Exploring the Synthesis and Reactivity of Phosphinoboranes and Organophosphorus-based Lewis Acids

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemistry
University of Toronto

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2019

Abstract

Advances in main group chemistry are challenging the status of the transition metals. Small-molecule activations necessary in many catalytic reactions have traditionally been the province of the transition metals owing to their large atomic radii, available d-orbital electrons, vacant coordination sites, and accessible orbital energies. Increasingly however, main group species are being discovered with accessible donor and acceptor sites capable of activating small molecules in analogous and complementary reactions to the transition metals. The first portion of this thesis explores the synthesis of phosphinoboranes and their reactivity towards a number of small molecules: acyl phosphone and chloroborane synthesis was achieved from reactions with benzoyl chloride, reactions with carbon dioxide produced single addition and diphospha-urea products, and addition reactions were observed with diazomethanes and diazobenzene. In the latter case, subsequent intramolecular frustrated Lewis pair chemistry of addition products with Lewis basic substrates yielded unique heterocyclic rings.

Main group chemistry has also made progress in Lewis acid catalysis, where transition metals have traditionally been applied. Synthetic strategies for attaching highly electron-withdrawing substituents to main group element centres and the design of weakly coordinating anions have led to the development of main group Lewis super acids. The second part of this thesis explores the design and reactivity of phosphonium Lewis acids: fluorine-substituted phenoxy rings were applied to achieve more robust yet reactive compounds, a phenoxyphosphonium salt derivative was subsequently used to catalyze the double hydroarylation of diarylamines with alkynes, and steric considerations of the C₆F₅ group were compared to the 3,5-(CF₃)₂C₆H₃ group. Additionally, the development of main group Lewis acids containing ligands originally designed for transition
metals have demonstrated stability, selectivity, and reactivity. The third part of this thesis explores the synthesis and hemilabile reactivity of diiminopyridine, bipyridine, and terpyridine ligated phosphorus-based Lewis acids towards the catalytic allylation of aliphatic carbon-fluorine bonds.
This work is dedicated to my parents,

*Gordon and Sandra LaFortune*

in recognition of their contributions to my academic career.
Acknowledgements

From the outset I’d like to thank my parents Gordon and Sandra LaFortune for their love, support, and encouragement over the years. I’d also like to thank Kelsey Young for her love, support, patience, and joy through the peaks and valleys of graduate school.

I am very grateful to my supervisor Prof. Doug Stephan for his enthusiasm and support and for letting me pursue whatever projects I found interesting. I’d also like to thank my examination committee Prof. Thomas Baumgartner, Prof. Bob Morris, Prof. Datong Song, and Prof. Mark Taylor for their guidance and kindness.

I’d like to thank all of my collaborators for sharing chemistry with me. I’d particularly like to recognize Prof. Steve Westcott, Steve Geier, and Chris Vogels for their help and encouragement in the phosphinoboration projects as well as my undergraduate students Alina Trofimova, Haley Cummings, Farah Farinha, and Cathy Yao and my high school student Remi Free. I’ve had the great fortune of working with enthusiastic, talented, and fun people.

I’d like to thank the Stephan group, both past and present. Despite being a big and constantly rotating roster, it’s always been a good group of colleagues and friends. The movie, beer, and boardgame nights, the Flakey Peaches climbing crew, the Banana Cream Pie curling crew, and the squirrels made the lab more than just a workplace. Specific thanks go out to Shawn Postle for making my cover art and to Tim Johnstone for sharing so much of his time and love of chemistry with me. I’d also like to thank Shawn Postle, Jolie Lam, Diya Zhu, Chris Major, Leo Liu, Jiliang Zhou, and Kevin Szkop for editing chapters of my thesis.

I am grateful to the NMR facilities staff Darcy Burns, Jack Sheng, Karl Demmans, Shawn Postle, and Sergiy Nokhrin for designing experiments for me and for being so welcoming, the departmental crystallographer Alan Lough for helping me learn to use and troubleshoot the X-ray diffractometer, the AIMS lab staff Matthew Forbes and Fung Chung Woo for letting me constantly barrage them with requests and follow-ups, the ANALEST staff member Rose Balazs for her elemental analysis expertise, and the support of the whole Chemistry Department’s administrative staff.

This Ph.D. was not done alone and I appreciate everyone’s help along the way.
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<td>electron affinity</td>
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<tr>
<td>Å</td>
<td>angstrom, $10^{-10}$ m</td>
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<tr>
<td>AN</td>
<td>Gutmann-Beckett acceptor number</td>
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<td>atmosphere</td>
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<td>alpha</td>
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d doublet
D3 Dispersion damping function 3
Def2-SVP default2-single valence polarized
Def2-TZVPP default2-triple zeta valence polarized polarized
Def2-QZVP default2-quadruple zeta valence polarized
DART direct analysis in real time
DCE 1,2-dichloroethane
DCM dichloromethane
Dip 2,6-diisopropylphenyl
DippIminopyridine (1E,1'E)-1,1'-(pyridine-2,6-diyl)bis(N-(2,6-diisopropylphenyl)ethan-1-imine
DMSO dimethylsulfoxide
Dur 2,3,5,6-tetramethylphenyl
δ delta, chemical shift
Δ delta, difference
Δ delta, heat
ΔH change in enthalpy
EA elemental analysis
EI electron ionization
EPC electrophilic phosphonium cation
ESI electrospray ionization
Et ethyl
eq equivalent
Eqn equation
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<td>EXSY</td>
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<td>fluoride ion affinity</td>
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<tr>
<td>FLP</td>
<td>frustrated Lewis pair</td>
</tr>
<tr>
<td>$f^*(\rho)$</td>
<td>Fukui function for the addition of an electron to a molecule</td>
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<td>G</td>
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<td>GC-MS</td>
<td>gas chromatography-mass spectrometry</td>
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<td>GEI</td>
<td>global electrophilicity index</td>
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<td>h</td>
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<tr>
<td>HIA</td>
<td>hydride ion affinity</td>
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<tr>
<td>HMBC</td>
<td>heteronuclear multiple bond correlation</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
</tr>
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<td>heteronuclear single quantum coherence</td>
</tr>
<tr>
<td>$hv$</td>
<td>light</td>
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<tr>
<td>Hz</td>
<td>hertz</td>
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<tr>
<td>I</td>
<td>ionization energy</td>
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<tr>
<td>IMes</td>
<td>1,3-Dimesitylimidazol-2-ylidene</td>
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<td>iPr</td>
<td>isopropyl</td>
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<td>infrared spectroscopy</td>
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<td>IRC</td>
<td>intrinsic reaction coordinate</td>
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<tr>
<td>$^nJ_{xy}$</td>
<td>n-bond scalar coupling between nuclei x and y</td>
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<tr>
<td>$k$</td>
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Chapter 1

Introduction

1.1 Moving to the Main Group

Modern society’s needs and luxuries come from the manipulation of raw materials – from chemistry. The use of raw materials has grown significantly with increased demands for consumer goods. This has prompted several reports outlining “endangered elements” that are predicted to become at risk due to limited supply or their extraction becoming economically nonviable.\(^1\)\(^-\)\(^4\) While recycling of materials and improving their efficiencies and lifetimes are productive approaches to addressing these issues, the development of methods using alternative elements to satisfy the needs of “endangered elements” remains an ideal goal. Lists of “endangered elements” include some main group elements, many of the rare earth elements, and many of the transition metals such as platinum, rhodium, palladium, osmium, and iridium, which are used as catalysts in the pharmaceuticals and fine chemicals industries.\(^5\)\(^-\)\(^7\) In addition to being “endangered elements,” these metals are expensive\(^8\) and generally pose toxicity concerns – their removal from drugs is both challenging and costly.\(^9\),\(^10\) While iron is a reasonable replacement in various applications, as it is not considered endangered or particularly toxic and its chemistry has seen remarkable growth,\(^11\) main group species are becoming increasingly viable alternatives.\(^12\)\(^-\)\(^15\)

1.2 Brief Introduction to Phosphorus

Phosphorus, meaning light-bearing, is a non-metallic p-block element belonging to the group 15 pnictogens. It was first isolated by Brand in 1669 from the distillation of urine, yielding a white solid that glowed in the dark and combusted in air. The red and black allotropes of phosphorus were later discovered by Von Schrotter in 1848 and by Bridgman in 1914,\(^16\) respectively. Though urine was the only source of phosphorus for nearly 100 years, it was later isolated from bones and subsequently from minerals including apatites. The Earth’s crust is estimated to contain 0.1% by weight of phosphorus, making it the 11\(^{th}\) most abundant element ahead of carbon in the 12\(^{th}\) place.\(^17\)

The history of phosphorus-containing compounds has been sordid. Exposure to white phosphorus leads to phossy jaw,\(^18\) phosphorus-based nerve agents including sarin gas were researched in World War II,\(^19\) and white and red phosphorus remain controlled substances in the U.S.A. for their use in the production of methamphetamine.\(^20\) Nevertheless, phosphorus is essential to all life and
is present in lipids, bones, teeth, blood, and nucleic acids.\textsuperscript{21, 22} The global demand for phosphorus is 20 million tonnes per year, 90\% of which is used as fertilizer.\textsuperscript{3} The irreplaceability of phosphorus in fertilizers and the inefficiency of current fertilization techniques has caused phosphorus to be considered an “endangered element,” although efforts are being made to address the latter issue.\textsuperscript{3}

The synthesis of organophosphorus compounds begins with the processing of mineral ores such as fluorapatite at 800 to 1200 °C in the presence of sand and coke to yield white phosphorus. Subsequent reactions with elemental chlorine or bromine yield phosphorus trichloride or phosphorus tribromide, respectively (Scheme 1.1).\textsuperscript{17, 23} These and other halophosphines are used as starting materials in a wide variety of reactions to produce organophosphorus compounds.

![Scheme 1.1 Syntheses of white phosphorus from fluorapatite (top) and phosphorus trichloride and phosphorus tribromide from white phosphorus (bottom).](image)

The chemistry of organophosphorus compounds is very rich. Phosphorus’ oxidation states range from -3 to +5 and it has a maximum coordination of six. While phosphorus has been applied in materials\textsuperscript{24} and polymers\textsuperscript{25} chemistry, trivalent organophosphorus compounds are commonly used as Lewis basic ligands to tune reactivity and selectivity in organometallic complexes.\textsuperscript{17} Their strongly σ-donating and weakly π-accepting electronic influences can be tuned by changing the electron donating or withdrawing ability of the substituents on the phosphine, with variations also impacting the ligands’ steric demands. Tolman quantified these effects with the Tolman electronic parameter (TEP), derived from the IR stretching frequency of the carbonyl groups in Ni(CO)\textsubscript{3}PR\textsubscript{3},\textsuperscript{26} and with the Tolman cone angle, measured as the apex angle of a cylindrical cone.
centred 2.28 Å from the phosphorus atom which just touches the van der Waals radii of the outermost atoms on phosphorus’ substituents.\(^{27}\)

Organophosphorus species are also known to be Lewis acidic. Phosphenium cations are two-coordinate phosphorus compounds stabilized by π-donor substituents with a vacant \(p\)-orbital and a lone pair of electrons, and thus are isolobal and isoelectronic with singlet carbenes. As such, they also display both Lewis acidic and basic character. While their Lewis basic character was first demonstrated by Cowley,\(^ {28}\) Paine,\(^ {29}\) and Parry\(^ {30}\) in reports of phosphenium ligands in organometallic salt complexes, their Lewis acidic character was first demonstrated by Parry when a mixture of \([(\text{NMe}_2)_2\text{P}][\text{AlCl}_4]\) and \((\text{NMe}_2)_3\text{P}\) was found to form an adduct.\(^ {31}\) Cowley\(^ {32}\) and Baxter\(^ {33}\) subsequently reported reactions of 1,3-dienes with phosphenium cations resulting from the ambiphilic nature of the phosphorus centre (Scheme 1.2). Kinjo has recently reported the use of a phosphenium cation as a Lewis acid catalyst in the hydroboration of pyridines.\(^ {34}\)

\[
\begin{align*}
\text{[PF}_6\text{]} & \quad + \quad \text{Fe(CO)}_5 \\
\text{[PF}_6\text{]} & \quad -\text{CO}
\end{align*}
\]

\[
\begin{align*}
\text{[AlCl}_4\text{]} & \quad + \quad \text{[N+P:N]} \\
\text{[AlCl}_4\text{]}
\end{align*}
\]

\[
\begin{align*}
\text{[AlCl}_4\text{]} & \quad + \quad \text{[N+P:N]} \\
\text{[AlCl}_4\text{]}
\end{align*}
\]

**Scheme 1.2** Examples of Lewis basic (top), Lewis acidic (middle), and ambiphilic (bottom) character of phosphenium cations.
Another ambiphilic phosphorus species is phosphinidene, a mono-valent phosphorus atom with two lone pairs and a vacant orbital. While triplet phosphinidenes are generally unstable, Bertrand reported the synthesis of a singlet phosphinidene with the use of very sterically bulky and electron donating substituents and demonstrated its ambiphilic reactivity. Both Lewis acidity and basicity at a phosphorus centre has also been achieved in strained species. By distorting the geometry about a three-coordinate phosphorus centre from pyramidal to distorted square pyramidal, Radosevich was able to make both the lone pair of electrons and the LUMO accessible to substrates. In reactivity analogous to transition metals (vide infra), this strained trivalent phosphorus species was seen to effect transfer hydrogenation from ammonia borane to diazobenzene to produce the diphenylhydrazine through a pentavalent dihydridophosphorane intermediate (Scheme 1.3).

![Scheme 1.3](image)

Scheme 1.3 Catalytic two-electron redox reaction of a P(III)/P(V) redox species.

Radosevich has since expanded this approach to include other strained substituents to similar effect. Recently, Radosevich has also applied a strained geometry to pentavalent phosphonium cations. In this case, distortion from the standard pseudo tetrahedral geometry to a square pyramidal geometry is achieved with the use of a planar four-coordinate corrole ligand. The resulting five-coordinate phosphacorroles were found to be robust, tunable, and catalytically active Lewis acids (Figure 1.1).
1.3 Phosphonium Salts as Organocatalysts

While organophosphorus compounds are ubiquitous Lewis bases in metal-catalyzed organic reactions, their application in Lewis acid catalysis is relatively underexplored. One of the earliest examples of Lewis acidic pentavalent phosphorus (P(V)) reactivity was Wittig’s stoichiometric use of electrophilic phosphorus ylides to convert aldehydes and ketones to alkenes (Scheme 1.4).\(^41, 42\) Shortly thereafter, the Lewis acidity of neutral P(V) species was demonstrated by their ability to form stable adducts with a variety of Lewis basic substrates.\(^43\)

Since these early reports, research in phosphorus-based Lewis acids has focused primarily on phosphonium salts – four-coordinate P(V) species bearing a positive charge. These easily accessible Lewis acidic cations are able to participate in hypervalent interactions with Lewis basic
substrates through a σ* orbital on the phosphorus centre. This orbital is made energetically accessible by the electron-deficient nature of the cationic phosphorus centre and the hypervalent interaction is further stabilized when an electron-withdrawing substituent occupies the axial position on the phosphorus centre (Scheme 1.5).

![Scheme 1.5 Phosphonium cation adduct formation](image)

Interest in phosphonium salts as organocatalysts has led to the development of many different salts (Scheme 1.6) with applications in a broad scope of reactions. While the groups of Lee and Szu have applied \([\text{Ph}_3\text{PCH}_2\text{C(O)Me}][\text{Br}]\) to catalyze the protection of alcohols as substituted ethers, the addition of TMSCN to aldehydes catalyzed by \([\text{Ph}_3\text{PMe}][\text{I}]\) and \([\text{Ph}_3\text{PBn}][\text{Cl}]\) was reported by the groups of Plumet and Tian, respectively. The Diels-Alder reaction of α,β-unsaturated amides and cyclopentadiene with several catechol-containing phosphonium salts was reported by Kouchi. Various phosphonium salts have also been applied to the catalytic insertion of \(\text{CO}_2\) into oxiranes.

Dicationic diphosphonium salts of the form \([\text{R}_3\text{POPR}_3][\text{OTf}]_2\) (R = Ph, Bu) have been used by Kouichi and Shigekazu to catalyze Aldol and Michael reactions of carbonyl compounds as well as reactions of imines with ketene silyl acetals. Phosphonium salts have also found importance as a class of ionic liquids and have been used by the groups of Robertson, Andersen, and Karodia as both solvent and Lewis acid catalyst for Henry nitroaldol reactions, hydroformylation, transfer hydrogenation, and Diels-Alder reactions. Further, Sasson has applied alumina- and silica-supported molten alkyl phosphonium salts to catalyze gas phase halogen exchange between alkyl chlorides and alkyl bromides. Auner recently demonstrated the catalytic cleavage of disilanes by \([n\text{Bu}_4\text{P}][\text{Cl}]\) while Suga reported that \([(4\text{-MeOC}_6\text{H}_4)_4\text{P}][\text{I}]\) catalyzes the cyclization reaction of glycidol with isocyanates. It should be noted that these species are all weakly Lewis acidic as the electron-deficiency at phosphorus is primarily derived only from its cationic charge.
1.4 Brief Introduction to Boron

Boron, meaning white, is a metalloid p-block element belonging to the group 13 triels or icosagens. Its first uses date back to antiquity, with the boron-containing mineral borax being used to make glazes, glass, and used in the working of gold.\textsuperscript{66} Impure elemental boron was first discovered in 1808 by Gay-Lussac and Thénard from electrolysis of wet boric acid and independently by Davy from heating reactions of boric acid with potassium metal.\textsuperscript{67, 68} It was not until 1909 that pure boron was isolated by Weintraub from the reaction of boron halides with hydrogen gas.\textsuperscript{69} Since then, other methods have been developed and a multitude of boron allotropes have been synthesized, the most recent of which are B\textsubscript{12} and B\textsubscript{2} as reported by Oganov.\textsuperscript{70} Boron is the 40\textsuperscript{th} most abundant element on the Earth’s crust and is isolated from borax and kernite. Boron is necessary for the nutrition of plants and is an essential ingredient in glass and ceramics. For the latter application, and because it is only found in high concentrations in few places, it is considered an “endangered element.”\textsuperscript{3}

Preparation of organoboron starting materials is a multistep process (Scheme 1.7). First, borax is reacted with sulfuric acid above 750 °C to produce boron oxide which is then reacted at high
temperature with reducing metals to yield elemental boron. While elemental boron reacts with F₂ at ambient temperature to yield BF₃, elevated temperatures of 400 and 600 °C are required to promote reactions with Cl₂ and Br₂ to give BCl₃ and BBr₃, respectively. Subsequent reactions with sodium, lithium, or aluminum hydride produce diborane B₂H₆. These haloboranes and diborane are used as starting materials in the synthesis of other organoboron reagents.⁶⁶

\[
\text{[Na]₂[B₄O₅(OH)₄] + H₂SO₂} \xrightarrow{\Delta} 2 \text{ eq B}_2\text{O}_3 + \text{ Na}_2\text{SO}_₄ + 3 \text{ eq H}_₂\text{O}
\]

\[
2 \text{ eq B} + 3 \text{ eq } X₂ \xrightarrow{X = F, X = Cl, 400 °C; X = Br, 600 °C} 2 \text{ eq BX₃}
\]

\[
8 \text{ eq BF₃} + 6 \text{ eq LiH} \xrightarrow{\text{NaOH, -NaI}} \text{ B}_2\text{H}_₆ + 6 \text{ eq LiBF}_₄
\]

Scheme 1.7 Syntheses of organoboron precursors.

The chemistry of organoboron compounds is also rich, with boron having four coordination sites and oxidation states ranging from -5 to +3, however three- or four-coordinate neutral or negatively charged species are the most common. While organoboron reagents have found extensive use in cross couplings and hydroborations,⁷¹ neutral three-coordinate boranes are also ubiquitous as Lewis acids, finding use as catalysts in a broad scope of reactions (Scheme 1.8, Scheme 1.9).⁷², ⁷³ Their Lewis acidity is derived from a vacant \(p\)-orbital at the boron centre that can be made more accessible with reduced sterics about the boron centre and increased electron withdrawing ability of the substituents. Of particular note is B(C₆F₅)₃, a strong Lewis acid catalyst due to the electron withdrawing perfluorophenyl rings. B(C₆F₅)₃ has gained significant attention lately, especially in the context of frustrated Lewis pair chemistry pioneered by Stephan and Erker.⁷⁴, ⁷⁵

\[
\text{Ph} + \text{Octyl-B}=\text{B} \xrightarrow{3 \text{ mol\% Pd(PPh}_₃)_₄ / \text{NaOH, -NaI}} \text{Ph-Octyl} + \text{HO-B}=\text{B}
\]

Scheme 1.8 Example of reactions involving organoboron reagents: cross coupling.
Remarkable advances in the chemistry of low valent boron species have been made recently. The first Lewis basic boron species was reported by Yamashita and Nozaki as a two-coordinate boryl anion isoelectronic with carbenes.\textsuperscript{76} Subsequently, Bertrand reported a Lewis basic monovalent boron species stabilized by two cyclic alkyl amino carbene (CAAC) substituents that is isoelectronic with amines and phosphines.\textsuperscript{77} Using arylborylenes stabilized by a CAAC ligand, Braunschweig was able to bind, reduce, and couple dinitrogen gas (Scheme 1.10).\textsuperscript{78, 79} These studies represent the first examples of p-block species reacting with dinitrogen – reactions that were thought to be the province of the transition metals.

