray Data

Single crystals were coated with Paratone-N oil, and mounted using a glass fibre pin under a cold N\textsubscript{2} stream. Data sets were collected on a Bruker Kappa Apex II CCD X-ray diffractometer using a graphite monochromator with MoK\textsubscript{α} 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 reduction was performed using the Bruker SMART software package and data sets were corrected for absorption effects using the SADABS routine (empirical multi-scan method). The structures were solved by direct methods using XS and refined by full-matrix. Least-squares on F\textsuperscript{2} using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically unless otherwise noted. Hydrogen atoms bonded to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

**Table 3.4.1: Crystallographic Data for Compound 3-1**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Z</th>
<th>Wt.</th>
<th>Cryst. syst.</th>
<th>Space group</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V(Å\text.superscript{3})</th>
<th>µ, mm\textsuperscript{-1}</th>
<th>R(int)</th>
<th>R(&gt;2σ)</th>
<th>R\textsubscript{w}</th>
<th>GOOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{39}H\textsubscript{36}BrF\textsubscript{10}N\textsubscript{2}P•(CH\textsubscript{2}Cl\textsubscript{2})</td>
<td>4</td>
<td>918.50</td>
<td>Monoclinic</td>
<td>P\textsubscript{2}\textsubscript{1}/n</td>
<td>16.2129(11)</td>
<td>13.1419(9)</td>
<td>19.3227(12)</td>
<td>90</td>
<td>100.335(2)</td>
<td>90</td>
<td>4050.3(5)</td>
<td>1.265</td>
<td>0.0391</td>
<td>9334</td>
<td>0.0402</td>
<td>0.0854</td>
</tr>
</tbody>
</table>
Chapter 4
Conclusions

4.1 Thesis Summary
This thesis has examined the use of pentachlorophenyl substituents as a means to develop air stable phosphonium cations capable of performing as Lewis acid catalysts and as Lewis acids in FLP-type reactions.

Fluorophosphonium cations of the form $[(C_{6}Cl_{5})_{n}PFPh_{3-n}][B(C_{6}F_{5})_{4}]$ and $[(C_{6}Cl_{5})_{n}PF(C_{6}F_{5})_{3-n}][B(C_{6}F_{5})_{4}]$ ($n = 1, 2$) were synthesized from their precursor difluorophosphoranes and phosphines, and have shown to be competent Lewis acid catalysts in a host of prototypical reactions. These reactions include: hydrodefluorination, hydrodeoxygenation, hydrosilylation, dehydrocoupling, and Friedel-Crafts type reactions. The reactivity trend discovered was $[(C_{6}Cl_{5})PF(C_{6}F_{5})_{2}]^+ > [(C_{6}Cl_{5})_{2}PF(C_{6}F_{5})]^+ > [(C_{6}Cl_{5})_{2}PFPh]^+ > [(C_{6}Cl_{5})PFPh_{2}]^+$. Qualitative air stability testing was also undertaken with a solution of each of the fluorophosphonium species in $C_{6}H_{5}Br$ being exposed to air for successively longer intervals, uncovering the following trend for the onset of hydrolysis – from most to least stable: $[(C_{6}Cl_{5})_{2}PFPh]^+ > [(C_{6}Cl_{5})PFPh_{2}]^+ > [(C_{6}Cl_{5})_{2}PF(C_{6}F_{5})]^+ > [(C_{6}Cl_{5})PF(C_{6}F_{5})_{2}]^+$. These trends suggest that: (1) A $C_{6}F_{5}$ substituent enhances Lewis acidity to a greater degree than a $C_{6}Cl_{5}$ or a phenyl substituent but this comes at the expense of air stability. (2) The steric protection offered by the ortho-chlorine atoms of a $C_{6}Cl_{5}$ moiety are a viable approach to air stability via protection of the P-F bond. (3) $C_{6}Cl_{5}$ groups enhance Lewis acidity compared to phenyl substituents and also increase the air stability of the fluorophosphonium cation due to the added steric protection.