**Scheme 1.9** Examples of reactions involving organoboron reagents: hydroboration (top) and frustrated Lewis pair catalyzed hydrogenation (bottom).

**Scheme 1.10** Trapping of dinitrogen with monovalent boron species.

### 1.5 Hypervalent Interactions

The term hypervalent was first used by Mushers in 1969\textsuperscript{80} to describe molecules of the heavier main group elements that exceed the expected valency for their group. Examples of such molecules
include those with strongly electronegative groups participating at the extremities of the bond in question such as PF₅, SF₆, and ClF₃ (Figure 1.2). Early explanations for this behaviour include expanding the octet of the central atom by involving \(d\)-orbital hybridization\(^{81}\) and maintaining the octet by requiring the hypervalent species be charge separated instead of covalently bound.\(^{82}\)

![Figure 1.2](image1.png)

**Figure 1.2** Bonding depictions of PF₅: expanded octet (left) and charge separated (right).

A third view, put forward by Rundle\(^{83}\) and Pimentel,\(^{84}\) used molecular orbital theory to invoke a three-centre four-electron bond. This requires three \(p\)-atomic orbitals to combine colinearly to form a bonding, a nonbonding, and an antibonding orbital. In this view, only two of the four electrons involved occupy a bonding orbital, with the other two occupying a nonbonding orbital, thereby making each bond a collinear two-centre one-electron bond (Figure 1.3). As computational chemistry became more powerful, the contributions of \(d\)-orbitals were shown not to be very meaningful in hypervalent bonds,\(^{85}\) a view which is supported by the isolation of hypervalent molecules from the second period of the periodic table whose \(d\)-orbitals should be inaccessible.\(^{86}\) As a result, the three-centre four-electron model of hypervalency is currently the most widely accepted model.

![Figure 1.3](image2.png)

**Figure 1.3** Molecular orbital diagram of hypervalent bonding involving \(p\)-orbitals in PF₅.
1.6 Main Group Element-Element Bond Reactivity

Advances in main group chemistry are encroaching on transformations that traditionally belong to the transition metals. The reactivity characteristic of the transition metals results from their large atomic radii, available d-orbital electrons, vacant coordination sites, and accessible orbital energies that are able to interact with small molecules. The cleavage of H$_2$, for example, is a necessary step in the reaction cycles of many transition metal catalyzed hydrogenation reactions.$^{87,88}$ As more main group species are being developed, more are being discovered with accessible frontier orbitals, resulting in reactivity towards small molecules akin to that known for the transition metals. Examples of such reactivity have grown considerably in recent years. By imposing steric or conformational restrictions on the frontier orbitals, Stephan reported the activation of H$_2$ with frustrated Lewis pairs$^{89}$ and Bertrand and Schoeller showed analogous chemistry with a CAAC.$^{90}$ Frontier orbital accessibility is also achieved in heavier main group element-element bonded species. The first heavier main group species bearing a multiple element-element bond was a distannylene isolated by Lappert.$^{91,92}$ Subsequently, the isolation of disilene, diphosphene, and silaethene were achieved by West,$^{93}$ Yoshifuji,$^{94}$ and Brook,$^{95}$ respectively (Scheme 1.11).

![Scheme 1.11](image)

**Scheme 1.11** Early main group compounds with element-element multiple bond character.

When moving below the second period of the periodic table, atomic size increases and the element centres become more pyramidalized. This results in poor orbital overlap and a maintenance of
accessible donor and acceptor orbitals analogous to transition metal species. Small-molecule activation by a multiply bonded heavier element-element species was first reported by Power who found that \( \text{H}_2 \) and \( \text{NH}_3 \) added across a digermyne\(^{96} \) and subsequently across a digallyne\(^{97} \) under ambient conditions. Computations affirmed mechanisms involving cooperative interaction of the main group species’ donor and acceptor sites. Since then, a number of element-element bonds have been shown to activate small molecules (Scheme 1.12, Scheme 1.13). While Power has also reported that a triply bonded distannyne reacts irreversibly with \( \text{H}_2 \)^{98} but reversibly with ethylene,\(^{99} \) Inoue reported the synthesis of a dialumene and found that its double bond undergoes addition reactions with ethylene and phenyl acetylene to form heterocycles.\(^{100} \) Rieger and Inoue also found reactions of \( \text{H}_2, \text{N}_2\text{O}, \text{CO}_2, \text{O}_2, \) and \( \text{NH}_3 \) with a disilene.\(^{101, 102} \) This reactivity has recently been demonstrated with element-element bonds from the second period of the period table as well, with Braunschweig’s report of \( \text{H}_2 \) activation at a boron-boron centre with multiple bond character\(^{103} \) and a subsequent report by Yamashita and Lin demonstrating \( \text{H}_2 \) activation with a singly bonded B-B compound.\(^{104} \) As the library of main group element-element bonded species continues to grow,\(^{105, 106} \) new and interesting reactivities are sure to abound and continue to offer alternative and complementary chemistry to the transition metals.\(^{87, 107} \)

![Scheme 1.12](image.png)

**Scheme 1.12** Selected small-molecule activations by main group element-element bonded species continued.
1.7 Main Group Lewis Acids

Advances in main group Lewis acid chemistry are also striving to supplant transition metals. Lewis acids and bases were defined in 1923 by Gilbert Lewis as species that accept and donate a pair of electrons, respectively.\(^{81}\) Lewis acids are essential components of the synthetic chemist’s repertoire because a broad variety of reactions are facilitated by coordination of substrates to an electrophilic site. The low electronegativities and large atomic radii\(^{108}\) of the transition metals have made them traditional sources of Lewis acids for stoichiometric and catalytic transformations. This role has been cemented by decades of research into the fundamental coordination chemistry of the transition metals, which revealed ligand design principles (e.g. hemilability, redox non-innocence, chelate effect) that enable catalyst tuning for imparting or improving desirable features such as stability, selectivity, and reactivity.\(^{88}\) By comparison, although the coordination chemistry of p-block elements is less well-developed, catalysis with neutral (e.g. BX\(_3\), AlX\(_3\), GaX\(_3\))\(^{109-111}\) and cationic (e.g. CX\(_3^+\), SiX\(_3^+\), PX\(_4^+\))\(^{112-115}\) p-block acceptors is ubiquitous in organic synthesis. The evolution of p-block Lewis acid catalysts has been driven by new synthetic strategies for appending highly electron-withdrawing substituents to element centres and the design of ever more weakly coordination anions. Examples of such Lewis acids include perhaloaryl-substituted silicon centres reported by Greb, Bergman, and Tilley, as well as trifluoromethyl- and OTeF\(_5\)-substituted aluminum centres reported by Krossing and Riedel, respectively (Figure 1.4, top).\(^{116-120}\) Examples of such anions include perhalo-substituted borates, carboranes, and pnictogenates reported by Massey and Park,\(^{121}\) Stibr and Reed,\(^{122, 123}\) and Schrobilgen, respectively (Figure 1.4, bottom).\(^{124-127}\)

As a result, several main group Lewis superacids have been discovered,\(^{128}\) some of which show catalytic behaviour in transformations involving even strong C-F \(\sigma\) bonds.\(^{129-131}\)

**Scheme 1.13** Selected small-molecule activations by main group element-element bonded species.
Figure 1.4   Selected Lewis acids bearing highly electron-withdrawing substituents (top) and selected weakly coordinating anions (bottom).

The strength of a Lewis acid, however, does not alone predict its ultimate utility as a catalyst in commercial settings. Ease of synthesis, stability under atmospheric conditions, and tunability are equally important considerations to promote broad adoption of main group Lewis acid catalysts. However, in the context of p-block chemistry, these factors have received limited attention with greater emphasis placed on making stronger Lewis acids by introducing more perhalogenated substituents and developing less coordinating anions. Notable exceptions are found in the field of Group 13 and 15 element mediated catalysis where the use of modular O/N-based salen or porphyrin ligands, initially developed for transition metal acceptors, has led to the synthesis of designer p-block Lewis acid catalysts that exhibit lower electrophilicity than the prototypical derivatives EX3 (E = B, Al, Ga, I; X = F, Cl, Br, I, O1.5), but introduce air-stability, chirality, and excellent tunability.14,132 These include reports from Loh of the synthesis of chiral indium (III) complexes with PYBOX ligands for enantioselective allylation of aldehydes133 and from Jiang of O/N-based salen ligands used to make aluminum (III) complexes which catalyze the synthesis of cyclic carbonates from carbon dioxide and epoxides.134 In group 15 elements, Arduengo reported
phosphorus (III), arsenic (III), and antimony (III) complexes bearing a tridentate O-N-O substituent to achieve ambiphilic reactivity characteristic of transition metals. More recently, Stephan reported a phosphorus dication bearing a cyclopentadienyl ligand while Chitnis reported a bismuth complex of a tridentate triamine substituent whose electronic structure is best described as bismuth (I) but whose reactivity more closely resembles bismuth (III) (Figure 1.5). As advances are made in main group Lewis acid catalysts, they are becoming more reasonable to adopt, with Al(salen) complexes having led to several patented polymerization systems.

Figure 1.5 Selected coordination complexes of Group 13 and 15 elements.

1.8 Metrics of Lewis Acidity

Lewis acids have found use not only in catalysis but also in materials, sensors, and medications. When designing new Lewis acids for such applications, quantitatively assessing the Lewis acidic strength is often critical. This is also, however, quite difficult. Unlike Brønsted acids, which are characterized by proton donation quantifiable by \( pK_a \), the broadness of Lewis acid interactions has no universally quantifying measure. Efforts to rank order Lewis acids have led to the development of a number of measures based on spectroscopic data, reactivity trends, and computational data, with the assumption that trends observed within each measure are representative of trends in Lewis...
acidity generally. However, relative Lewis acidities derived from reactivity measurements can be misleading as they depend heavily on a Lewis acid’s ability to interact with the Lewis basic substrate in question, which is complicated both by the sterics around a Lewis acid’s reactive site and by a Lewis acid’s affinity for the given Lewis base. Divergent Lewis acidity has been observed in comparisons of [Et₃Si]⁺ and [Ph₃C]⁺ cations by fluoride ion affinity (FIA) and hydride ion affinity (HIA), with [Et₃Si]⁺ being the stronger Lewis acid by FIA but weaker by HIA. Additionally, BCl₃ was found to interact more strongly with NH₃ than with CO whereas the opposite was found for BF₃. While these differences can be generally attributed to the hard soft acids and bases principle, which states that hard acids interact more favourably with hard bases and soft acids with soft bases, sterics around the Lewis acidic sites must also be considered. Therefore, a number of measures should be applied and considered holistically to obtain a clear picture of relative Lewis acid strengths.

Comparing the catalytic reactivity of Lewis acids is a powerful way to compare Lewis acidities, as the goal of ranking Lewis acid strength is often to predict relative reactivity. When developing new Lewis acids, the Stephan group routinely compares their efficacy in sets of Lewis acid catalyzed reactions under similar conditions. The Stephan group has also performed competition reactions to directly compare the Lewis acidities of two species by mixing the fluoride adduct of a Lewis acid with an additional Lewis acid, allowing the mixture to equilibrate, and probing the mixture by NMR spectroscopy (Scheme 1.14). Whether added as the free Lewis acid or as the adduct, the stronger of the two Lewis acids dominates as the fluoride adduct. While these approaches are informative, they are also taxing as they require performing several reactions with a variety of substrates, some of them exotic as in the case of competition reactions.

\[
\text{LA1–F} + \text{LA2} \rightleftharpoons \text{LA1} + \text{LA2–F}
\]

Scheme 1.14 Competition reaction for Lewis acid strength comparison between two species.

Less taxing measures of Lewis acidity include analysis of spectroscopic data. When comparing fluorophosphonium salts, the Stephan group has used ³¹P and ¹⁹F NMR data to gauge relative Lewis acidities, with chemical shifts and coupling constants being assessed. However, this specific approach is limited to fluorophosphonium species and cannot be used to compare with
other Lewis acids. More general approaches comparing spectroscopic data resulting from a Lewis acid’s interaction with a given Lewis base have also been developed. Sivaev established scales for polyhedral boron hydrides by comparing the $^1$H NMR shifts of $\alpha$-hydrogens of complexed Lewis bases including dimethylsulfide, oxirane, and benzyl amide.\textsuperscript{146} Very recently, Caputo and Baumgartner developed a method based on the fluorescence of adducts between Lewis acids and dithienophosphole oxides with applicability to a broad range of Lewis acids and good correlation with other methods.\textsuperscript{147} However, the most widely adopted methods currently include the Childs’ method, the Gutmann-Beckett method, and fluoride ion affinity.

### 1.8.1 Childs’ Method

In the Childs’ method, an equimolar solution of a Lewis acid and the soft base $\text{trans}$-crotonaldehyde is made in DCM at -20 °C (Scheme 1.15) and the $^1$H NMR spectrum is obtained at that temperature.\textsuperscript{148} $\text{trans}$-crotonaldehyde was chosen as it showed the most sensitivity to Lewis acid changes. On adduct formation, the signal corresponding to H$^3$ experiences a downfield shift that correlates with Lewis acid strength. While this method is widely adopted, the necessity to make and measure the solution at -20 °C is inconvenient. Additionally, fluorophosphonium salts developed by the Stephan group have been shown to react with $\text{trans}$-crotonaldehyde instead of simply coordinating to it.\textsuperscript{145, 149}

![Scheme 1.15](image)

**Scheme 1.15** Child’s method for Lewis acid strength determination.

### 1.8.2 Gutmann-Beckett Method

The Gutmann-Beckett method has seen greater adoption than the Childs’ method.\textsuperscript{114, 150} Gutmann first proposed a method to rank order the electrophilic character of solvents to develop a guide to select solvents for a given reaction. By measuring the $^{31}$P NMR shift of the hard base Et$_3$PO in different solvents and at different concentrations, Gutmann developed an acceptor number (AN) scale, referenced against Et$_3$PO in hexane ($\delta = 41.0$ ppm, AN = 0) and in SbCl$_5$ ($\delta = 100$ ppm, AN = 86.1).\textsuperscript{151, 152} Triethylphosphine oxide was chosen because it is soluble in many solvents and its only basic site is at the oxygen atom. Coordination weakens the P-O bond, resulting in a particularly broad distribution of $^{31}$P NMR shifts in different solvents, with more coordinating...
solvents resulting in more downfield shifts. This scale was later extended by Beckett to include Lewis acids (Scheme 1.16). Beckett found that the Gutmann AN results correlated well with results from the Child’s method without the need for measuring various concentrations.\(^{153}\) The Gutmann-Beckett AN for Lewis acids is calculated with Equation 1-1, where \(\delta_{\text{sample}}\) is the \(^{31}\)P NMR chemical shift of the Lewis acid/Et\(_3\)PO adduct and 86.1 and 41.0 are the \(^{31}\)P NMR shifts of Et\(_3\)PO in hexane and SbCl\(_5\), respectively.

\[
AN = (\delta_{\text{sample}} - 41.0) \times \left(\frac{100}{86.1 - 41.0}\right)
\]

Eqn 1-1

\[\text{Scheme 1.16}\] Gutmann-Beckett method for Lewis acid strength determination.

In applying the Gutmann-Beckett method to a series of strongly Lewis acidic boranes, Britovsek\(^ {154}\) found that solvent effects were insignificant when sufficiently strong Lewis acids were applied, with consistent values being measured in benzene, THF, and CDCl\(_3\). However, he found that the Gutmann-Beckett method and the Childs’ method gave divergent results, with harder borane Lewis acids interacting more strongly with the hard base Et\(_3\)PO than with the soft base trans-crotonaldehyde.

1.8.3 Fluoride Ion Affinity

As computational power increased, and quantum chemical calculations became more accessible and accurate, computationally derived measures of Lewis acidity were developed. These have been useful both as a complimentary measure of Lewis acidity to include in a holistic consideration and as a means to predict the Lewis acidities of species not yet synthesized. One of the most popular methods is fluoride ion affinity (FIA) developed by Christe.\(^ {155}\) By this method, the enthalpy of the adduct formation reaction between a Lewis acid and its fluoride adduct is calculated, FIA being the negative of the enthalpy value and greater values corresponding to stronger Lewis acidity (Scheme 1.17). The method avoids using a fluoride anion directly due to difficulties in consistently computationally modelling its energy. Instead, [COF\(_3\)]\(^+\) is used as a fluoride anion source, as the enthalpy of the fluoride adduct formation reaction of F\(_2\)CO is experimentally known.
Scheme 1.17 Calculation of fluoride ion affinity for Lewis acid strength determination.

1.9 Scope of Thesis

The objective of this thesis is to explore the design and reactivity of organophosphorus compounds for interesting stoichiometric reactivity, catalyst design, and catalytic application. Chapter 2 explores the synthesis of phosphinoboranes and their reactivity towards benzoyl chloride, CO$_2$, diazobenzene, and diazomethanes, leading to various 1,1- and 1,2-addition products and diphospha-urea products. The frustrated Lewis pair reactivity of several of these phosphinoboration products is investigated. In Chapter 3, derivatives of electrophilic phenoxyphosphonium salts are synthesized to improve moisture tolerance, a dicationic phenoxyphosphonium salt is found to catalyze the Friedel-Crafts double hydroarylation of diarylamines with alkynes, and a sterically accessible electrophilic phosphonium salt bearing (CF$_3$)$_2$C$_6$H$_3$-substituents is studied. Chapter 4 investigates the synthesis of doubly cationic phosphorus coordination complexes and their application towards the reaction of aliphatic carbon-fluorine bonds with allylsilanes.

This thesis contains work performed collaboratively:

In Chapter 2, Section 2.1, the reaction of Ph$_3$PBpin with benzoyl chloride and the synthesis of 2-11 was performed by B.Sc. Maia Murphy, synthesis of some phosphinoboranes and their subsequent reactivity with benzoyl chloride was performed by B.Sc. Alina Trofimova, some starting material was provided by B.Sc. Karlee L. Bamford, and guidance was provided by Dr. Chris Vogels and Prof. Stephen A. Westcott. In Chapter 2, Section 2.2, the initial synthesis of 2-12 was performed by Dr. Steve J. Geier, computational work was performed by Dr. Zheng-Wang Qu, and some starting material and guidance was provided by Dr. Steve J. Geier and Prof. Stephen A. Westcott. In Chapter 2, Section 2.3, syntheses were performed in part by B.Sc. Alina Trofimova, synthesis
of 2-20 and 2-24 were performed by Haley Cummings, and some starting material and guidance was provided by Prof. Stephen A. Westcott. All other synthetic, analytical, and computational work herein was performed by the author. In Chapter 3, Section 3.1, computational work was performed by Dr. Tim Johnstone, and instruction and guidance was provided by Dr. Tim Johnstone, Dr. Manuel Pérez, Dr. Daniel Winkelhaus, and M.Sc. Vitali Podgorny. In Chapter 3, Section 3.2, dications of phenoxyphosphonium salt was provided by B.Sc. Julia Bayne, computational work was performed with guidance from by Dr. Tim Johnstone, and instruction and guidance was provided by Dr. Louie Fan. In Chapter 3, Section 3.3, syntheses of 3-23 and 3-24 were first performed by B.Sc. Kevin M. Szkop, syntheses and reactivity studies were performed in part by Farah E. Farinha, computational work and self-exchange reactions were performed in part by Dr. Timothy C. Johnstone, and instruction and guidance was provided by Dr. Shawn Postle. In Chapter 4, reactivity of 4-2 was performed by Dr. Saurabh S. Chitnis. Computational work was performed by Dr. Liu L. Liu. Some starting material synthesis was performed by Haley Cummings and B.Sc. Ryan Andrews. Elemental analysis and high-resolution mass spectrometry were performed in-house by the ANALEST and AIMS laboratories, respectively.

Portions of this thesis have been published at the time of writing:


1.10 References


3. B. Miller, presented in part at the 5th Chemical Sciences and Society Summit (CS3), Narita, Japan, 2013.


144. S. W. Postle, Chemistry Ph.D., University of Toronto, 2017.


Chapter 2

Section 2.1 - Synthesis of Phosphinoboranes and Reactions with Benzoyl Chloride

2.1 Brief Introduction to Phosphinoboranes

Some of the most well explored moieties in organic chemistry are C-C bonds which range from alkanes (R_3C-CR’_3), alkynes (RC≡CR’), and arenes (-CR=CR’)_n (benzene: R, R’ = H, n = 3) (Figure 2.1, top). Significant research has also been done on the analogous N-B bonds as they are the heteroatomic and isoelectronic derivatives of the C-C bond. Species with N-B bonds include ammine boranes ([R_3N-BR’_3]), aminoboranes (R_2N=BR’_2), iminoboranes (RN≡BR’), and borazines ([RN=BR’_3]), being isoelectronic and often isostructural with alkanes, alkenes, alkynes, and benzene, respectively (Figure 2.1, middle). The heavier isoelectronic phosphorus-containing analogues have also gained attention (Figure 2.1, bottom).

While phosphine boranes ([R_3P-BR’_3], isoelectronic with alkanes) are readily synthesized from mixtures of phosphines and boranes and synthetic strategies to phosphinoboranes (R_2P-BR’_2, isoelectronic with alkenes) have been known for some time, phosphinidene boranes (RP=BR’_2, isoelectronic with alkynes) have been less explored due primarily to synthetic challenges.

![Chemical Structures]

Figure 2.1  C-C bonded species (top) and their isoelectronic N-B (middle) and P-B (bottom) analogues.
In contrast to the strong multiple bond character displayed by alkenes, aminoboranes, alkynes, and iminoboranes, phosphinoboranes and phosphinidene boranes generally show less $\pi$-bonding. While this might be expected to arise from poor orbital overlap between atoms on different periods of the periodic table (boron: 2nd, phosphorus: 3rd), it is more likely a result of the high inversion barrier of the phosphorus with respect to the nitrogen centres. This general inability for P-B moieties to form strong $\pi$ bonding leaves an accessible lone pair and a vacant $p$-orbital on the phosphorus and boron centres, respectively.\textsuperscript{22, 23} As a result, and particularly for phosphinidene boranes, their isolation often requires base stabilization of the vacant $p$-orbital or is otherwise complicated by dimerization or oligomerization.\textsuperscript{16-20} Despite being isoelectronic, these groups display significantly different reactivity owing in large part to differences in the bond polarity between the C-C (Pauling electronegativity: $\chi_{\text{Pauling}} = 2.55$) and N-B ($\chi_{\text{Pauling, nitrogen}} = 3.04$, $\chi_{\text{Pauling, boron}} = 2.04$) moieties\textsuperscript{24, 25} and the available Lewis acidic and basic sites on P-B moieties as well as the minimal charge separation between the phosphorus ($\chi_{\text{Pauling}} = 2.19$) and boron ($\chi_{\text{Pauling}} = 2.04$) centres.

The reactivity of phosphine boranes has been explored both stoichiometrically and catalytically in a variety of reactions,\textsuperscript{25} seeing new interest in the context of frustrated Lewis pair chemistry (see Chapter 2, Section 2.3). However, the reactivity of phosphinoboranes has been relatively underexplored (Scheme 2.1)\textsuperscript{26} compared to analogous C-C and N-B moieties. Early work by N"oth includes reactions of (NMe$_2$)$_2$B-PEt$_2$ with a variety of strongly reactive species including HCl, BCl$_3$, MeI, aniline, and ethanol to yield the corresponding dissociated phosphine borane species.\textsuperscript{27} While Scheer reported reactions of H$_2$P-BH$_2$ stabilized by NMe$_3$ with S$_8$, Se$_8$, and Me$_3$NO to yield the oxidized phosphinoboranes,\textsuperscript{28} the Stephan group demonstrated H$_2$ cleavage and dehydrogenation of ammonia borane with phosphinoboranes of the form R$_2$P-B(C$_6$F$_5$)$_2$ (R = tBu, Cy, Mes).\textsuperscript{15, 29} Additionally, the Su group reported that tBu$_2$P-B(biphenyl) cleaves H$_2$ and undergoes 1,2-addition reactions with benzophenone, dimethylbutadiene, and acetonitrile.\textsuperscript{30} Following these advances, the Westcott group synthesized phosphinoboranes of the form R$_2$PBpin (R = Ph, Cy) and Ph$_2$PBcat and demonstrated their addition reactions with aldehydes, ketones, imines, pyridines, and heteroallenes.\textsuperscript{14, 31-33}
2.2 Brief Introduction to Acyl Phosphines

While amides are a common class of molecules readily synthesized from condensation reactions of carboxylic acids and amines, their phosphorus analogues, acyl phosphines, are less common. In contrast to amides, which show a significant amount of π delocalization in the N-C=O fragment, acyl phosphines show little π delocalization, leaving a pyramidal geometry about the phosphorus.
centre. When exposed to UV-Vis radiation, acyl phosphines and acyl phosphine oxides generate highly reactive radicals from the cleavage of the P-CO bond (Scheme 2.2).\textsuperscript{35, 36} This has led to the use of acyl phosphines and acyl phosphine oxides as photoinitiators in polymerization reactions and radiation curable compositions.\textsuperscript{37, 38}

![Scheme 2.2](image)

**Scheme 2.2**  Photoinitiation mechanism of an acyl phosphine and an acyl phosphine oxide.

Synthetic strategies to metal-bound acyl phosphines are known (Figure 2.2), with Roper reporting reactions of phosphine-substituted osmium complexes\textsuperscript{39, 40} and Antiñolo and Otero reporting reactions of phosphine-substituted niobium complexes\textsuperscript{41} with benzoyl chloride as well as Chauvin’s report of reactions of acyl-substituted iron complexes with chlorophosphines.\textsuperscript{42, 43} Metal-free routes to acyl phosphines are also known (Figure 2.2, Figure 2.3) from reactions of P(TMS)\textsubscript{3} with acyl chlorides,\textsuperscript{44, 45} as reported by Becker, and from reactions of reactions of lithium, sodium, or potassium salts of phosphines with esters,\textsuperscript{46, 47} as reported by Liotta and Becker, and with acyl chlorides,\textsuperscript{48, 49} as reported by Grützmacher and Mézailles. Additionally, [PCO]\textsuperscript{-} has been used with various reagents by the Grützmacher and Goicoechea groups\textsuperscript{50} and the Cummins and Stephan groups have used a phosphinidene precursor with acyl chlorides.\textsuperscript{51}

![Figure 2.2](image)

**Figure 2.2**  Selected reagents used in the synthesis of acyl phosphines.
2.3 Results and Discussion

2.3.1 Synthesis of Phosphinoboranes

Throughout this chapter, various phosphinoboranes are used to probe substituent effects in the phosphinoboration reactions with a variety of substrates. To fulfill this need, the synthesis of new phosphinoboranes was undertaken. Following similar procedures to those used by Westcott,\textsuperscript{14} Stephan,\textsuperscript{15} and Power,\textsuperscript{13} the phosphines $t$BuPH, Mes$_2$PH, and Ph$_2$PH were lithiated with either $n$BuLi or $t$BuLi and subsequently reacted with $i$PrOBpin, FBMe$_2$, ClBcat, or BrB(9,10-phenanthrenediol) (BrBquin \textbf{2-1}, synthesized according to a modified literature procedure)\textsuperscript{52} to yield the phosphinoboranes $t$Bu$_2$PBpin (\textbf{2-2}), $t$Bu$_2$PBMes$_2$ (\textbf{2-3}), $t$Bu$_2$PBcat (\textbf{2-4}), Mes$_2$PBcat (\textbf{2-5}), and Ph$_2$PBquin (\textbf{2-6}) in 89, 68, 76, 86, and 58% yields, respectively, with concomitant lithium salt formation (Scheme 2.3). While the majority of these phosphinoboranes are colourless, as is the case with Ph$_2$PBpin, Ph$_2$PBcat, and Cy$_2$PBpin,\textsuperscript{14} the phosphinoborane \textbf{2-3} was isolated as a yellow solid, resembling Mes$_2$PB(C$_6$F$_5$)$_2$\textsuperscript{15} and Ph$_2$PBMes$_2$.\textsuperscript{12} The $^{11}$B\{\textsuperscript{1}H\} NMR spectra show broad singlets at 35.6, 56.6, 37.2, 37.7, and 37.1 ppm for \textbf{2-2} to \textbf{2-6}, respectively, while the $^{31}$P\{\textsuperscript{1}H\}
NMR signals appear at -15.8, 75.9, -16.4, -106.1, and -66.1 ppm for 2-2 to 2-6, respectively. The majority of the \(^{31}\text{P}\{^1\text{H}\}\) NMR signals appear as broad singlets with the exception of 2-2 which appears as a doublet with a \(J\)-coupling of 77 Hz.

**Scheme 2.3** Synthesis of phosphinoboranes 2-2 to 2-6.

Single crystals of 2-2 to 2-5 as well as Ph\(_2\)PBcat\(^{14}\) and Mes\(_2\)PB(C\(_6\)F\(_5\))\(_2\),\(^{15}\) prepared according to literature methods, suitable for X-ray diffraction were grown from \(n\)-pentane. Diffraction studies revealed that 2-2 to 2-4 and Mes\(_2\)PB(C\(_6\)F\(_5\))\(_2\) each crystallize with one molecule in the asymmetric unit while 2-5 and Ph\(_2\)PBcat crystallize with two and four molecules, respectively, revealing P-B bond lengths of 1.935(4); 1.849(2); 1.915(2); 1.916(8) and 1.915(8); 1.94(1), 1.95(1), 1.87(1), and 1.89(1); and 1.783(2) Å for 2-2 to 2-5 and Mes\(_2\)PB(C\(_6\)F\(_5\))\(_2\), respectively (Figure 2.4, Figure 2.5, Figure 2.6, Figure 2.7). These span the range from a P-B single bond (1.92 – 2.0 Å) to double bond (1.79 – 1.86 Å).\(^{13, 16, 21-23, 30, 53-55}\) The geometry about the phosphorus centres varies from clearly pyramidal in the cases of 2-2, 2-4, 2-5, and Ph\(_2\)PBcat to a more trigonal planar geometry in the cases of 2-3 and Mes\(_2\)PB(C\(_6\)F\(_5\))\(_2\), implying multiple bond character between the P and B atoms. Analysis of the crystallographic data (Table 2.1, entries 1 to 5 and 8) revealed twist angles between the R-P-R and R'-B-R' planes of 69.3; 30.9; 58.4; 63.2 and 65.3; 65.9, 66.2, 63.4, 69.8, and 68.33; and 1.1° as well as sums of angles around the phosphorus centres of 317.2; 352.1; 321.1; 321.7 and 320.6; 307.4, 307.0, 307.1, and 307.8; and 359.6° for 2-2 to 2-5, Ph\(_2\)PBcat, and Mes\(_2\)PB(C\(_6\)F\(_5\))\(_2\), respectively. Comparing to crystallographic data for Ph\(_2\)PBpin (P-B bond = 1.9274(14) Å, twist angle = 65.9°, sum of angles at P = 310.0°)\(^{14}\) and Ph\(_2\)PBMes\(_2\) (P-B bond = 1.859(3) Å, twist angle = 1.6°, sum of angles at P = 339.4°),\(^{12}\) which are recognized to have single and significant double bond character, respectively, the crystallographic metrics reported herein further support the P-B double bond character in 2-3 and Mes\(_2\)PB(C\(_6\)F\(_5\))\(_2\) as well as the single bond character in 2-2, 2-4, 2-5, and Ph\(_2\)PBcat (Table 2.1).
<table>
<thead>
<tr>
<th>Entry</th>
<th>Phosphinoborane</th>
<th>P-B distance (Å)</th>
<th>Twist angle between R-P-R and R'-B-R’ planes (°)</th>
<th>Sum of angles at P (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-2</td>
<td>1.935(4)</td>
<td>69.3</td>
<td>317.2</td>
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<tr>
<td>2</td>
<td>2-3</td>
<td>1.849(2)</td>
<td>30.9</td>
<td>352.1</td>
</tr>
<tr>
<td>3</td>
<td>2-4</td>
<td>1.915(2)</td>
<td>58.4</td>
<td>321.1</td>
</tr>
<tr>
<td>4</td>
<td>2-5</td>
<td>1.916(8)</td>
<td>63.2</td>
<td>321.7</td>
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<td>5</td>
<td>Ph₂PBcat</td>
<td>1.94(1)</td>
<td>66.2</td>
<td>307.4</td>
</tr>
<tr>
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<td>63.4</td>
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<td></td>
<td></td>
<td>1.89(1)</td>
<td>68.3</td>
<td>307.8</td>
</tr>
<tr>
<td>6</td>
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<td>65.9</td>
<td>310.0</td>
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<td>Ph₂PBMes₂¹²</td>
<td>1.859(3)</td>
<td>1.6</td>
<td>339.4</td>
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<tr>
<td>8</td>
<td>Mes₂PB(C₆F₅)₂</td>
<td>1.783(2)</td>
<td>1.1</td>
<td>359.6</td>
</tr>
</tbody>
</table>

Figure 2.4  ORTEP depictions of 2-2 viewed from above (left) and from the side (right) showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. P: orange, O: red, B: yellow-green, C: black.
Figure 2.5  ORTEP depictions of 2-3 viewed from above (top left) and from the side (top right) and of 2-4 viewed from above (bottom left) and from the side (bottom right) showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. P: orange, O: red, B: yellow-green, C: black.
Figure 2.6  ORTEP depictions of 2-5 viewed from above (top left) and from the side (top right) and of Ph₂PBCat viewed from above (bottom left) and from the side (bottom right) showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. P: orange, O: red, B: yellow-green, C: black.
Figure 2.7  ORTEP depiction of Mes$_2$PB(C$_6$F$_5$)$_2$ viewed from above (left) and from the side (right) showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. P: orange, B: yellow-green, C: black, F: spicy pink.

To further probe the potential for P-B multiple bond character, the structures of each phosphinoborane crystallized herein as well as those of Ph$_2$PBpin and Ph$_2$PBMes$_2$ were computed using the Gaussian 16$^{56}$ package at the BP86/Def2-TZVP$^{57-60}$ level of theory, revealing P-B bond lengths of 1.93, 1.84, 1.92, 1.90, 1.92, 1.81, 1.93, and 1.87 Å, twist angles between the R-P-R and R’-B-R’ planes of 58.8, 16.3, 60.0, 43.9, 61.5, 61.5, 7.5, 60.2, and 26.6°, and sums of angles about the phosphorus centres of 320.3, 360.0, 319.6, 329.1, 311.2, 311.3, 360.0, 312.1, and 345.9° for 2-2 to 2-6, Ph$_2$PBcat, Mes$_2$PB(C$_6$F$_5$)$_2$, Ph$_2$PBpin, and Ph$_2$PBMes$_2$, respectively. Additionally, natural population analysis using NBO 6.0$^{61}$ at the M06-2X/Def2-TZVP$^{62}$ level of theory was performed on each, revealing P-B Wiberg bond indices of 1.246, 1.133, and 1.218 for 2-3, Ph$_2$PBMes$_2$, and Mes$_2$PB(C$_6$F$_5$)$_2$, respectively, whereas 2-2, 2-4 to 2-6, Ph$_2$PBcat, and Ph$_2$PBpin have P-B bond indices of 0.953, 0.957, 0.968, 0.922, 0.922, and 0.913, respectively. These computational data (Table 2.2) agree well with crystallographic data (vide supra, Table 2.1) and
are consistent with the planarity apparent in the computed and crystallographically determined structures of 2-3, Ph₂PBMes₂, and Mes₂PB(C₆F₅)₂ attributable to double bond character.

Table 2.2  Selected computational data for the structures of 2-2 to 2-6, Ph₂PBcat, Ph₂PBpin, Ph₂PBMes₂, and Mes₂PB(C₆F₅)₂.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Phosphinoborane</th>
<th>P-B distance (Å)</th>
<th>P-B Wiberg Bond Order</th>
<th>Twist angle between R-P-R and R'-B-R' planes (°)</th>
<th>Sum of angles at P (°)</th>
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<td>1</td>
<td>2-2</td>
<td>1.93</td>
<td>0.953</td>
<td>58.8</td>
<td>320.3</td>
</tr>
<tr>
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<td>1.246</td>
<td>16.3</td>
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<td>3</td>
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<td>0.957</td>
<td>60.0</td>
<td>319.6</td>
</tr>
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<td>0.968</td>
<td>43.9</td>
<td>329.1</td>
</tr>
<tr>
<td>5</td>
<td>2-6</td>
<td>1.92</td>
<td>0.922</td>
<td>61.5</td>
<td>311.2</td>
</tr>
<tr>
<td>6</td>
<td>Ph₂PBcat</td>
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<td>0.922</td>
<td>61.5</td>
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<td>0.913</td>
<td>60.2</td>
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<tr>
<td>8</td>
<td>Ph₂PBMes₂</td>
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<td>1.133</td>
<td>26.6</td>
<td>345.9</td>
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<tr>
<td>9</td>
<td>Mes₂PB(C₆F₅)₂</td>
<td>1.81</td>
<td>1.218</td>
<td>7.5</td>
<td>360.0</td>
</tr>
</tbody>
</table>

These phosphinoboranes were chosen for their ease of synthesis and breadth of steric and electronic parameters. On the phosphorus centre, steric bulk and electron donating ability decrease in the order of tBu, Mes, Ph, while on the boron centre, steric decrease in the order of Mes, C₆F₅, pin, quin, cat while electron donating ability decreases in the order of pin, quin, cat, Mes, C₆F₅. As such, this set of phosphinoboranes spans a range of sterics and electronics at the phosphorus and boron centres and is suitable for exploration of substituent effects in phosphinoboration reactions.

2.3.2 Phosphinoboration of Benzoyl Chloride

The reactions of Ph₂PBpin with one equivalent of benzoyl chloride in toluene proceeds at ambient temperature over 24 hours to give a yellow solution. Analysis of the reaction mixture by $^{11}$B{$^1$H} NMR revealed a peak at 28 ppm, consistent with a chlorine-bound Bpin group. After removing the solvent in vacuo and recrystallizing from n-pentane, a yellow solid (2-7) was isolated in 95% yield (Scheme 2.4). While the isolated product’s $^{31}$P{$^1$H} NMR spectrum showed a signal at 14.1 ppm, the $^{11}$B{$^1$H} NMR spectrum showed no signals. Additionally, the $^1$H and $^{13}$C{$^1$H} NMR spectra only show signals corresponding to aromatic nuclei. This is consistent with the formulation of 2-7 as the acyl phosphine PhC(O)PPh₂, resulting from a formal P-B/C-Cl bond metathesis and the formation of ClBpin as a by-product. This notion was affirmed by elemental analysis data.
Analogous reactivity was observed from combinations of Ph₂PBcat and Ph₂PBMes₂ with one equivalent of benzoyl chloride in DCM at ambient temperature for 24 hours (Scheme 2.4). The \(^{11}\text{B}\{^{1}\text{H}\}\) NMR spectra of the crude yellow-coloured reaction mixtures showed peaks at 28.0 and 69.3 ppm for reactions with Ph₂PBcat and Ph₂PBMes₂, respectively, consistent with chlorine-bound Bcat\(^{63}\) and BMes\(^{64}\) groups, respectively. Upon workup, yellow solids were isolated in 96 and 94% yields for reactions with Ph₂PBcat and Ph₂PBMes₂, respectively. The \(^1\text{H}\), \(^{13}\text{C}\{^{1}\text{H}\}\), \(^{11}\text{B}\{^{1}\text{H}\}\), and \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectra and the elemental analysis data were identical to that of 2-7. These phosphinoboration reactions must therefore also proceed through a formal P-B/C-Cl bond metathesis, producing 2-7 as well as ClBcat and ClBMes₂ as by-products. It is noteworthy that these reactions provide facile routes to the syntheses of chloroboranes.

\[
\text{Ph}_2\text{PBR}_2 + \text{O}_\text{Cl} \rightarrow \text{DCM, rt, 24 h} \rightarrow \begin{array}{c}
\text{Ph}_2\text{PO} \\
\text{PBR}_2
\end{array}
\]

\[
\text{R}_2 = \text{pin: (95\%)} \\
\text{R}_2 = \text{cat: (96\%)} \\
\text{R} = \text{Mes: (94\%)}
\]

**Scheme 2.4** Reactions of Ph₂PBpin, Ph₂PBcat, and Ph₂PBMes₂ with benzoyl chloride.

Related reactions of 2-3 and 2-4 with benzoyl chloride also proceeded in DCM at ambient temperature over 24 hours to give yellow solutions. Analysis of the crude \(^{11}\text{B}\{^{1}\text{H}\}\) NMR spectra revealed identical signals to those seen in the reactions with the diphenylphospine-substituted phosphinoboranes, indicating that the same chloroborane by-products were generated. Upon workup, yellow oils (2-8) were isolated in 92 and 94% yields for the reactions with 2-3 and 2-4, respectively (Scheme 2.5). The \(^{11}\text{B}\{^{1}\text{H}\}\) NMR spectra of the isolated materials were both silent but displayed \(^{31}\text{P}\{^{1}\text{H}\}\) NMR signals at 39.5 ppm. These, as well as the \(^1\text{H}\) and \(^{13}\text{C}\{^{1}\text{H}\}\) NMR spectra and the elemental analysis data, confirm that both reactions produce the same product 2-8 and affirm it as the acyl phosphine PhC(O)PrBu₂.
Scheme 2.5  Reactions of 2-3 and 2-4 with benzoyl chloride.

The corresponding reaction of 2-5 with one equivalent of benzoyl chloride under the same conditions also reacted to give a yellow solution that displayed a $^{11}$B{${}^1$H} NMR signal consistent with ClBcat. A yellow solid (2-9), isolated in 94% yield, displayed a $^{31}$P{${}^1$H} NMR signal at -2.9 ppm but no signals in the $^{11}$B{${}^1$H} NMR spectrum (Scheme 2.6). The $^1$H and $^{13}$C{${}^1$H} NMR spectra and the elemental analysis data are consistent with the formulation of 2-9 as the acyl phosphine PhC(O)PPh₂. Single crystals suitable for X-ray diffraction were grown from n-pentane. The diffraction study affirmed the formulation of 2-9 and revealed the trigonal pyramidal geometry about the central carbon atom (Figure 2.8). The P-C and C-O bond lengths were found to be 1.860(1) and 1.219(2) Å, respectively, while the sum of the angles about the central carbon was found to be 358.5°, consistent with maintenance of the C-O double bond.