Efforts to form FLPs of $[(C_{6}Cl_{5})_{2}PFPh]^+$ and $[(C_{6}Cl_{5})PFPh_{2}]^+$ with the weakly Lewis basic PPh$_3$ or TMP in order to activate $H_2$ or $CO_2$ were unsuccessful. Reacting the stronger Lewis bases P(t-Bu)$_3$ or triisopropyl proazaphosphatrane yielded a mixture of unidentifiable products, and were not conducive to FLP reactivity.

The thesis has also examined the development of pentafluorophenyl-substituted NHC-stabilized phosphenium cations and their viability as Lewis acid catalysts.
The phosphenium compounds $[(\text{IDipp})\text{P}(\text{C}_6\text{F}_5)_2]\text{[Br]}$ and $[(\text{IDipp})\text{P}(\text{C}_6\text{F}_5)_2]\text{[B(\text{C}_6\text{F}_5)_4]}$ were synthesized and characterized. Attempts to oxidize the latter to a difluorophosphorane were unsuccessful. $[(\text{IDipp})\text{P}(\text{C}_6\text{F}_5)_2]\text{[B(\text{C}_6\text{F}_5)_4]}$ has also shown some capacity in the reactions outlined above, most notably in hydrodefluorination, hydrodeoxygenation, and Friedel-Crafts cyclodimerization reactivity, whereas the former was unsuccessful as a Lewis acid catalyst likely due to the more coordinating nature of the bromide counter-anion. $[(\text{IDipp})\text{P}(\text{C}_6\text{F}_5)_2]\text{[B(\text{C}_6\text{F}_5)_4]}$ has also qualitatively been shown to be air stable in a solution of $\text{C}_6\text{D}_5\text{Br}$ that has been exposed to air for four days.

More insight is needed into the mechanism of the reactivity of the phosphenium species, and calculations on the HOMO, LUMO, and LUMO + 1 molecular orbitals suggest that the site of Lewis acidity is not localized around the P atom but rather more delocalized about the imidazolylidene ring. Future theoretical and experimental work can focus on uncovering the nature of the observed catalysis.
4.2 Future Work

Further attempts to synthesize the dication [(IDipp)PF\((C_6F_5)_2\)][B(C_6F_5)_4] could be attempted utilizing various electrophilic fluorinating reagents such as: Selectfluor, \(N\)-fluorobenzenesulfonylimide (NFSI), \(N\)-fluoro-\(o\)-benzenedisulfonylimide (NFOBS), and \(N\)-Fluoropyridinium triflate. This would effectively bypass the need to abstract a fluorine from the corresponding difluorophosphorane. Subsequently, Lewis acidity and reactivity testing could be performed on the dication species; this dication would have the potential to be a very strong Lewis acid.

Synthesizing and isolating [(SIMes)P\((C_6F_5)_2\)][B(C_6F_5)_4] cleanly with a slightly modified version of the established methodology developed for the IDipp analog detailed in this thesis seems plausible. The possibility of developing the fluorophosphonium dication from this species would then serve as a direct comparison to the established highly Lewis acidic [(SIMes)PFPh\(_2\)][B(C_6F_5)_4] developed by our group. It would have a strong chance to surpass its capacity as a Lewis acid catalyst, given its employment of the highly electron withdrawing \(C_6F_5\) groups, allowing perhaps for more facile reactivity.

It would also be of interest to develop a family of carbene-stabilized phosphenium cations, perhaps containing \(C_6F_5\) groups as were developed in this thesis, in order to study their structural components such as changes to their bond lengths, geometries, and NMR parameters, before utilizing them as ligands in designing metal catalysts.

Further mechanistic and computational studies are needed to understand the reactivity of [(IDipp)P\((C_6F_5)_2\)][B(C_6F_5)_4] as a Lewis acid, and would aid in uncovering the prospect of a new class of catalysis, one that is performed by a P(III) compound.
References


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