Scheme 2.6  Reaction of 2-5 with benzoyl chloride.
2.3.3 Phosphinoboration of Acyl Phosphine

Taking note of the reported phosphinoboration reactions with ketones, aldehydes, and imines,\textsuperscript{14} the phosphinoboration reactions with the acyl phosphines synthesized herein were explored. The reaction of two equivalents of Ph\textsubscript{2}PBcat with benzoyl chloride proceeded in DCM at ambient temperature over 24 hours. By contrast, analogous reaction of Ph\textsubscript{2}PBpin with benzoyl chloride was less facile, requiring heating for 96 hours at 100 °C in toluene. Upon workup, the reactions of Ph\textsubscript{2}PBcat gave a colourless solid 2-10 in 90% yield while the reaction of Ph\textsubscript{2}PBpin gave a yellow solid 2-11 in 77% yield (Scheme 2.7). While the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra of 2-10 and 2-11 revealed a signals at 12.3 and 14.0 ppm, the \textsuperscript{11}B{\textsuperscript{1}H} NMR spectra revealed signals at 21.4 and 20 ppm, consistent with oxygen-bound Bcat and Bpin groups,\textsuperscript{14} respectively. In both cases, the \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra as well as the elemental analysis data were consistent with a 1:1 combination of the starting materials, indicating that an addition reaction had occurred and
affirming the formulations of 2-10 and 2-11 as PhC(OBcat)(PPh₂)₂ and PhC(OBpin)(PPh₂)₂, respectively.

Scheme 2.7  Reactions of two equivalents of Ph₂PBcat and Ph₂PBpin with benzoyl chloride.

Single crystals of 2-10 suitable for X-ray diffraction were grown from n-pentane. The diffraction study confirmed the formulation of 2-10 as PhC(OBcat)(PPh₂)₂, revealing a pseudo-tetrahedral geometry about the central carbon atom (Figure 2.9). The P-C bond lengths were found to be 1.940(3) and 1.917(2) Å while the B-O and C-O bond lengths were found to be 1.353(3) and 1.445(3) Å, respectively. Interestingly, no interaction is apparent between the boron and either phosphorus centre, with neither lone pair on phosphorus directed towards the vacant p-orbital on boron. Additionally, P-B distances were found to be 3.246(3) and 3.569(2) Å. These are within the sum of the van der Waals radii for P and B (3.98 Å) but well outside the sum of the covalent radii for P and B (1.98 Å).⁶⁵
Figure 2.9  ORTEP depiction of 2-10 showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. P: orange, O: red, B: yellow-green, C: black.

Inspired by these double addition reactions, we sought to extend this chemistry to other phosphinoboranes in an effort to probe their substituent effects. While a second equivalent of \( \text{Ph}_2\text{PBcat} \) reacted with 2-7 at ambient temperature over 24 hours to give 2-10, every mixture iteration of 2-7 with 2-2 to 2-5 and \( \text{Ph}_2\text{PBMes}_2 \) in DCM at ambient temperature or at 50 °C proved unreactive. Mixtures of 2-8 and 2-9 with 2-2 to 2-5, \( \text{Ph}_2\text{PBcat}, \text{Ph}_2\text{PBpin} \), and \( \text{Ph}_2\text{PBMes}_2 \) proved similarly unreactive under these conditions (Scheme 2.8), as did mixtures of benzoyl chloride with two equivalents of these phosphinoboranes.
2.4 Conclusions

The synthesis of a variety of new phosphinoboranes is reported herein. Crystallographic data was gathered for most of the phosphinoboranes synthesized herein and on the previously reported Ph$_2$PBcat and Mes$_2$PB(C$_6$F$_5$)$_2$ and computational investigations of these as well as Ph$_2$PBMes$_2$ were carried out. Analysis of the crystallographic and computed bond and angle metrics were used to investigate the P-B bond orders, with 2-3, Ph$_2$PBMes$_2$, and Mes$_2$PB(C$_6$F$_5$)$_2$ displaying double bond character and the other phosphinoboranes displaying single bond character. The phosphinoboration reaction of benzoyl chloride was investigated for most of these phosphinoboranes and was found to give a formal P-B/C-Cl bond metathesis to yield the corresponding acyl phosphines 2-7 to 2-9 with chloroborane by-product formation. It is worth noting that these reactions represent a facile synthetic route to acyl phosphines and to chloroboranes. Addition of two equivalents of Ph$_2$PBcat or Ph$_2$PBpin to benzoyl chloride resulted in the double addition products 2-10 and 2-11, with 2-10 also synthesizable from the reaction of 2-7 with a second equivalent of Ph$_2$PBcat. Attempts to extend this phosphinoboration reaction to other combinations of phosphinoborane and acyl phosphate were unsuccessful.

Scheme 2.8 Attempted synthesis of other double addition compounds.

2.5 Experimental

2.5.1 General Experimental Methods

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N$_2$. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (DCM, toluene, and $n$-pentane) were prepared using an Innovative Technologies solvent purification system or...
deoxygenated and distilled over sodium benzophenone under inert atmosphere. CDCl$_3$ (Aldrich) was deoxygenated, distilled over CaH$_2$, then stored over 3 Å molecular sieves before use. C$_6$D$_6$ (Aldrich) was deoxygenated, distilled over sodium benzophenone under inert atmosphere, then stored over 3 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. Ph$_2$PBpin,$^{14}$ Ph$_2$PBcat,$^{14}$ Ph$_2$PBMes$_2$,$^{12}$ and Mes$_2$PB(C$_6$F$_5$)$_2$$^{15}$ were prepared according to literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz or a Varian Mercury-300 MHz spectrometer. $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H}, $^{19}$F, and $^{11}$B{$^1$H} NMR chemical shifts (δ/ppm) are referenced to Me$_4$Si, Me$_4$Si, H$_3$PO$_4$, CFCl$_3$, and BF$_3$•OEt$_2$, respectively. Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI), a GCT Premier (EI), 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.

2.5.2 X-ray Diffraction Studies

Single crystals were coated with Paratone oil, mounted on a CryoLoop, and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-Kα (0.71073 Å) radiation. Data were collected using Bruker APEX-2 or APEX-3 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 or APEX-3 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.
Table 2.3 X-ray table for 2-1, 2-2, and 2-3.

<table>
<thead>
<tr>
<th></th>
<th>BrBquin (2-1)</th>
<th>tBu₂PBpin (2-2)</th>
<th>tBu₂PBMes₂ (2-3)</th>
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<tr>
<td><strong>Empirical Formula</strong></td>
<td>C₁₄H₈BBrO₂</td>
<td>C₁₄H₃₀BO₂P</td>
<td>C₂₀H₄₀BP</td>
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<td><strong>Weight (g/mol)</strong></td>
<td>298.92</td>
<td>272.16</td>
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<td><strong>Crystal System</strong></td>
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<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>Pbca</td>
<td>Pca2₁</td>
<td>P₂₁/n</td>
</tr>
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<td><strong>a (Å)</strong></td>
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<td>12.0762(7)</td>
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<td>90</td>
<td>90</td>
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<td><strong>β (°)</strong></td>
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<td>90</td>
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<tr>
<td><strong>γ (°)</strong></td>
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<td>90</td>
<td>90</td>
</tr>
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<td>4</td>
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<td>864</td>
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<td>Mo Kα</td>
<td>Mo Kα</td>
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<td>3.039 to 27.876</td>
<td>1.931 to 32.031</td>
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<td><strong>T (K)</strong></td>
<td>296(2)</td>
<td>150(2)</td>
<td>150(2)</td>
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<td><strong>Reflections Collected</strong></td>
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<td>16670</td>
<td>75798</td>
</tr>
<tr>
<td><strong>Independent Reflections</strong></td>
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<td>3870</td>
<td>8511</td>
</tr>
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<td>0.0730</td>
<td>0.1203</td>
</tr>
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<td><strong>GOF (F²)</strong></td>
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<td><strong>R1 indices [I&gt;2σ(I)]</strong></td>
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<td><strong>wR2 indices (all data)</strong></td>
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<td>0.1787</td>
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<td><strong>Largest diff. peak and hole (e. Å⁻³)</strong></td>
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<td>0.342 &amp; -0.367</td>
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<td><strong>CCDC No.</strong></td>
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Table 2.4  X-ray table for 2-4, 2-5, and Ph₂PBcat.

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<th>tBu₂PBcat (2-4)</th>
<th>Mes₂PBcat (2-5)</th>
<th>Ph₂PBcat</th>
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<tr>
<td><strong>Empirical Formula</strong></td>
<td>C₁₄H₂₂BO₂P</td>
<td>C₂₄H₂₆BO₂P</td>
<td>C₁₈H₁₄BO₂P</td>
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<td><strong>Weight (g/mol)</strong></td>
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<td><strong>Crystal System</strong></td>
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<td>Pna₂₁</td>
<td>Cc</td>
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<td><strong>a (Å)</strong></td>
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<td>18.6804(11)</td>
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<td>9.6887(8)</td>
<td>13.435(5)</td>
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<td><strong>c (Å)</strong></td>
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<td>24.173(9)</td>
<td>33.562(2)</td>
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<td><strong>α (°)</strong></td>
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<td>90</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
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<td>92.018(4)</td>
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<td><strong>γ (°)</strong></td>
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<td><strong>F(000)</strong></td>
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<td>2528</td>
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<td><strong>Radiation</strong></td>
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<td>Mo Kα</td>
<td>Mo Kα</td>
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<td>150(2)</td>
<td>150(2)</td>
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<td><strong>Reflections Collected</strong></td>
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Table 2.5 X-ray table for Mes$_2$PB(C$_6$F$_5$)$_2$, 2-9, and 2-11.

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<th>Mes$_2$PB(C$_6$F$_5$)$_2$</th>
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<th>PhC(OBcat)(PPh$_2$)$_2$ (2-11)</th>
</tr>
</thead>
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<td><strong>Empirical Formula</strong></td>
<td>C$<em>{30}$H$</em>{22}$BF$_{10}$P</td>
<td>C$<em>{25}$H$</em>{27}$OP</td>
<td>C$<em>{37}$H$</em>{29}$BO$_3$P</td>
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<td><strong>Weight (g/mol)</strong></td>
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<td>Triclinic</td>
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<td>$P\bar{1}$</td>
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<tr>
<td>$b$ (Å)</td>
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</tr>
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<td>$c$ (Å)</td>
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<td>$\beta$ (°)</td>
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<td>$\gamma$ (°)</td>
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<td>2</td>
</tr>
<tr>
<td>$\rho$ (calcd.) (Mg/m$^3$)</td>
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<tr>
<td>$\mu$ (mm$^{-1}$)</td>
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<td>0.181</td>
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<td>$F(000)$</td>
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<td>620</td>
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<td>Mo Kα</td>
<td>Mo Kα</td>
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<td>150(2)</td>
<td>150(2)</td>
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<td><strong>Reflections Collected</strong></td>
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<td>43828</td>
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<td><strong>CCDC No.</strong></td>
<td>1935189</td>
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2.5.1 Synthesis of Phosphinoboranes

2-1 2-Bromophanthro[9,10-d]-1,3,2-dioxaborole (BrBquin)

In a 100 mL Schlenk flask, a mixture of 9,10-phenanthrene-diol (0.57 mmol, 119.3 mg, 1 eq.) was prepared in DCM (30 mL) and cooled to 0 °C. A bubbler was attached with the outlet connected into a solution of NaOH in water. Boron tribromide (0.62 mmol, 0.06 mL, 1.1 eq.) was added dropwise slowly and the mixture was allowed to stir overnight. The mixture was dried in vacuo and the residue was sublimed in vacuo at 70 °C to afford a colourless crystalline product (108.2 mg, 64% isolated yield). Crystals suitable for single crystal X-ray diffraction were grown from sublimation. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.60 - 7.75$ (m, 4H), 8.10 (d, $J = 8$ Hz, 2H), 8.63 (d, $J = 8$ Hz, 2H) ppm. $^{11}$B$^1$H NMR (128 MHz, CDCl$_3$): $\delta = 27.2$ (s) ppm. $^{13}$C$^1$H NMR (100 MHz, CDCl$_3$): $\delta = 120.5, 122.0, 123.5, 126.1, 127.5, 128.0, 141.0$ ppm. HRMS (DART-TOF+): m/z [M-(BBr)+H] 209.06059 (calc’d for C$_{14}$H$_9$O$_2$: 209.06025).

2-2 Di-tert-butyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphine (tBu$_2$PBpin)

In a 20 mL vial, a suspension of tBu$_2$PLi (0.85 mmol, 124.1 mg, 1 eq.) was prepared in toluene (4 mL), cooled to -35 °C, and 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.70 mmol, 0.3 mL, 2 eq.) was added dropwise. The reaction mixture was stirred at ambient temperature for 4 hours. The solution was then filtered, dried in vacuo, and recrystallized from minimal n-pentane to afford a colourless crystalline solid (205.6 mg, 89% isolated yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.25$ (s, 12H), 1.28 (s, 9H), 1.31 (s, 9H) ppm. $^{11}$B$^1$H NMR (128 MHz, CDCl$_3$): $\delta = 35.6$ (s, br) ppm. $^{31}$P$^1$H NMR (162 MHz, CDCl$_3$): $\delta = -15.8$ (d, br, $^1J_{PB} = 77$ Hz) ppm. $^{13}$C$^1$H NMR (100 MHz, CDCl$_3$): $\delta = 25.0$ (s, 4C), 31.4 (d, $^1J_{PC} = 13$ Hz, 2C), 32.3 (d, $^2J_{PC} = 12$ Hz, 6C), 83.7 (s, 2C) ppm. HRMS (EI-TOF+): m/z [M] 272.2082 (calc’d for C$_{14}$H$_{30}$B$_1$O$_2$P$_1$: 272.2076).
2-3  **Di-tert-butyl(dimesitylboranyl)phosphine (tBu₂PBMes₂)**

In a 20 mL vial, a solution of tBu₂PH (0.30 mmol, 44.4 mg, 1 eq.) was prepared in toluene (4 mL). N-butyl lithium (1.6 M in hexane, 0.3 mmol, 0.19 mL, 1 eq.) was added dropwise and the solution was stirred at ambient temperature overnight. A solution of FBMes₂ (0.3 mmol, 80.5 mg, 1 eq.) in toluene (4 mL) was then added dropwise and the reaction mixture was stirred at ambient temperature for 4 hours. The solution was then filtered, dried *in vacuo*, and recrystallized from minimal *n*-pentane to afford a yellow crystalline solid (72.2 mg, 68% isolated yield).

**1H NMR (500 MHz, CDCl₃):** δ = 1.27 (d, 3J₁H = 14 Hz, 18H), 2.21 (s, 2H), 2.46 (s, 4H), 6.72 (m, 4H) ppm. **11B{1H} NMR (128 MHz, CDCl₃):** δ = 56.6 (s, br) ppm. **31P{1H} NMR (162 MHz, CDCl₃):** δ = 75.9 (s, br) ppm. **13C{1H} NMR (125 MHz, CDCl₃):** δ = 21.1 (s, 2C), 24.6 (s, 4C), 33.4 (d, 2Jₚ₋₋₋ₚ = 2 Hz, 6C), 38.2 (d, 1Jₚ₋₋₋ₚ = 17 Hz, 2C), 128.3 (s, 4C), 136.4 (s, 2C), 139.9 (s, 2C), 140.0 (s, 2C), 142.2 (s, br), 2C) ppm. **HRMS (EI-TOF+):** m/z [M] 394.2958 (calc’d for C₂₆H₄₀B₁P₁: 394.2961).

2-4  **Benzo[d][1,3,2]dioxaborol-2-yldi-tert-butylphosphine (tBu₂PBcat)**

In a 500 mL Schlenk flask, a solution of tBu₂PH (6.84 mmol, 1.0010 g, 1 eq.) was prepared in toluene (30 mL) and cooled to -78 °C in a dry ice isopropanol bath. Tert-butyl lithium (1.7 M in pentane, 6.84 mmol, 4.03 mL, 1 eq.) was added dropwise and the solution was stirred for 1 h at -78 °C and then was allowed to warm to ambient temperature over 2 h, after which time the solution was cooled back down to -78 °C. A solution of ClBcat (6.50 mmol, 1.0033 g, 0.95 eq.) in toluene (12 mL) was added dropwise and the reaction mixture was left to warm to room temperature while stir overnight. The solution was then filtered, dried *in vacuo*, and recrystallized from minimal *n*-pentane to afford a colourless crystalline solid (1.3740 g, 76% isolated yield).

**1H NMR (500 MHz, CDCl₃):** δ = 1.43 (d, 3J₁H = 12 Hz, 18H), 7.10 (dd, 3J₁H₁ = 6 Hz, 4J₁H₂ = 3 Hz, 2H), 7.27 (dd, 3J₁H₁ = 6 Hz, 4J₁H₂ = 3 Hz, 2H) ppm. **11B{1H} NMR (128 MHz, CDCl₃):** δ = 37.2 (s, br) ppm. **31P{1H} NMR (162 MHz, CDCl₃):** δ = -16.4 (s, br) ppm. **13C{1H} NMR (125 MHz, CDCl₃):** δ = 32.4 (d, 2Jₚ₋₋₋ₚ = 12 Hz, 6C), 112.5 (s, 2C), 122.8 (s, 2C), 148.3 (s, 2C) ppm, ipso-carbon on tert-butyl group was not observed. **HRMS (EI-TOF+):** m/z [M] 264.1451 (calc’d for C₁₄H₂₂B₁O₂P₁: 264.1450).
Benzo[\textit{d}][1,3,2]-dioxaborol-2-yldimesitylphosphine (\textit{Mes}_2\textit{PBcat})

In a 20 mL vial, a solution of \textit{Mes}_2\textit{PH} (1.54 mmol, 415.3 mg, 1 eq.) was prepared in toluene (4 mL). \textit{N}-butyl lithium (1.6 M in hexane, 1.54 mmol, 0.96 mL, 1 eq.) was added dropwise and the solution was stirred at ambient temperature overnight. A solution of Cl\textit{BCat} (1.54 mmol, 237.1 mg, 1 eq.) in toluene (4 mL) was then added dropwise and the reaction mixture was stirred at ambient temperature for 4 hours. The solution was then filtered, dried \textit{in vacuo}, and recrystallized from minimal \textit{n}-pentane to afford a yellow crystalline solid (512.1 mg, 86% isolated yield). \textit{\textit{H} NMR (500 MHz, CDCl}_3): \(\delta = 2.28 \ (s, \ 6H), 2.31 \ (s, \ 12H), 6.88 \ (d, \ 4J_{PH} = 4 \ Hz, \ 4H), 7.08 \ (d d d, \ 3J_{HH} = 6 \ Hz, \ 4J_{HH} = 3 \ Hz, \ 5J_{HH} = 1 \ Hz, \ 2H), 7.22 \ (d d d, \ 3J_{HH} = 6 \ Hz, \ 4J_{HH} = 3 \ Hz, \ 5J_{HH} = 1 \ Hz, \ 2H) \ ppm. \textit{\textit{B}^{[\textit{\textit{H}}]}} NMR (128 MHz, CDCl}_3): \(\delta = 37.7 \ (s, \ br) \ ppm. \textit{\textit{P}^{[\textit{\textit{H}}]}} NMR (162 MHz, CDCl}_3): \(\delta = -106.1 \ (s, \ br) \ ppm. \textit{\textit{C}^{[\textit{\textit{H}}]}} NMR (125 MHz, CDCl}_3): \(\delta = 21.1 \ (s, \ 2C), 23.8 \ (s, \ 2C), 23.9 \ (s, \ 2C), 112.8 \ (s, \ 2C), 122.9 \ (s, \ 2C), 127.6 \ (d, \ 4J_{PC} = 3 \ Hz, \ 2C), 129.7 \ (d, \ 3J_{PC} = 5 \ Hz, \ 4C), 138.2 \ (s, \ 2C), 143.3 \ (d, \ 2J_{PC} = 14 \ Hz, \ 4C), 148.8 \ (d, \ 1J_{PC} = 2 \ Hz, \ 2C) \ ppm. \textit{HRMS (EI-TOF+)}: m/z [M] 388.1765 (calc’d for \textit{C}_{24}\textit{H}_{26}\textit{B}_{1}\textit{O}_{2}\textit{P}: 388.1763).

Phenanthro[9,10-\textit{d}]-1,3,2-dioxaborole diphenylphosphine (\textit{Ph}_2\textit{PBquin})

In a 20 mL vial, a solution of \textit{Ph}_2\textit{PH} (0.20 mmol, 37.1 mg, 1 eq.) was prepared in \textit{n}-pentane (4 mL), cooled to \(-35 ^\circ\text{C}, and \textit{n}-butyllithium (0.20 mmol, 0.12 mL, 1 eq.) was added dropwise. The reaction mixture was stirred at ambient temperature for 2 hours. The solution was then cooled to \(-35 ^\circ\text{C}, \textit{BrBquin} (0.20 mmol, 62.2 mg, 1 eq.) was added, and the mixture was stirred at ambient temperature for 16 hours. The mixture was filtered, dried \textit{in vacuo}, and recrystallized from minimal \textit{n}-pentane to afford a colourless solid (46.7 mg, 58% isolated yield). \textit{\textit{H} NMR (500 MHz, CDCl}_3): \(\delta = 7.33 – 7.45 \ (m, \ 5H), 7.60 – 7.74 \ (m, \ 9H), 8.11 – 8.21 \ (m, \ 2H), 8.71 \ (d d, \ J = 8 \ Hz, \ 1 Hz, \ 2H) \ ppm. \textit{\textit{B}^{[\textit{\textit{H}}]}} NMR (128 MHz, CDCl}_3): \(\delta = 37.1 \ (s, \ br) \ ppm. \textit{\textit{P}^{[\textit{\textit{H}}]}} NMR (162 MHz, CDCl}_3): \(\delta = -66.10 \ (s, \ br) \ ppm. \textit{\textit{C}^{[\textit{\textit{H}}]}} NMR (126 MHz, CDCl}_3): \(\delta = 120.6, 120.8, 122.7, 123.5, 125.8, 127.3, 128.0, 128.6, 128.9 \ (d, \ J = 8 \ Hz), 132.8 \ (d, \ J = 3 \ Hz), 134.9 \ (d, \ J = 18 \ Hz), 140.9 \ ppm. \textit{HRMS (DART ESI+)}: m/z [M] 405.12087 (calc’d for \textit{C}_{36}\textit{H}_{19}\textit{B}_{1}\textit{O}_{2}\textit{P}: 405.12157).
2.5.2 Phosphinoborations of benzoyl chloride

2-7 (Diphenylphosphinyl)(phenyl)methanone (PhC(O)PPh₂)

In a 20 mL vial, a solution of the given phosphinoborane (Ph₂PBpin, Ph₂PBcat, or Ph₂PBMes₂) (0.1 mmol, 1 eq.) was prepared in DCM (3 mL). A solution of benzoyl chloride (0.1 mmol, 14.1 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) to afford a yellow solid (Ph₂PBpin: 27.6 mg, 95% isolated yield, Ph₂PBcat: 27.8 mg, 96% isolated yield, Ph₂PBMes₂: 27.2 mg, 94% isolated yield). ¹H NMR (400 MHz, CDCl₃) δ = 7.32 – 7.48 (m, 13H), 7.97 (m, 2H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃) δ = 14.1 ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 128.4 (d, J = 9 Hz), 128.6, 128.8 (d, J = 9 Hz), 129.6, 132.8 (d, J = 6 Hz), 133.3, 135.0 (d, J = 19 Hz), 139.3 (d, J = 35 Hz), 213.0 (d, J = 37 Hz) ppm. EA: calcd (%) for C₁₉H₁₅OP: C, 78.61; H, 5.21; found: C, 79.87; H, 6.87.

2-8 (Di-tert-butyolphosphinyl)(phenyl)methanone (PhC(O)PrBu₂)

In a 20 mL vial, a solution of the given phosphinoborane (tBu₂PBcat or tBu₂PBMes₂) (0.1 mmol, 1 eq.) was prepared in DCM (3 mL). A solution of benzoyl chloride (0.1 mmol, 14.1 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) to afford a yellow oil (tBu₂PBcat: 23.0 mg, 92% isolated yield, tBu₂PBMes₂: 23.5 mg, 94% isolated yield). ¹H NMR (500 MHz, C₆D₆) δ = 1.23 (dd, J = 12, 2 Hz, 18H), 6.97 – 7.13 (m, 3H), 8.25 (ddt, J = 9, 3, 2 Hz, 2H) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ = 39.46 ppm. ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 30.5 (d, J = 13 Hz), 33.4 (d, J = 22 Hz), 128.6 (d, J = 2 Hz), 129.1 (d, J = 13 Hz), 133.1 (d, J = 2 Hz), 144.2 (d, J = 35 Hz), 218.2 (d, J = 40 Hz) ppm. EA: calcd (%) for C₁₅H₂₃OP: C, 71.97; H, 9.26; found: C, 71.98; H, 9.26.
In a 20 mL vial, a solution of Mes₂PBcat (0.1 mmol, 38.8 mg, 1 eq.) was prepared in DCM (3 mL). A solution of benzoyl chloride (0.1 mmol, 14.1 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) to afford a yellow solid (35.1 mg, 94% isolated yield). Crystals suitable for X-ray diffraction were grown from n-pentane. ¹H NMR (500 MHz, C₆D₆) δ = 2.00 (s, 6H), 2.35 (s, 12H), 6.70 – 6.66 (m, 4H), 6.89 – 6.98 (m, 3H), 8.08 – 8.12 (m, 2H) ppm. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ = -2.85 ppm. ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 21.0, 23.5 (d, J = 14 Hz), 128.0 (d, J = 2 Hz), 128.4, 128.6 (d, J = 1 Hz), 130.3 (d, J = 5 Hz), 132.6 (d, J = 2 Hz), 139.4 (d, J = 1 Hz), 141.3 (d, J = 43 Hz), 143.9 (d, J = 15 Hz), 211.0 (d, J = 37 Hz) ppm. EA: calcd (%) for C₂₅H₂₇OP: C, 80.19; H, 7.27; found: C, 80.07; H, 7.34.

2.5.3 Phosphinoboration of Acyl Phosphone

In a 20 mL vial, a solution of Ph₂PBcat (0.2 mmol, 60.8 mg, 2 eq.) was prepared in DCM (3 mL). A solution of benzoyl chloride (0.1 mmol, 14.1 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) to afford a colourless crystalline solid (53.5 mg, 90% isolated yield). ¹H NMR (500 MHz, CDCl₃) δ = 6.78 – 6.90 (m, 4H), 6.95 – 7.01 (m, 3H), 7.07 – 7.24 (m, 14H), 7.53 – 7.66 (m, 8H) ppm. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = 21.4 (s, br) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 12.3 ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 88.5 (t, J = 43 Hz), 111.6, 121.8, 126.0 (d, J = 1 Hz), 126.8, 127.0 (t, J = 7 Hz), 127.9 (dt, J = 6, 4 Hz), 129.1, 129.6, 133.4 (t, J = 6 Hz), 134.2 (t, J = 5 Hz), 136.2 (dt, J = 34, 12 Hz), 139.8 (t, J = 3 Hz), 147.7 ppm. EA: calcd (%) for C₃₇H₂₉BO₃P₂: C, 74.77; H, 4.92; found: C, 74.93; H, 4.88.
In a 20 mL vial, a solution of Ph3PBpin (1.49 mmol, 466 mg, 2 eq.) was prepared in toluene (1.5 mL). A solution of benzoyl chloride (0.71 mmol, 100 mg, 1 eq.) in toluene (1.5 mL) was added at ambient temperature and the reaction mixture was heated at 100 °C for 5 days. The solution was then dried in vacuo and triturated with hexane (2 mL) to afford a yellow solid (328 mg, 77% isolated yield); mp 126-128°C.

\[ \text{1H NMR} (400 \text{ MHz, CDCl}_3) \delta = 0.75 (s, 12H), 6.84 – 6.87 (m, 3H), 6.94 (m, 2H), 7.09 (t, J = 7.3 Hz, 4H), 7.17 (t, J = 7.8 Hz, 2H), 7.21 – 7.26 (m, 6H), 7.37 (m, 4H), 7.64 (m, 4H) \text{ ppm.} \]

\[ \text{11B NMR} (128 \text{ MHz, CDCl}_3) \delta = 20 (s, \text{ br}) \text{ ppm.} \]

\[ \text{31P\{1H\} NMR} (162 \text{ MHz, CDCl}_3) \delta = 14.0 \text{ ppm.} \]

\[ \text{13C\{1H\} NMR} (400 \text{ MHz, CDCl}_3) \delta = 24.4, 82.7, 86.6 (t, J = 41 Hz), 125.4, 126.3, 127.4 (t, J = 6 Hz), 127.5 (t, J = 4 Hz), 128.0 (t, J_{CP} = 4 Hz), 128.6, 128.8, 135.2 (t, J = 6 Hz), 135.6 (t, J = 3 Hz), 135.7 (t, J = 13 Hz), 136.7 (t, J = 13 Hz), 140.6, (t, J = 13 Hz) \text{ ppm.} \]

EA: calcd (%) for C_{37}H_{37}BO_{3}P: C, 73.77; H, 6.19; found: C, 73.53; H, 6.24.

### 2.5.4 Computational Details

Geometry optimizations and frequency calculations were performed with the Gaussian 16 package with the BP86 functional and the polarized triple-zeta basis set Def2-TZVP. The absence of any imaginary frequency with an absolute magnitude greater than 10 cm$^{-1}$ confirmed that each optimized structure was indeed located at a minimum on its potential energy hypersurface. Natural bond orbital and natural population analyses were performed on optimized structures using NBO at the M06-2X/Def2-TZVP level of theory. X-ray coordinates were used as the starting geometry for geometry optimizations where possible.

### 2.6 References


25. A. Staubitz, A. P. M. Robertson, M. E. Sloan and I. Manners, *Chem. Rev.*, 2010, **110**, 4023-4078.


Section 2.2 - Double Phosphinoboration of CO$_2$: A Facile Route to Diphospha-ureas

2.7 Introduction to Carbon Dioxide Reactivity

As the levels of anthropogenic CO$_2$ continue to climb in the atmosphere, the natural cycle of CO$_2$ emission and uptake is becoming overwhelmed causing impacts on the Earth’s environment.$^{1-3}$ Attempts to address this problem have spurred significant research efforts into carbon capture and storage,$^{4-7}$ its conversion into C1 chemical feedstocks,$^{8-11}$ and its direct use as a reagent in chemical synthesis. In the latter context, CO$_2$ is used industrially as a reagent in the syntheses of urea (105 million tonnes CO$_2$), salicylic acid (90,000 tonnes CO$_2$), cyclic carbonates (80,000 tonnes CO$_2$), and polypropylene carbonate (70,000 tonnes CO$_2$).$^{12}$ While strongly nucleophilic metal-based compounds have traditionally been used for these transformations,$^{12, 13}$ transition metal-based catalysts have also been applied,$^{14-18}$ with Boogaerts and Nolan reporting carboxylations mediated by gold-based catalysts$^{19-21}$ and Inoue performing cyclizations of unsaturated compounds mediated by palladium$^{22, 23}$ and nickel-based$^{24, 25}$ catalysts (Scheme 2.9).

![Scheme 2.9](image)

Scheme 2.9 Transition metal-catalyzed carboxylation (top) and cyclization (bottom) reactions with CO$_2$.

Reactions of main group-based systems have also been developed with CO$_2$, providing alternative approaches to its activation. Since the initial report by Stephan, Erker, and Grimme of P/B-based frustrated Lewis pairs (FLPs) being applied to the stoichiometric capture and release of CO$_2$ (Scheme 2.10),$^{26}$ several other FLP systems have been developed to capture CO$_2$ or to effect its stoichiometric or catalytic reduction. While Ashley, O’Hare, and Piers focused on B/N-based...
FLPs,\textsuperscript{27,28} Fontaine, Maron, and Stephan developed B/P-based FLPs.\textsuperscript{29-32} Moving down one period in the periodic table, Al/P-based FLPs\textsuperscript{33,34} have been developed by Stephan while investigations into Si/P-based FLPs\textsuperscript{35,36} have been carried out by Stephan and Müller. Strongly basic main group species have also shown productive CO\textsubscript{2} chemistry, with Dielmann demonstrating capture with particularly basic phosphines,\textsuperscript{37-39} Louie reporting carboxylation reactions of N-heterocyclic carbenes,\textsuperscript{40} and Kemp reporting carboxylation reactions of germanium- and tin-silyl amides (Figure 2.10).\textsuperscript{41}

\begin{equation*}
\begin{aligned}
\text{PtBu}_3 &+ \text{B(C}_6\text{F}_5)_3 &\xrightleftharpoons{\text{CO}_2, \text{25 °C}} &\text{tBu}_3^+\text{P}^\ominus\text{B(C}_6\text{F}_5)_3 \\
\text{Mes}_2\text{P} &+ \text{B(C}_6\text{F}_5)_2 &\xrightleftharpoons{\text{CO}_2, \text{25 °C}} &\text{Mes}_2^+\text{P}^\ominus\text{B(C}_6\text{F}_5)_2
\end{aligned}
\end{equation*}

**Scheme 2.10** Initial report of FLP activation of CO\textsubscript{2}.

\begin{equation*}
\begin{aligned}
\begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{N}
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{PPh}_2
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{Bcat}
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{AlX}_3
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{TMSOTf}
\end{array}
\end{array}
\end{array}
\end{aligned}
\end{equation*}

Ashley, O’Hare, and Piers Fontaine Stephan Stephan X = Cl, Br Stephan

\begin{equation*}
\begin{aligned}
\begin{array}{c}
\begin{array}{c}
\text{[Me}_3\text{C}_6\text{Si]}^+
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{B(C}_6\text{F}_5)_4
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{N}\cdots\text{Ni/Pr}
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{TMS}
\end{array}
\end{array} &
\begin{array}{c}
\begin{array}{c}
\text{N}^\ominus\text{TMS}
\end{array}
\end{array}
\end{array}
\end{aligned}
\end{equation*}

Müller Dielmann Louie Kemp

M = Ge, Sn

**Figure 2.10** Selected main group-based systems that undergo reaction with CO\textsubscript{2}.
Synthetic strategies to ureas have also benefited from the use of CO₂ as a reagent. While the direct reaction of CO₂ with amines requires high temperatures and pressures,²⁴-²⁵ transition metal-based catalysts¹⁸,⁴⁶ have been shown to mediate reactions from silylamines and cesium-based catalysts from aliphatic amines to ureas.⁴⁷-⁴⁹ Main group-based reactions have also been reported, with stoichiometric synthesis of ureas using amines and (PhO)₂P(O)H from the Yamazaki group⁴³ and the use of silylamines with supercritical CO₂ from the Holmes group.⁴² Catalytic syntheses from CO₂ have also been reported using sulfonium cations generated from DMSO to catalyze urea synthesis from alkyl and aryl amines⁵⁰ and indium-based Lewis acids catalyzing the reaction from silylamines.⁵¹

In contrast to ureas, the phosphorus analogues, diphospha-ureas, (R₂P)₂C=O are rare (Figure 2.11, Figure 2.12). In the first example of a diphospha-urea, Becher and Langer prepared (Ph₂P)₂C=O in low yield by the reaction of Ph₂PSiMe₃ with phosgene at -110 °C.⁵² Transition metal-supported diphospha-ureas have also been reported by Ruiz, Glueck, King, and Holt.⁵³-⁶³ The reduction of dimeric phosphaketenes, RP=C=O was reported by Schmutzler, Appel, and Paulen to give an alternative route to diphospha-ureas,⁶⁴-⁶⁷ and Stephan has described a synthetic route exploiting nucleophilic attack of the phosphaketene Ph₃GeP=C=O by phosphides and subsequent alkylation to form tBu₂PC(O)PMe₂ as well as the first crystallographically characterized free diphospha-ureas tBu₂PC(O)P(Ph₂Ge)₂Me and tBu₂PC(O)P(Ph₂Ge)₂.⁶⁸

![Chemical structures](image)

**Figure 2.11** Exhaustive list of previously reported diphospha-ureas.
Figure 2.12 Exhaustive list of previously reported diphospha-ureas continued.

Drawing inspiration from advances in phosphinoboration and diphospha-urea chemistry, this section explores the reactivity of a variety of phosphinoboranes with CO$_2$. Substituent effects are found to direct the chemistry either to a 1,2-addition product or to a diphospha-urea product. The mechanism of this reaction is probed computationally for several phosphinoboranes and is supported by the crystallographic characterization of a reaction intermediate.

2.8 Results and Discussion

2.8.1 Phosphinoboration of CO$_2$

Our most recent efforts in phosphinoboration chemistry began with the study of their reactivity towards CO$_2$ in collaboration with the Westcott group. The reaction of Ph$_2$PBpin with 4 atm CO$_2$ in benzene proceeds at ambient temperature over 4 days to give, upon workup, a light yellow solid (2-12) in 35% yield (Scheme 2.11). While the $^{11}$B{$^{1}$H} NMR spectrum shows a broad singlet at 22 ppm, consistent with an oxygen-bound Bpin group, the $^{13}$C{$^{1}$H} and $^{31}$P{$^{1}$H} NMR spectra show doublets in the $^{13}$C-labelled product centred at 177.5 and -0.7 ppm, respectively, each with a $J$-coupling of 16 Hz. These data are consistent with a 1,2-addition product wherein the P-B bond is broken to form P-C and B-O bonds. Additionally, FT-IR spectroscopy revealed a stretching frequency at 1705 cm$^{-1}$, consistent with the presence of a C=O group. Single crystals suitable for X-ray diffraction were grown from cold n-pentane and a diffraction study confirmed the formulation of 2-12 as Ph$_2$PC(O)OBpin with a slightly distorted trigonal planar geometry at the central carbon which results in a P-C-O angle of 111.12(16)$^\circ$ (Figure 2.13). The newly formed P-C and B-O bonds were found to be 1.850(2) and 1.383(3) Å, respectively, while the C-O bonds were found to be 1.197(3) and 1.360(3) Å, consistent with formal double and single bonds, respectively.
Scheme 2.11  Reaction of Ph$_2$PBpin with CO$_2$.

Figure 2.13  ORTEP depiction of 2-12 showing thermal ellipsoids at 50% probability. Hydrogen atoms and minor disorder omitted for clarity. P: orange, O: red, B: yellow-green, C: black.

While attempting to grow crystals of 2-12, we found that exposure of 2-12 to an excess of Ph$_2$PBpin in *n*-pentane at -35 °C for approximately 1 year produced colourless crystals (2-13) in relatively low yields. All efforts to obtain HRMS or NMR data of 2-13 were unsuccessful due to its instability in DCM or toluene solutions at -35 °C, as evidenced by NMR spectroscopy, and in the solid state at ambient temperature. However, the original crystalline product was suitable for single crystal X-ray diffraction. The subsequent diffraction study confirmed its formulation as (Ph$_2$P)$_2$C(OBpin)$_2$ as well as the pseudo-tetrahedral geometry about the central carbon atom.
The newly formed P-C bond lengths were found to be 1.9116(17) and 1.9388(18) Å while the newly formed B-O bond lengths were found to be 1.370(2) and 1.364(2) Å.

Figure 2.14  ORTEP depiction of 2-13 showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. P: orange, O: red, B: yellow-green, C: black.

The isolation of 2-13 sparked an investigation into the further reactivity of R$_2$PBR$_2^1$ and of R$_2$PC(O)OB$R_2^1$ compounds with CO$_2$. To probe substituent effects in this reaction, Mes$_2$PB(C$_6$F$_5$)$_2$ was subjected to 4 atm of CO$_2$ in DCM at ambient temperature, at 50 °C, or in toluene at 100 °C and monitored by NMR spectroscopy. Unfortunately, no reactivity was observed other than slight decomposition with adventitious water. The corresponding reaction of Ph$_2$PBMes$_2$ with 4 atm of CO$_2$ in DCM at ambient temperature proceeded over 3 days to give, upon workup, a white solid 2-14 in 86% yield (Scheme 2.12). The $^{13}$C{$_1$H} and $^{31}$P{$_1$H} NMR spectra are quite similar to those of 2-12, showing doublets in the $^{13}$C-labelled product centred at 178.1 and -1.5 ppm, respectively, each with a J-coupling of 19 Hz, while the $^{11}$B{$_1$H} NMR spectrum shows a broad singlet at 53.1 ppm, consistent with an oxygen-bound BMes$_2$ group. 70 In
addition, the FT-IR spectrum revealed a C=O stretching frequency at 1662 cm\(^{-1}\). Single crystals suitable for X-ray diffraction were grown from \(n\)-pentane and a diffraction study confirmed the formulation of 2-14 as Ph\(_2\)PC(O)OBMes\(_2\) (Figure 2.15), with a similar geometry to that seen in 2-12. The newly formed P-C and O-B bonds were found to be 1.859(2) and 1.410(2) Å, respectively, while the C-O bonds were found to be 1.200(2) and 1.362(2) Å, again consistent with formal double and single bonds, respectively.

![Scheme 2.12 Reaction of Ph\(_2\)PBMes\(_2\) with CO\(_2\).](image)

**Scheme 2.12** Reaction of Ph\(_2\)PBMes\(_2\) with CO\(_2\).

![Figure 2.15 ORTEP depiction of 2-14 showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. P: orange, O: red, B: yellow-green, C: black.](image)
Reactions of 2-2 and 2-3 with CO₂ proceeded in DCM at ambient temperature overnight and for 3 days to give the analogous 1,2-addition products 2-15 and 2-16 as a white solid and a yellow oil in 89 and 82% isolated yields, respectively (Scheme 2.13). In the ¹³C-labelled products, the ³¹P{¹H} NMR spectra of 2-15 and 2-16 exhibit doublets centred at 48.2 and 47.3 ppm with J-couplings of 35 and 40 Hz, respectively, while the corresponding ¹³C{¹H} NMR doublets appear centred at 178.2 and 179.3 ppm, respectively. Interestingly, 2-15 and 2-16 exhibit greater J-coupling constants than 2-12 and 2-14 between the P and C=O atoms, consistent with increased P-C bond strengths resulting from the more basic tBu₂P group. The FT-IR spectra show stretching frequencies at 1670 and 1695 cm⁻¹ for 2-15 and 2-16, respectively, consistent with the presence of C=O groups. Considering the characterizations of 2-12 and 2-14, these data are consistent with the formulations of 2-15 and 2-16 as tBu₂PC(O)OBpin and tBu₂PC(O)OBMes₂, respectively.

Scheme 2.13  Reactions of 2-2 and 2-3 with CO₂.

Related reactions with phosphinoboranes of the form R₂PBcat (R = Ph, tBu 2-4, Mes 2-5) were performed with 4 atm CO₂ in DCM at ambient temperature for several days but gave products distinct from 2-12 and 2-14 to 2-16. The phosphinoborane Ph₂PBcat was seen to react with CO₂ to give a yellow solution (Scheme 2.14). Monitoring the reaction in situ by NMR spectroscopy showed the appearance of a signal in the ¹¹B{¹H} NMR spectrum at 24.4 ppm, consistent with an oxygen-bound Bcat group.⁶⁹ In the ¹³C-labelled reaction mixture, the ³¹P{¹H} NMR spectrum showed a doublet at 30.5 ppm while the ¹³C{¹H} NMR spectrum showed the corresponding triplet at 239.0 ppm, each with a J-coupling of 70 Hz. These data are consistent with the generation of the diphospha-urea (Ph₂P)₂C=O (2-17) with concomitant formation of O(Bcat)₂. Efforts to isolate 2-17 were plagued by its thermal and photochemical instability which was also noted by the authors in the initial report of its synthesis.⁵²
The corresponding reactions of 2-4 and 2-5 with CO$_2$ also proceeded over several days to produce yellow solutions that displayed $^{11}$B{$_1$H} NMR signals at 22.5 and 21.9 ppm and $^{31}$P{$_1$H} NMR signals at 75.5 and 14.4 ppm, respectively. From these mixtures, yellow solids (2-18) and (2-19) were isolated in 43 and 34% yields, respectively (Scheme 2.14). The FT-IR spectra of 2-18 and 2-19 revealed C=O bond stretches of 1672 and 1662 cm$^{-1}$, respectively, while the $^{31}$P{$_1$H} NMR signals became doublets in the $^{13}$C-labelled analogues with the corresponding $^{13}$C{$_1$H} NMR triplets appearing at 245.5 and 227.5 ppm, each with J-coupling of 83 and 73 Hz. While the IR stretching frequencies are similar to those observed for 2-15 and 2-16, the J-couplings are consistent with decreasing P-C bond strengths in the order of $t$Bu$_2$P-, Mes$_2$P-, Ph$_2$P-substituted systems.

![Scheme 2.14](image)

**Scheme 2.14** Reactions of R$_2$PBcat (R = Ph, $t$Bu 2-4, Mes 2-5) with CO$_2$.

Crystals suitable for single crystal X-ray diffractometry were grown from $n$-pentane solutions. The diffraction studies of 2-18 and 2-19 were performed at -123 °C in the dark due to their photochemical instability, confirming their formulation as ($t$Bu$_2$P)$_2$C=O and (Mes$_2$P)$_2$C=O, respectively (Figure 2.16). In the case of 2-18, two molecules appear in the asymmetric unit, whose P-CO bond lengths were found to be 1.887(5), 1.893(5), 1.902(5), and 1.898(5) Å and the C=O bond lengths were found to be 1.224(6) and 1.213(6) Å. The resulting P-C-P angles were found to be 116.8(2) and 117.0(2)° and the P-C=O angles were found to be 121.0(3), 122.2(3), 121.1(3), and 121.9(3)°, with each summing to 360°. In the case of 2-19, the P-CO bond lengths were found to be 1.914(4) and 1.905(2) Å and the C=O bond length was found to be 1.192(2) Å. The resulting P-C-P angle was found to be 102.29(10)° and the two P-C=O angles were found to be 130.03(16) and 127.65(16)°, summing to nearly 360° and confirming the trigonal planar geometry about the central carbon atom. These parameters are comparable to those recently reported for
Given that different types of compounds are isolated from the reactions of phosphinoboranes with CO2 depending on substituent effects, further reactivity of 2-12 and 2-14 to 2-16 with phosphinoboranes was probed. Although every mixture iteration of 2-12 and 2-14 to 2-16 with an
equivalent of 2-2 to 2-6, Ph₂PBcat, Ph₂PBpin, and Ph₂PBMes₂ was performed in DCM at ambient temperature and at 50 °C or in toluene at 100 °C in an attempt to make mixed diphospha-ureas, no productive reactivity was observed (Scheme 2.15).

\[
\begin{align*}
\text{R}_2\text{P} \quad \text{O} \quad \text{BR}_2^1 + \text{R}^2\text{P} \quad \text{O} \quad \text{BR}_2^3 \\
\to 1) \text{DCM, rt} \\
2) \text{DCM, 50 °C} \\
3) \text{Tol, 100 °C} \\
\text{R} = \text{Ph, tBu} \\
\text{R}_2^1 = \text{pin, Mes} \\
\text{R}_2^3 = \text{pin, cat, Mes} \\
\text{R}^2 = \text{Ph, tBu, Mes}
\end{align*}
\]

**Scheme 2.15** Attempted synthesis of mixed diphospha-urea compounds.

### 2.8.2 UV Radiation Induced Reactions with Diphospha-ureas

Formyl-phosphines and diphospha-ureas are well known to produce diphosphines and CO gas on exposure to UV radiation.\(^{67, 68, 71, 72}\) As such, this reactivity was probed with the two isolable diphospha-ureas, 2-18 and 2-19 (Scheme 2.16). In sealed NMR tubes, a solution of either 2-18 in \text{n-pentane} or \text{in situ} generated 2-19 in DCM was subjected to UV light for 2 hours, resulting in the disappearance of each the solution’s yellow colour. Analysis of the sealed reaction mixtures by NMR spectroscopy revealed a signal at 181.0 ppm in the \(^{13}\text{C}\{^1\text{H}\}\) NMR in each, corresponding to dissolved CO gas,\(^{73}\) and signals at 40.0 and -30.4 ppm in the \(^{31}\text{P}\{^1\text{H}\}\) NMR corresponding to \text{tBu}_2\text{P}-\text{PrBu}_2\(^{74}\) and \text{Mes}_2\text{P}-\text{PMes}_2,\(^{75}\) respectively. Crystals suitable for singe crystal X-ray diffractometry of \text{Mes}_2\text{P}-\text{PMes}_2 were grown from slow evaporation of the crude DCM solution and the diffraction study confirmed the formulation of \text{Mes}_2\text{P}-\text{PMes}_2 by comparison of the unit cell parameters to reported values.\(^{76}\)

\[
\begin{align*}
\text{R}_2\text{P} \quad \text{O} \quad \text{P} \quad \text{R} \\
\to \text{UV light} \\
\to \text{rt, 2h} \\
\text{n-pentane, R = tBu 2-18} \\
\text{or DCM, R = Mes 2-19}
\end{align*}
\]

**Scheme 2.16** Reactions of 2-18 and 2-19 induced by UV radiation.
2.8.3 Mechanistic Insights

The mechanism of the reactions of Ph₂PBpin, Ph₂PBcat, and 2-4 with CO₂ were probed computationally with the TURBOMOLE 7.3 suite,77 with geometry optimizations and frequency calculations at the PW6B95-D3/Def2-QZVP + COSMO-RS78-82 level of theory with DCM solvation and single-point calculations at the TPSS-D3/Def2-TZVP + COSMO82-84 level of theory with DCM solvation85 (Figure 2.17). In the case of Ph₂PBpin, the direct addition of P-B across a C=O bond in CO₂ is -2.3 kcal/mol exergonic over a barrier of 23.4 kcal/mol via the first transition state (TS) structure TS1 to afford the single addition product 2-12 with a cis-arrangement of the Bpin and Ph₂P fragments. The cis-arrangement was found to be only slightly more favourable than the crystallographically observed trans-arrangement by 0.3 kcal/mol. Addition of a second equivalent of Ph₂PBpin to the C=O bond of 2-12 is -3.3 kcal/mol exergonic over a larger barrier of 28.2 kcal/mol via TS2 to give INT 2-13. The elimination of O(Bpin)₂ from 2-13 to give 2-17 is -20.7 kcal/mol exergonic over a barrier of 24.1 kcal/mol via TS3, resulting in the full reaction being exergonic by -26.3 kcal/mol. A competing reaction pathway of P-B/C-O bond metathesis between 2-12 and the second equivalent of Ph₂PBpin was found to proceed over a larger barrier of 31.6 kcal/mol via TS4 and is therefore unlikely. These computations are consistent with the observed formation of 2-12 with no further reactivity observed at ambient temperature. Further, the isolation of 2-13 validates the reaction intermediate calculated in this mechanism. Although the isolation of 2-13 is surprising given that the barrier for it to eliminate O(Bpin)₂ is computed to be lower than the barrier for its formation, it should be noted that the computations were performed using DCM solvation and that 2-13 was only found to be stable when suspended in n-pentane at -35 °C.
Very similar paths for the reactions of Ph$_2$PBcat and 2-4 with CO$_2$ were found computationally. Introduction of a more Lewis acidic Bcat group (Figure 2.17, in parentheses) results in the first addition being -1.4 kcal/mol exergonic over a similar barrier of 23.3 kcal/mol while the more Lewis basic tBu$_2$P group results in the first addition being 2.5 kcal/mol endergonic over a much smaller barrier of 17.1 kcal/mol via TS1 to the cis-arranged single addition products Ph$_2$PC(O)OBcat and tBu$_2$PC(O)Bcat, respectively. Rotation to the trans-arranged products are endergonic by 0.3 kcal/mol but exergonic by -2.9 kcal/mol for Ph$_2$PC(O)OBcat and tBu$_2$PC(O)Bcat, respectively. Subsequent reaction of Ph$_2$PC(O)OBcat with a second equivalent of Ph$_2$PBcat was found to follow the same reaction pathway as for 2-12, with smaller barriers of 22.1 and 19.6 kcal/mol via TS2 and TS3, respectively, to give 2-17 with an overall reaction that is exergonic by -26.7 kcal/mol. This is consistent with the production of 2-17 from the reaction of CO$_2$ with Ph$_2$PBcat but not with Ph$_2$PBpin. In contrast, the subsequent reaction of tBu$_2$PC(O)OBcat with a second equivalent of 2-4 is computed to have a high overall barrier of 34.9 kcal/mol via TS2 and TS3, precluding this reaction pathway (Figure 2.17, in brackets).
Instead, P-B/C-O bond metathesis over a barrier of 31.5 kcal/mol via TS4 is more likely to afford 2-18, consistent with the slower formation of 2-18 with respect to 2-17.

2.8.4 Conclusions

The reactions of a series of phosphinoboranes with CO2 was explored. Products of the form R2PC(O)OBR2 were isolated from a variety of phosphinoboranes while products of the form (R2P)2C=O were isolated from phosphinoboranes bearing a Bcat group. The mechanism of diphospha-urea synthesis was probed computationally and found to proceed either through two consecutive additions of phosphinoborane to C=O double bonds with subsequent elimination of O(BR2)2, as in the cases of Ph2PBpin and Ph2PBcat, or by an addition of phosphinoborane to one C=O double bond with subsequent P-B/C-O bond metathesis, as is the case for 2-4. The computed mechanism is supported by qualitatively observed reaction rates as well as the isolation and crystallographic characterization of a reaction computed intermediate 2-13. This work represents a unique and simple route to the synthesis of symmetric diphospha-ureas.

2.9 Experimental

2.9.1 General Experimental Methods

All manipulations were performed in a MB Unilab glove box produced by MBraun 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 (toluene, and n-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone under inert atmosphere. DCM and CDCl3 (Aldrich) was deoxygenated, distilled over CaH2, then stored over 3 Å molecular sieves before use. C6D6 (Aldrich) was deoxygenated, distilled over CaH2, then stored over 3 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. Ph2PBpin, Ph2PBcat, Ph2PBMes, and Mes2PB(C6F5)2 were prepared according to literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz or a Varian Mercury-300 MHz spectrometer. 1H, 13C{1H}, 31P{1H}, 19F, and 11B{1H} NMR chemical shifts (δ/ppm) are referenced to Me4Si, Me4Si, H3PO4, CFCl3, and BF3•OEt2, respectively.
Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI), a GCT Premier (EI), or a JEOL AccuTOF (DART) mass spectrometer. Fourier-transform infrared spectra (FT-IR) were obtained on a Bruker Alpha Platinum ATR infrared spectrophotometer. Ultraviolet (UV) radiation was produced from a medium pressure mercury ACE glass 7825-34 immersion UV lamp (450 Watt, 121.92 mm arc length, 244.35 mm overall length) inside a photochemical reaction cabinet.

2.9.2 X-Ray Diffraction Studies

Single crystals were coated with Paratone oil, mounted on a CryoLoop, and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-Kα (0.71073 Å) radiation. Data were collected using Bruker APEX-2 or APEX-3 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 or APEX-3 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre. In the case of 2-18, the diffraction study was complicated by its heavy twinning and its photochemical instability despite being collected at -123 °C in the dark. Nevertheless, preliminary data confirms the connectivity and formulation of 2-18 as (tBu₂P)₂C=O.
Table 2.6  X-ray table for 2-12 and 2-13.

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<th>Ph₂PC(O)OBpin (2-12)</th>
<th>(Ph₂P)₂C(OBpin)₂ (2-13)</th>
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<td>C₃₇H₄₈B₂O₆P₂</td>
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</tr>
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<td>12.4881(11)</td>
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<td>c (Å)</td>
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<td>Independent Reflections</td>
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<td>9035</td>
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Table 2.7  X-ray table for 2-18 and 2-19.

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<th>(Mes₂P)₂C=O (2-19)</th>
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<td>C₃₇H₄₄OP₂</td>
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<td><strong>ρ (calcd.) (Mg/m³)</strong></td>
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<td>Mo Kα</td>
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<td>1.343 to 28.281</td>
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<td><strong>CCDC No.</strong></td>
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2.9.3 Phosphinoboration Reactions of CO$_2$

2-12 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl diphenylphosphinecarboxylate (Ph$_2$PC(O)OBpin)

In a 50 mL Schlenk flask, a solution of Ph$_2$PBpin (0.32 mmol, 100.0 mg) was prepared in C$_6$H$_6$ (3 mL). The solution was degassed by three freeze, pump, thaw cycles, charged with 1 atm CO$_2$, and allowed to react at ambient temperature for 4 days. The solution was then dried in vacuo and recrystallized from pentane (2 mL) to afford a light yellow solid (40.0 mg, 35% isolated yield). Crystals suitable for single crystal X-ray diffraction were grown from pentane. $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 0.94 (s, 12H; C$_3$H$_3$), 6.98 – 7.02 (m, 6H; o-Ph and p-Ph), 7.54 – 7.60 (m, 4H; m-Ph) ppm. $^{11}$B$[^1$H] NMR (128 Hz, C$_6$D$_6$): $\delta$ = 22.7 (s) ppm. $^{31}$P$[^1$H] NMR (202 MHz, C$_6$D$_6$): $\delta$ = -0.7 (s) ppm. $^{13}$C$[^1$H] NMR (125 MHz, C$_6$D$_6$): $\delta$ = 24.5 (s, 4C; C$_3$H$_3$), 84.2 (s, 2C; OC(CH$_3$)$_2$), 128.9 (d, $^2$J$_{PC}$ = 8 Hz, 4C; o-Ph), 129.8 (s, 2C; p-Ph), 132.8 (d, $^1$J$_{PC}$ = 5 Hz, 2C; i-Ph), 135.0 (d, $^3$J$_{PC}$ = 20 Hz, 4C; m-Ph), 177.5 (d, $^1$J$_{PC}$ = 16 Hz, 1C; C=O) ppm. HRMS (EI-TOF+): m/z [M] 356.1355 (calc’d for C$_{19}$H$_{22}$BO$_4$P: 356.1349). FT-IR (ATR): 1705 (m, C=O) cm$^{-1}$. EA: calcd (%) for C$_{19}$H$_{22}$BO$_4$P: C, 64.07; H, 6.23; found: C, 64.27; H, 6.27.

2-13 Bis(diphenylphosphinyl)bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methane ((Ph$_2$P)$_2$C(OBpin)$_2$)

Single crystals suitable for X-ray diffraction were grown from a solution of Ph$_2$PCO$_2$Bpin (0.17 mmol, 60.0 mg) in n-pentane (10 mL) that was cooled to -35 °C for 1 year. The crystals were thermally sensitive as rapid decomposition to a yellow and then colourless solid product was visually observed upon warming to ambient temperature. The crystals were also unstable in solution as gas evolution was observed when crystals were dissolved in either CDCl$_3$ or toluene-d$_8$ at -35 °C. $^{13}$C$[^1$H] NMR (151 MHz, CDCl$_3$, -35 °C, 12500 scans) showed no evidence of a PCP triplet.
In a J. Young NMR tube, a solution of Ph₂PBpin₂ (0.09 mmol, 40.0 mg) was prepared in DCM (0.6 mL). The solution was degassed by three freeze, pump, thaw cycles, charged with 4 atm CO₂, and allowed to react at ambient temperature for 3 days. The solution was then dried \textit{in vacuo} and recrystallized from pentane (2 mL) to afford a white solid (37.8 mg, 86% isolated yield). \( ^1H \) NMR (400 MHz, CDCl₃): \( \delta = 2.17 \text{ (s, 12H), } 2.27 \text{ (s, 6H), } 6.77 \text{ (s, 4H), } 7.35-7.40 \text{ (m, 6H), } 7.56 \text{ (ddd, } ^3J_{PH} = 9 \text{ Hz, } ^3J_{HH} = 7 \text{ Hz, } ^4J_{HH} = 2 \text{ Hz, 4H) ppm.} \)

\( ^11B\{^1H\} \) NMR (128 MHz, CDCl₃): \( \delta = 53.1 \text{ (s, br) ppm.} \)

\( ^{31}P\{^1H\} \) NMR (162 MHz, CDCl₃): \( \delta = -1.5 \text{ (d, } ^1J_{PC} = 19 \text{ Hz) ppm.} \)

\( ^{13}C\{^1H\} \) NMR (100 MHz, CDCl₃): \( \delta = 21.4, 22.7, 22.7, 125.0 \text{ (} ^{13}CO₂\text{), 128.5, 128.8 \text{ (d, } ^3J_{PC} = 8 \text{ Hz), 129.9, 131.8 \text{ (d, } ^4J_{PC} = 6 \text{ Hz), 134.8 \text{ (dd, } ^1J_{PC} = 20 \text{ Hz, } ^2J_{CC} = 3 \text{ Hz), 139.9, 141.7, 178.1 \text{ (d, } ^1J_{PC} = 19 \text{ Hz) ppm.} \)} \)

FT-IR (ATR): 1662 \text{ (m, C=O) cm}^{-1}. 

In a J. Young NMR tube, a solution of tBu₂PBpin₂ (0.20 mmol, 54.4 mg) was prepared in DCM (0.6 mL). The solution was degassed by three freeze, pump, thaw cycles, charged with 4 atm CO₂, and allowed to react at ambient temperature overnight. The solution was then dried \textit{in vacuo} to afford a slightly yellow oil (56.2 mg, 89% isolated yield). \( ^1H \) NMR (400 MHz, CDCl₃): \( \delta = 1.30 \text{ (s, 9H), } 1.31 \text{ (s, 12H), } 1.33 \text{ (s, 9H) ppm.} \)

\( ^11B\{^1H\} \) NMR (128 MHz, CDCl₃): \( \delta = 21.9 \text{ (s) ppm.} \)

\( ^{31}P\{^1H\} \) NMR (162 MHz, CDCl₃): \( \delta = 48.2 \text{ (d, } ^1J_{PC} = 35 \text{ Hz) ppm.} \)

\( ^{13}C\{^1H\} \) NMR (100 MHz, CDCl₃): \( \delta = 24.7, 30.2 \text{ (dd, } J = 13 \text{ Hz, 2 Hz), 33.4 \text{ (d, } J = 21 \text{ Hz), 84.2, 178.2 \text{ (d, } ^1J_{PC} = 35.1 \text{ Hz) ppm.} \)} \)

FT-IR (ATR): 1670 \text{ (m (br), C=O) cm}^{-1}. 

\( 4,4,5,5\)-tetramethyl-1,3,2-dioxaborolan-2-yl di-tert-butylphosphinecarboxylate \( \text{(tBu₂PC(O)OBpin)} \)
In a 50 mL Strauss flask, a solution of \( \text{tBu}_2\text{PBMe}_2 \) (0.23 mmol, 90.2 mg) was prepared in DCM (5 mL). The solution was degassed by three freeze, pump, thaw cycles, charged with 4 atm CO\(_2\), and allowed to react at ambient temperature for 3 days. The solution was then dried in vacuo and recrystallized from pentane (2 mL) to afford a white solid (82.2 mg, 82\% isolated yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.31 \) (d, \( J_{PH} = 12 \) Hz, 18H), 2.02 (s, 6H), 2.29 (s, 12H), 6.77 (s, 4H) ppm. \(^{11}\)B\(^{\text{1H}}\) NMR (128 MHz, CDCl\(_3\)): \( \delta = 52.0 \) (s, br) ppm. \(^{31}\)P\(^{\text{1H}}\) NMR (162 MHz, CDCl\(_3\)): \( \delta = 46.9 \) (s) ppm. \(^{31}\)P\(^{\text{1H}}\) NMR (162 MHz, CH\(_2\)Cl\(_2\)): \( \delta = 30.5 \) (d, \( J_{PC} = 70 \) Hz; P(CO)P) ppm. \(^{13}\)C\(^{\text{1H}}\) NMR (125 MHz, CDCl\(_3\)): \( \delta = 21.4 \) (s, 2C), 22.8 (s, 2C), 22.9 (s, 2C), 30.3 (d, \( J_{PC} = 12 \) Hz, 6C), 33.8 (d, \( J_{PC} = 21 \) Hz, 2C), 128.3 (s, 2C), 128.7 (s, 2C), 135.6 (s, br, 2C), 139.4 (s, 2C), 141.2 (s, 4C), 179.3 (d, \( J_{PC} = 39 \) Hz, 1C) ppm. FT-IR (ATR): 1695 (m, C=O) cm\(^{-1}\). HRMS (EI-TOF+): m/z [M] 438.2866 (calc’d for C\(_{27}\)H\(_{40}\)B\(_1\)O\(_2\)P\(_1\): 438.2859).

**2-17** Bis(diphenylphosphinyl)methanone ((Ph\(_2\)P)\(_2\)C=O)

In a J. Young NMR tube, a solution of Ph\(_2\)PBcat (0.10 mmol, 30.4 mg) was prepared in DCM (0.6 mL). The solution was degassed by three freeze, pump, thaw cycles, charged with 4 atm CO\(_2\), and allowed to react at ambient temperature for several days. The solution turned yellow within 1 h. Monitoring of the solution in situ demonstrated characteristic peaks for the generation of the diphospha-urea product. \(^{31}\)P\(^{\text{1H}}\) NMR (162 MHz, CH\(_2\)Cl\(_2\)): \( \delta = 30.5 \) (d, \( J_{PC} = 70 \) Hz; P(CO)P) ppm. \(^{13}\)C\(^{\text{1H}}\) NMR (100 MHz, CH\(_2\)Cl\(_2\)): \( \delta = 239.0 \) (t, \( J_{PC} = 70 \) Hz, 1C; C=O) ppm.

**2-18** \( \text{bis(di-}\text{-}\text{tert}-\text{butylphosphinyl)}\text{methanone ((tBu}_2\text{P})_2\text{C}=\text{O}) \)

In a J. Young NMR tube, a solution of tBu\(_2\)PBcat (2-4) (0.37 mmol, 103.2 mg) was prepared in DCM (0.6 mL). The solution was degassed by three freeze, pump, thaw cycles, charged with 4 atm CO\(_2\), and allowed to react at
ambient temperature for 96 h. The solution was then filtered, dried in vacuo, and recrystallized from minimal pentane to afford a yellow solid (50.4 mg, 43% isolated yield). ¹H NMR (500 MHz, C₆D₆): δ = 1.37 – 1.39 (m, 36H) ppm. ¹¹B{¹H} NMR (128 MHz, CH₂Cl₂): δ = 22.5 ppm (s(br)). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ = 74.6 ppm. ³¹P{¹H} NMR (200 MHz, CH₂Cl₂): δ = 75.5 (d, JₚC = 83 Hz) ppm. ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 31.3 (t, JₚC = 8 Hz), 35.0 (dd, J = 14 Hz, 11 Hz), 245.1 (t, JₚC = 83 Hz, C=O) ppm. FT-IR (ATR): 1672 (w (br), C=O) cm⁻¹.

2-19 Bis(dimesitylphosphinyl)methanone ((Mes₂P)₂C=O)

In a J. Young NMR tube, a solution of Mes₂PBcat (2-5) (0.2 mmol, 77.6 mg) was prepared in DCM (0.6 mL). The solution was degassed by three freeze, pump, thaw cycles, charged with 4 atm CO₂, and allowed to react at ambient temperature for 6 days. The solution was then filtered, dried in vacuo, and washed with cold pentane (3 x 2 mL). The pentane washings were concentrated and cooled to -35 °C to afford a yellow solid (70.3 mg, 62% isolated yield). ¹H NMR (500 MHz, Tol-d₈): δ = 2.04 (s, 12H), 2.13 (s, 24H), 6.63 (s, 8H) ppm. ³¹P{¹H} NMR (162 MHz, Tol-d₈): δ = 12.6 (s) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 14.4 (d, JₚC = 73 Hz) ppm. ¹³C{¹H} NMR (125 MHz, Tol-d₈): δ = 20.9, 23.6 (t, J = 7 Hz), 130.0, 138.8, 144.0 (t, J = 7 Hz), 224.0 ppm. Ipso-carbon signals were not observed. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 227.5 (t, JₚC = 73 Hz, C=O) ppm. FT-IR (ATR): 1662 (m, C=O) cm⁻¹.

2.9.4 Exposure of (tBu₂P)₂CO to UV Radiation

In a sealed NMR tube, a solution of 2-18 was prepared in n-pentane and subjected to UV light for 2 hours. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 40.0 (tBu₂P-P-tBu₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 181.0 (C≡O) ppm.

2.9.5 Exposure of (Mes₂P)₂CO to UV Radiation

In a sealed NMR tube, a solution of 2-19 generated in situ from reaction of Mes₂PBcat with CO₂ in CH₂Cl₂ was subjected to UV light for 2 hours. Single crystals of Mes₂P-PMes₂ were grown from slow evaporation of the crude DCM solution and confirmed by comparison of the unit cell parameters to reported values.⁷⁶ ³¹P{¹H} NMR (162 MHz, CH₂Cl₂): δ = -30.4 (Mes₂P-PMes₂) ppm. ¹³C{¹H} NMR (100 MHz, CH₂Cl₂): δ = 181.0 (C≡O) ppm.
2.9.6 Computational Details

The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.3 suite of programs\textsuperscript{88} The structures are fully optimized at the TPSS-D3/Def2-TZVP + COSMO(CH\textsubscript{2}Cl\textsubscript{2}) level of theory, which combines the TPSS meta-GGA density functional\textsuperscript{83} with the BJ-damped DFT-D3 dispersion correction\textsuperscript{79, 80} and the Def2-TZVP basis set,\textsuperscript{81, 82} using the Conductor-like Screening Model (COSMO) continuum solvation model\textsuperscript{85} for CH\textsubscript{2}Cl\textsubscript{2} solvent (dielectric constant $\varepsilon = 8.93$ and solvent diameter $R_{\text{solv}} = 2.94$ Å). The density-fitting RI-J approach\textsuperscript{81, 89, 90} is used to accelerate the geometry optimization and numerical harmonic frequency calculations\textsuperscript{91} in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model.\textsuperscript{92}

The final solvation free energies in CH\textsubscript{2}Cl\textsubscript{2} are computed with the COSMO-RS solvation model\textsuperscript{93} (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm program package\textsuperscript{94} on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol\textsuperscript{−1} to account for higher reference solute concentration of 1 mol·L\textsuperscript{−1} usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the TPSS-D3\textsuperscript{83} and hybrid PW6B95-D3\textsuperscript{78} levels are performed using a larger Def2-QZVP basis set.\textsuperscript{82, 84} The final reaction Gibbs free energies ($\Delta G$) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. As expected, the results from both DFT functionals are in good mutual agreement of $−0.1 \pm 1.6$ kcal/mol, despite 4.4 ± 1.9 kcal/mol higher reactions barriers are found at the hybrid PW6B95-D3 level. In our discussion, the final PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L standard state concentration) will be used in our discussion unless specified otherwise.

2.10 References

22. Y. Inoue, T. Hibi, M. Satake and H. Hashimoto, 1979, **1979**.


Section 2.3 - Phosphinoboration of Diazobenzene: Intramolecular FLP Synthon for PN$_2$B-derived Heterocycles

2.11 Brief Introduction to Frustrated Lewis Pairs

Acids and bases have been categorized by three major classifications: Arrhenius, Brønsted, and Lewis. Arrhenius acids and bases are species that donate hydrogen cations and hydroxide anions, respectively, while Brønsted acids and bases are species that donate and accept hydrogen cations, respectively.\(^1\) Amongst the three classes, the refined definition proposed by Lewis is perhaps the most comprehensive as it includes dissolution in nonaqueous solvents. Lewis acids and bases are defined as species that accept and donate a pair of electrons, respectively.\(^2\) Combinations of Arrhenius or Brønsted acid/base pairs typically result in a salt and often water production. In contrast, due to the inclusive nature of the Lewis definition, combinations of Lewis acids and bases simply result in acid/base adduct formation. (Scheme 2.17). Lewis acids, such as boranes, have found applications as catalysts for organic transformations\(^3\)\(^-\)\(^8\) while Lewis bases, such as phosphines, have been used as ligands in transition metal-based catalysts.\(^9\)\(^-\)\(^13\)

\[
\begin{align*}
\text{HCl} & \quad + \quad \text{H} & \quad \text{N} & \quad \text{H} & \quad \rightarrow & \quad \left[ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{N} \\
\text{H} \\
\end{array} \right] \\
\text{B} & \quad + \quad \text{H} & \quad \text{N} & \quad \text{H} & \quad \rightarrow & \quad \left[ \begin{array}{c}
\text{B} \\
\text{H} \\
\text{N} \\
\text{H} \\
\end{array} \right]
\end{align*}
\]

Scheme 2.17 Quenching reactions of pairs of Brønsted (top) and Lewis (bottom) acids and bases.

Although Lewis acid/base adduct formation is the norm, exceptions have been reported (Scheme 2.18). The first deviation from the rule was Brown’s report that lutidine and BMe$_3$ do not form an adduct in contrast to most other combinations of pyridines and boranes. The authors attribute this result to the steric bulk present between the acid and base.\(^{14,15}\) Wittig and Benz subsequently found that a mixture of PPh$_3$ and BPh$_3$, presumably forming a Lewis acid/base adduct, reacts with benzyne to form an ortho-disubstituted zwitterionic arene species.\(^{16}\) Later, Tochtermann found
that a mixture of butadiene, BPh₃, and [Na][Ph₃C], instead of forming the expected polybutadiene, resulted in 1,2-addition of the Lewis acid and base across the olefin. Tochtermann termed such unquenched Lewis acid/base pair reactivity as “antagonisches Paar” or antagonistic pairs.¹⁷ In 2006, Stephan found that a para-disubstituted arene species bearing a phosphine and borane, which was sterically precluded from forming a Lewis acid/base adduct, was able to reversibly activate H₂.¹⁸ Stephan termed such Lewis acid/base pairs with unquenched reactivity “frustrated Lewis pairs” (FLPs) (Figure 2.18). 

![Scheme 2.18 Early examples of Lewis acids and bases that do not form stable adducts.](image)

![Figure 2.18 Depiction of a frustrated Lewis pair.](image)

Emboldened by the first discovery of a non-transition metal-based system that reversibly activates H₂, frustrated Lewis pair chemistry has since expanded considerably,¹⁹-²⁷ achieving stoichiometric
and catalytic activations of a broad scope of small molecules including but not limited to \( \text{H}_2, \text{CO, CO}_2, \text{NO, NO}_2, \text{N}_2\text{O}, \text{SO}_2, \) alkyl C-F bonds, olefins, alkynes, and cyclopropanes. Intermolecular FLP combinations (Figure 2.19) including P/B, P/Al, P/Si, N/B, C/B, and O/B have been developed by the groups of Stephan, Erker, Repo, Rieger, and Tamm and have been applied in FLP chemistry by their groups and by the groups of Young, Aldridge, Piers, Berke, Alcarazo, and Ashley.

![Figure 2.19](image)

**Figure 2.19** Selected intermolecular FLPs and the group that first reported each.

While the simplicity of using intermolecular systems makes them attractive in FLP chemistry, their simultaneous action in the activation of substrates implies an entropically unfavourable termolecular reaction mechanism. Investigations into the FLP activation of \( \text{H}_2 \) both computationally by Papai and Grimme and experimentally by Autrey and Holbrey and Swadźba-Kwaśny have found that the Lewis acid and base come together as a result of weak intermolecular interactions to form an encounter complex that can then undergo FLP chemistry. Intramolecular FLPs circumvent this need by pre-organizing the Lewis acidic and basic groups into an encounter complex on a shared molecular backbone. These have been prepared from combinations including P/B, P/Al, N/B, and S/B by the groups of Stephan, Erker, Uhl, Lammertsma, Fontaine, Rieger, and Repo (Figure 2.20).
Figure 2.20  Selected intramolecular FLPs.

The majority of intramolecular FLPs use a carbon-based linkage between the Lewis acidic and basic sites. While synthetic strategies to these FLPs are well established (vide supra), developing synthetic strategies to FLPs with heteroatom-containing linkages would offer new ways to tune the steric and electronics about the Lewis acidic and basic sites. In particular, including electron rich heteroatoms near the Lewis acidic site would reduce the Lewis acid’s strength, an effect that is desirable for the FLP catalyzed reduction of CO₂ as noted by Fontaine. To date, only a few intramolecular FLPs incorporating heteroatom linkers have been reported (Scheme 2.19, Scheme 2.20), with Stephan describing the FLP reactivity of a CN-linked boron amidinate with CO₂, CO, RC≡N, RN≡C, alkyne, and aldehyde, the active species of which is believed to be the ring-opened species. Stephan has also reported the catalytic reduction of CO₂ by a ring-expanded product of a phosphine-containing NHC and 9-BBN. More recently Wang has used the oxygen-linked Mes₂POB(C₆F₅)₂ to effect activation of H₂ and cyclizations with CO₂ and olefins.

Scheme 2.19  Reactivity of heteroatom-linked intramolecular FLPs.
Scheme 2.20 Reactivity of heteroatom-linked intramolecular FLPs continued.

Taking inspiration from phosphinoboration chemistry and seeking to target intramolecular FLPs with heteroatom linkages, we herein report the reactions of diazobenzene and diazomethanes with phosphinoboranes to form 1,2- and 1,1-addition products, respectively. The mechanism of the 1,2-phosphinoboration reactions is probed computationally. Despite the weak Lewis acidity of the boron centres, the N$_2$-linked species 2-20 and 2-21 are found to give FLP reactivity to yield unique five-, six-, and eight-membered heterocyclic rings. By contrast, the N-linked species 2-30 and 2-31 are not found to behave as FLPs. Investigations into the FLP reactivity of the CN-linked species 9-PPh$_2$-10-Bpin-dihydroacridine are also reported.

2.12 Results and Discussion

2.12.1 Phosphinoboration of Diazobenzene

The reaction of Ph$_2$PBcat and the structurally similar 2-6 with one equivalent of diazobenzene (PhN=NPh) in DCM proceeds at ambient temperature over 24 hours to give, upon workup, white solids 2-20 and 2-21 in 92 and 91 % yields, respectively (Scheme 2.21). The $^{11}$B${}^{1}$$H$ NMR spectra show singlet resonances at 27.6 and 26.3 ppm while the $^{31}$P${}^{1}$$H$ NMR spectra show singlet resonances at 69.4 and 70.9 ppm, respectively. The $^{1}$$H$ and $^{13}$C${}^{1}$$H$ NMR spectra as well as the HRMS data are consistent with the formulations of 2-20 and 2-21 as 1:1 combinations of the reactants.
Scheme 2.21  Reactions of Ph$_2$PBcat and 2-6 with PhN=NPh.

Single crystals suitable for X-ray diffraction were grown from layering $n$-pentane and DCM. The diffraction study confirmed the formulation of 2-20 as Ph$_2$P(PhNNPh)Bcat, resulting from a 1,2-phosphinoboration across the N=N double bond (Figure 2.21). Given this and the similar NMR and HRMS data between 2-20 and 2-21, the formulation of 2-21 was affirmed as Ph$_2$P(PhNNPh)Bquin. In the diffraction study, the newly formed P-N and B-N distances were found to be 1.7524(18) and 1.422(3) Å, respectively, while the N-N distance was found to be 1.409(2) Å. While the length of the N-N bond falls into the range of a single bond, the B-N bond distance implies double bond character. This is further supported by a twist angle of 17.7° between the O-B-O and C-N-N planes and by the sums of angles at B and at the C-N-N nitrogen of 350.0 and 359.7°, respectively. Additionally, the P-B distance was found to be 3.672(4) Å, only slightly less than the sum of the van der Waals radii for P and B (3.89 Å) but significantly greater than the sum of the covalent radii for P and B (1.98 Å). Indeed, the lone pair of electrons on phosphorus is directed away from the boron’s $p$-orbital, demonstrating that no bonding exists between the Lewis acidic boron and Lewis basic phosphorus sites.
The electronic structure of 2-20 was investigated computationally, with geometry optimizations performed with Gaussian 16\textsuperscript{92} using the BP86/Def2-TZVP\textsuperscript{93-96} level of theory and natural population analysis subsequently performed using NBO 6.0\textsuperscript{97} at the M06-2X/Def2-TZVP\textsuperscript{98} level of theory on the optimized structure (Figure 2.22). Modelling of the HOMO (reference 0.00 eV) revealed significant lobes on the phosphorus centre, whereas modelling of the LUMO (6.50 eV) revealed no contribution by the boron centre. It is not until the LUMO+10 (8.33 eV) that the boron centre bares any significant amount of the molecular orbital’s lobes. This is expected given that the boron centre has one nitrogen and two oxygen atom substituents that can donate electron density into its vacant $p$-orbital and that the B-N bond displays double bond character, resulting in a relatively saturated and particularly weakly Lewis acidic boron centre.
The analogous reactions of other phosphinoboranes proved less fruitful, with Ph$_2$PBMes$_2$ showing no reactivity with PhN=NPh in DCM at ambient temperature and at 50 °C or in toluene at 100 °C. In contrast, while Ph$_2$PBpin showed no reactivity with PhN=NPh in DCM at ambient temperature, heating at 70 °C for 2 days afforded productive reactivity (Scheme 2.22). Although the $^{31}$P{$^1$H} NMR spectrum of the crude reaction mixture showed multiple signals, the presence of the 1,2-addition product Ph$_2$P(PhNNPh)Bpin (2-22) was confirmed by HRMS data. Additionally, single crystals suitable for X-ray diffraction were grown from $n$-pentane. However, the diffraction study identified them as the oxidized 1,2-phosphinoboration product Ph$_2$P(O)(PhNNPh)Bpin (2-23) (Figure 2.23), presumably resulting from reaction with adventitious oxidant. The geometry of 2-23 is analogous to that of 2-20, with the newly formed P-N, B-N, and P-O distances in 2-23 found to be 1.735(2), 1.438(4), and 1.392(3) Å, respectively, while the N-N and P-B distances were found to be 1.410(2) and 3.589(3) Å, respectively. Like 2-20, the B-N bond in 2-23 displays double bond character, with a twist angle of 6.6° between the O-B-O and C-N-N planes, and sums of angles at B and at the C-N-N nitrogen of 360.0 and 359.8°, respectively. Unfortunately, attempts to isolate either phosphinoboration product were unsuccessful.
Scheme 2.22 Reaction of Ph$_2$PBpin with PhN=NPh.

Figure 2.23 ORTEP depiction of 2-23 showing thermal ellipsoids at 50% probability. Hydrogen atoms and minor disorder omitted. P: orange, O: red, N: blue, B: yellow-green, C: black.

2.12.2 Mechanistic Insights

The mechanism of the 1,2-addition reactions of Ph$_2$PBcat, Ph$_2$PBpin, and Ph$_2$PBMes$_2$ with PhN=NPh was probed computationally with the Gaussian 16$^{92}$ package at the BP86/Def2-TZVP$^{93-96}$ level of theory with the inclusion of PCM$^{99}$ solvation modeling for DCM. In each case, the reaction was found to proceed by adduct formation between the boron centre and a nitrogen atom on PhN=NPh followed by the concerted migration of the phosphorus centre to the other nitrogen atom (Figure 2.24). In the cases of Ph$_2$PBcat and Ph$_2$PBpin, formation of the adduct intermediates...
are 27.1 and 36.4 kcal/mol endergonic over barriers of 27.7 and 36.6 kcal/mol via TS1, respectively, while the concerted migration step is exergonic overall by 4.4 and 3.2 kcal/mol over barriers of 4.7 and 2.5 kcal/mol via TS2 to give 2-20 and 2-22, respectively. Overall, the activation barriers were found to be 31.8 and 38.9 kcal/mol for reactions with Ph2PBCat and Ph2PBpin, respectively. These barriers are consistent with the observed formation of 2-20 at ambient temperature while reaction of Ph2PBpin requires heating to 70 °C to promote phosphinoboration. By contrast, adduct formation with Ph2PBMes2 was found to be endergonic by 59.1 kcal/mol over a barrier of 66.3 kcal/mol via TS1 while the concerted migration step is exergonic overall by 0.2 kcal/mol over a barrier of 4.6 kcal/mol via TS2. The overall reaction barrier of 66.3 kcal/mol is consistent with the observed lack of reactivity of Ph2PBMes2 with PhN=NPPh even with prolonged heating at 100 °C.

Figure 2.24  Computed free energy paths in DCM solvation for the reactions of Ph2PBcat (red), Ph2PBpin (blue), and Ph2PBMes2 (green) with PhN=NPPh. Energies given in kcal/mol.
2.12.3 Frustrated Lewis Pair Reactivity of Ph$_2$P(PhNNPh)BR’$_2$ Species

The phosphinoboration products 2-20 and 2-21 represent unique N$_2$-linked intramolecular FLPs with unquenched Lewis acidic and basic sites. As such, their FLP reactivity was explored. It is worth noting that the boron centres are shown to be only weakly Lewis acidic (vide supra). While strongly Lewis acidic centres are generally sought after in the design of FLPs, Fontaine has previously shown that weak Lewis acids in carbon-linked intramolecular FLPs maintain FLP reactivity.\textsuperscript{42, 55, 85, 100} The FLP reactivity of 2-20 was initially probed with weakly donating substrates including HD, CO$_2$, MeI, 4-phenyl-3-buten-2-one, (4-Tol)C≡CH, and 1,3- and 1,4-cyclohexadiene but no reactivity was observed. By contrast, reactions occurred with exposure to more strongly donating substrates. The additions of a second equivalent of PhN=NPh to 2-20 and 2-21 each proceeded over 48 hours in DCM at ambient temperature to give, upon workup, yellow solids 2-24 and 2-25 in 86 and 91% yields, respectively (Scheme 2.23). While the $^{31}$P{$^1$H} NMR spectra show singlets at 43.7 and 41.8 ppm, the singlets appear in the $^{11}$B{$^1$H} NMR spectra at 11.7 and 12.6 ppm for 2-24 and 2-25, respectively. The corresponding $^1$H and $^{13}$C{$^1$H} NMR spectra as well as HRMS data confirmed a 1:1 ratio of the starting materials in each product.

\begin{center}
\includegraphics[width=\textwidth]{reaction Scheme.png}
\end{center}

\textbf{Scheme 2.23} FLP reactions of 2-20 and 2-21 with PhN=NPh.

Two sets of single crystals suitable for X-ray diffraction of 2-24 were grown from $n$-pentane and from toluene while single crystals suitable for X-ray diffraction of 2-25 were grown from $n$-pentane. The diffraction studies affirmed the formulations of 2-24 and 2-25 as the zwitterionic six-membered heterocyclic rings Ph$_2$P(PhNNPh)$_2$Bcat and Ph$_2$P(PhNNPh)$_2$Bquin, respectively (Figure 2.25, Figure 2.26). In each solid-state structure, the PN$_4$B ring system adopts a boat-like conformation in which two nitrogen atoms on opposite ends of the ring, one $\alpha$- to and another $\beta$-
to boron, are positioned above the plane of the ring. This minimizes steric clash between the phenyl groups and allows for $\pi$-stacking between two phenyl rings – one on phosphorus and another on one of the nitrogen atoms $\alpha$- to phosphorus. The P-N distances were found to be 1.6421(19) and 1.6565(18), 1.636(5) and 1.674(5), and 1.644(3) and 1.647(3) Å, the B-N distances were found to be 1.533(3) and 1.545(3), 1.536(9) and 1.550(9), and 1.538(6) and 1.535(6) Å, and the N-N distances were found to be 1.419(2) and 1.425(2), 1.430(7) and 1.429(7), and 1.423(4) and 1.428(5) Å in the crystals of 2-24 grown from n-pentane, from toluene, and of 2-25, respectively. While the N-N distances are similar to those seen in 2-20, the elongated P-N distances and shortened B-N distances in both solid-state structures of 2-24 compared to 2-20 are consistent with the formal positive and negative charges on the phosphorus and boron centres, respectively.

**Figure 2.25** ORTEP depiction of 2-24 from crystals grown in n-pentane showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted. P: orange, O: red, N: blue, B: yellow-green, C: black.
The analogous FLP reactions of 2-20 with 4-phenyl-1,2,4-triazole-3,5-dione and 1,10-phenanthroline-5,6-dione each proceeded over 24 hours in DCM at ambient temperature to give, upon workup, yellow solids 2-26 and 2-27 in 81 and 28% yields, respectively (Scheme 2.24). The $^1$H and $^{13}$C{$^1$H} NMR data are consistent with 1:1 combinations of starting materials, as supported by the HRMS data of 2-27. Unfortunately, 2-26 proved too unstable for analysis by HRMS. The $^{11}$B{$^1$H} NMR spectra revealed singlets at 13.9 and 15.2 ppm while the $^{31}$P{$^1$H} NMR spectra revealed singlets at 42.6 and 49.5 ppm for 2-26 and 2-27, respectively.
Scheme 2.24 FLP reactions of 2-20 with 4-phenyl-1,2,4-triazole-3,5-dione (top) and 1,10-phenanthroline-5,6-dione (bottom).

Single crystals suitable for X-ray diffraction of 2-26 and 2-27 were grown from layering n-pentane and DCM. The diffraction studies affirmed the formulations of 2-26 and 2-27 as Ph₂P(PhNNPh)(PhN(OCN)₂)Bcat and Ph₂P(PhNNPh)(O₂C₁₂H₆N₂)Bcat, respectively (Figure 2.27). In the case of 2-26, a zwitterionic six-membered heterocyclic ring was revealed with a boat-like conformation analogous to those seen in 2-24 and 2-25. The bond metrics were also found to be similar to those found in 2-24 and 2-25, with P-N distances of 1.634(2) and 1.685(2) Å, B-N distances of 1.548(3) and 1.576(3) Å, and N-N distances of 1.437(3) and 1.438(3) Å in the diazobenzene and triazole fragments, respectively. In the case of 2-27, a zwitterionic eight-membered heterocyclic core was revealed adopting a twisted boat-like conformation with the boron, boron-bound nitrogen, and phosphorus-bound oxygen atoms positioned above the plane of the ring. The newly formed B-O and P-O bond distances were found to be 1.488(6) and 1.587(3) Å.
Å, respectively, while the P-N, B-N, and N-N distances of 1.637(5), 1.536(8), and 1.419(6) Å, respectively, were found to be similar to those seen in 2-24 and 2-25.

**Figure 2.27**  ORTEP depictions of 2-26 (top) and 2-27 (bottom) showing thermal ellipsoids at 50% probability. Hydrogen atoms and solvents omitted for clarity. P: orange, O: red, N: blue, B: yellow-green, C: black.
Frustrated Lewis pair reactivity of \textbf{2-20} was also observed with benzyl azide, proceeding over 24 hours in DCM at ambient temperature to give, upon workup, a yellow solid \textbf{2-28} in 73\% yield (Scheme 2.25). Effervescence was observed during the reaction, signaling the loss of N\textsubscript{2}. While the \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR data are consistent with a 1:1 combination of starting materials, the HRMS data show a mass smaller than expected for a 1:1 combination that is consistent with the loss of N\textsubscript{2}. The \textsuperscript{11}B{\textsuperscript{1}H} and \textsuperscript{31}P{\textsuperscript{1}H} NMR signals appearing at 10.6 and 50.8 ppm, respectively, are similar to those obtained for \textbf{2-20} to \textbf{2-27}. Single crystals suitable for X-ray diffraction were grown from layering \textit{n}-pentane and DCM. The diffraction study confirmed the formulation of \textbf{2-28} as the zwitterionic five-membered heterocyclic ring Ph\textsubscript{2}P(PhNNPh)(NCH\textsubscript{2}Ph)Bcat adopting a pseudo planar geometry about the PN\textsubscript{3}B core (Figure 2.28). The B-N, N-N, and P-N bond lengths of the diazobenzene fragment were found to be 1.6765(17), 1.446(2), and 1.528(3) Å, respectively, while the newly formed B-N and P-N bonds were found to be 1.561(3) and 1.6145(16) Å, respectively.

\textbf{Scheme 2.25}  FLP reaction of \textbf{2-20} with benzyl azide.
Figure 2.28  ORTEP depiction of 2-28 showing thermal ellipsoids at 50% probability. Hydrogen atoms omitted. P: orange, O: red, N: blue, B: yellow-green, C: black.

The reaction of 2-20 with N,N-diphenylnitrous amide was also seen to proceed over 24 hours in DCM at ambient temperature to give, upon workup, a yellow solid 2-29 in 76% yield (Scheme 2.26). In this case, the HRMS data did not agree for a 1:1 combination of starting materials, instead showing a greater mass consistent with the inclusion of two protons. Indeed, the $^1$H and $^{13}$C{$^1$H} NMR data are consistent with 1:1 ratios of the starting materials with additional broad singlets at 5.88 – 5.92 and 6.51 – 6.55 ppm in the $^1$H NMR spectrum consistent with the presence of EH groups (E = N, O). Signals in the $^{11}$B{$^1$H} and $^{31}$P{$^1$H} NMR observed at 6.6 and 29.5 ppm, respectively, are shifted upfield relative to those of 2-20 to 2-28, indicating a more electron rich four-coordinate boron centre and a significantly different geometry about the phosphorus centre. As such, the formulation of 2-29 is proposed to be the acyclic Ph$_2$P(Ph$_2$NNH)(PhNNPh)(OH)Bcat with P-NH and B-OH bonds resulting from reaction of the transiently formed zwitterionic six-membered heterocyclic PN$_3$BO ring with adventitious water.
2.12.4 Phosphinoboration of Diazomethane

To further investigate nitrogen-linked FLPs, phosphinoboration reactions of diazomethanes were performed. While the mixture of 2-3 with diphenylidiazomethane showed no reactivity in DCM at ambient temperature over 24 hours, mixtures of Ph2PBpin, Ph2PBcat, and Ph2PBMes2 reacted with Ph2C=N=N over 3 hours in DCM at ambient temperature to yield addition products 2-30 to 2-32 as colourless solids in 95, 91, and 82% yields, respectively (Scheme 2.27). The analogous mixture of Ph2PBMes2 with fluorenyldiazomethane reacted similarly to give the addition product 2-33 as a white solid in 95% yield (Scheme 2.27). The $^{31}$P{$^1$H} NMR spectra revealed signals at 48.5, 49.8, 57.2, and 64.3 ppm while the $^{11}$B{$^1$H} NMR spectra revealed signals at 24.3, 25.6, 45.8, and 52.7 ppm for 2-30 and 2-33, respectively. The HRMS data of 2-32 and 2-33 as well as the $^1$H and $^{13}$C{$^1$H} NMR data were consistent with 2-30 to 2-33 consisting of a 1:1 combination of the phosphinoborane and the respective diazomethane.
Single crystals suitable for X-ray diffraction were grown from Et₂O. Diffraction studies confirmed the formulations of 2-31 to 2-33 as the 1,1-phosphinoboration products Ph₂C=NN(PPh₂)(Bcat), Ph₂C=NN(PPh₂)(BMes₂), and [fluorenyl]N=N(PPh₂)(BMes₂), respectively, displaying trigonal planar geometries about the P-N-B nitrogen atoms (Figure 2.29, Figure 2.30). Given the similar spectroscopic data between 2-30 and 2-31 to 2-33, the formulation of the former was found to be Ph₂C=NN(PPh₂)(Bpin). While the newly formed P-N bonds were found to be 1.729(2) and 1.730(1); 1.752(2); and 1.757(1) Å and the N-N bonds were found to be 1.445(2) and 1.443(2); 1.432(3); and 1.433(2) Å for 2-31 to 2-33, respectively, the newly formed B-N bonds were found to be 1.412(2) and 1.416(3); 1.429(3); and 1.441(2) Å for 2-31 to 2-33, respectively, indicative of B-N double bond character. The B-N double bond character is supported by the twist angle between the P-N-N and R’-B-R’ planes of 24.1 and 21.0; 12.1; and 28.4°, the sum of angles at B of 359.9 and 360.0; 360.0; and 359.9°, and the sum of angles at the P-N-B nitrogen of 355.4 and 356.3; 358.1; and 353.1° for 2-31 to 2-33, respectively. Additionally, no bonding is observed between the phosphorus and boron centres, with the lone pair of electrons on each phosphorus directed away from the boron’s p-orbital and P-B distances of 2.725(2) and 2.734(2); 2.762(3); and 2.761(2) Å measured in 2-31 to 2-33, respectively, being within the sum of the van der Waals radii for P and B (3.98 Å) but greater than the sum of the covalent radii for P and B (1.98 Å).

Figure 2.29 ORTEP depiction of 2-31 showing thermal ellipsoids at 50% probability. Hydrogen atoms and minor disorder omitted. P: orange, O: red, N: blue, B: yellow-green, C: black.
Figure 2.30  ORTEP depictions of 2-32 (top) and 2-33 (bottom) showing thermal ellipsoids at 50% probability. Hydrogen atoms and solvent omitted. P: orange, N: blue, B: yellow-green, C: black.
Given that the Lewis acidic and basic sites of 2-30 to 2-33 are similarly unquenched to those in the N2-linked species 2-24 and 2-25, the FLP reactivity of these geminal N-linked phosphinoboration products was investigated. Attempts to react 2-31 with CO showed no reaction while 4-phenyl-1,2,4-triazole-3,5-dione, 1,10-phenanthroline-5,6-dione, benzyl azide, or another equivalent of Ph2C≡N=N led to decomposition of the P-N-B moiety as characterized $^{31}$P{$^1$H} NMR spectra of the crude reaction mixtures. No signs of reactivity were observed by NMR spectroscopy upon exposure of 2-32 and 2-33 to H2, CO, CO2, N2O, O2, S8, [nBu4N][Ph3SiF2], benzyl azide, and 2-ethylxirane. While 2-31 showed immediate decomposition on exposure to water, 2-32 and 2-33 were found to be air and water stable, showing no signs of degradation in DCM/water mixtures even when heated to 80 °C for several days in the case of 2-32. Mixtures of 2-32 and 2-33 did show signs of reactivity when exposed to very reactive species including HCl, NaOH, H2O2, NFSI, [nBu4N][F], [NO][BF4], Me3NO, 4-phenyl-1,2,4-triazole-3,5-dione, and diazomethanes. However, analysis of the crude reaction mixtures by $^{31}$P{$^1$H} NMR revealed a multitude of peaks or, in each case of strong oxidants, decomposition to Ph2P(O)H and Ph2P(O)OH. No product of FLP reactivity could be isolated from any of the reaction mixtures.

### 2.12.5 Intramolecular FLPS with CN Linkages

Having found that 1,2-phosphinoboration products display FLP reactivity while the 1,1-phosphinoboration products synthesized herein do not, the FLP reactivity of phosphinoboration products where the phosphine and borane sites are more distantly held was explored. Noting that Westcott has published the 1,4-phosphinoboration of pyridines, 9-PPh2-10-Bpin-dihydroacridine was synthesized following their method.101 The FLP reactivity of this CN-linked phosphinoboration product was probed with a number of substrates including benzyl azide, p-nitrobenzaldehyde, phenol, 4-phenyl-1,2,4-triazole-3,5-dione, and o-quinones. However, $^{31}$P{$^1$H} NMR spectra of the crude reaction mixtures revealed complex mixtures and no product of FLP reactivity could be isolated. Indeed, diffraction studies of single crystals suitable for X-ray diffraction that were grown from these reaction mixtures contained the rearomatized acridine indicating decomposition. In hindsight, 9-PPh2-10-Bpin-dihydroacridine was a poor candidate for FLP reactivity given its proclivity for decomposition due to the stabilizing energy provided when rearomatizing the acridine ring. Future studies should focus instead on the 1,2-phosphinoboration products of imines, ketones, aldehydes,101 and various heteroallenes102 as these have also been synthesized and lack a similar decomposition pathway (Figure 2.31).
Figure 2.31 Candidate motifs for intramolecular FLPs produced by phosphinoboration reactions.

2.13 Conclusion

Reported herein are the 1,2-phosphinoboration reaction of PhN=NPh as well as the 1,1-phosphinoboration reaction of diazomethanes to yield unquenched Lewis acidic boron and Lewis basic phosphorus sites joined by N2- and N-linkers. The mechanism of the 1,2-phosphinoboration of PhN=NPh, investigated computationally, was found to proceed through an initial adduct formation between boron and a nitrogen atom on PhN=NPh followed by concerted migration of the phosphorus centre to the other nitrogen atom. Analysis of the HOMO and LUMOs of 2-20 using natural population analyses revealed that the boron centre is weakly Lewis acidic. Nevertheless, 2-20 and 2-21 behave as intramolecular FLPs, displaying small-molecule activation with the basic substrates PhN=NPh, 4-phenyl-1,2,4-triazole-3,5-dione, 1,10-phenanthroline-5,6-dione, and benzyl azide to form unique five-, six-, and eight-membered heterocyclic rings and with N,N-diphenylnitrous amide. Similar FLP investigations with the N-linked 2-31 to 2-33 resulted in either no reaction or decomposition. Efforts to extend the intramolecular FLP chemistry of phosphinoboration products to the CN-linked 9-PPh2-10-Bpin-dihydroacridine were similarly unsuccessful owing to the facile rearomatization of the acridine linker. Future studies applying the products of phosphinoboration reactions as heteroatom-linked intramolecular FLPs are encouraged provided judicious choice of the linker is made.
2.14 Experimental

2.14.1 General Experimental Methods

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N\textsubscript{2}. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (DCM, toluene, Et\textsubscript{2}O, and n-pentane) were prepared using an Innovative Technologies solvent purification system and degassed or distilled over sodium benzophenone under inert atmosphere. CDCl\textsubscript{3} (Aldrich) was deoxygenated, distilled over CaH\textsubscript{2}, then stored over 3 Å molecular sieves before use. C\textsubscript{6}D\textsubscript{6} (Aldrich) was deoxygenated, distilled over sodium benzophenone under inert atmosphere, then stored over 3 Å molecular sieves before use. DMSO-d\textsubscript{6} (Aldrich) was used without further purification. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. Ph\textsubscript{2}PBcat\textsuperscript{101}, Ph\textsubscript{2}PBpin\textsuperscript{101}, Ph\textsubscript{2}PBMes\textsubscript{2}\textsuperscript{103} and 9-PPh\textsubscript{2}-10-Bpin-dihydroacridine\textsuperscript{101} were prepared according to literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz or a Varian Mercury-300 MHz spectrometer. \textsuperscript{1}H, \textsuperscript{13}C{\textsuperscript{1}H}, \textsuperscript{31}P{\textsuperscript{1}H}, \textsuperscript{19}F, and \textsuperscript{11}B{\textsuperscript{1}H} NMR chemical shifts (δ/ppm) are referenced to Me\textsubscript{4}Si, Me\textsubscript{4}Si, H\textsubscript{3}PO\textsubscript{4}, CFCl\textsubscript{3}, and BF\textsubscript{3}•OEt\textsubscript{2}, respectively. Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI), a GCT Premier (EI), or a JEOL AccuTOF (DART) mass spectrometer.

2.14.2 X-Ray Diffraction Studies

Single crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-K\textsubscript{α} (0.71073 Å) or Cu-K\textsubscript{α} (1.54178 Å) radiation. Data were collected using Bruker APEX-2 or APEX-3 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 or APEX-3 program. All structures were solved and refined by direct methods within the SHELXLXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.
Table 2.8  X-ray table for 2-20, 2-23, and 2-24 grown from \( n \)-pentane.

<table>
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<th>Ph(_2)P(PhNNPh) Bcat (2-20)</th>
<th>Ph(_2)P(O)(PhNNPh) Bpin (2-23)</th>
<th>Ph(_2)P(PhNNPh)(_2) Bcat from ( n )-pentane (2-24)</th>
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<td>( P\overline{1} )</td>
<td>( P2_1/n )</td>
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Table 2.9  X-ray table for 2-24 grown from toluene, 2-25, and 2-26.

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<th>Ph$_2$P(PhNNPh)$_2$ (PhN(OCN)$_2$) Bcat (2-26)</th>
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<tr>
<td><strong>Empirical Formula</strong></td>
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<td>C$<em>{38}$H$</em>{29}$BN$_5$O$_4$P • (C$_7$H$<em>8$)$</em>{1.5}$</td>
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<td><strong>Weight (g/mol)</strong></td>
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<td>768.62</td>
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<td><strong>Crystal System</strong></td>
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<td>Monoclinic</td>
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<td><strong>Space Group</strong></td>
<td>Cc</td>
<td>Pbca</td>
<td>C2/c</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>13.2195(19)</td>
<td>18.0207(13)</td>
<td>31.4688(10)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>15.104(2)</td>
<td>18.4109(13)</td>
<td>16.7855(6)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>17.029(2)</td>
<td>23.1100(15)</td>
<td>20.4762(7)</td>
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<td><strong>α (°)</strong></td>
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<td>90</td>
<td>90</td>
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<tr>
<td><strong>β (°)</strong></td>
<td>91.838(3)</td>
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<td>128.6006(13)</td>
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<td><strong>γ (°)</strong></td>
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<td>90</td>
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<td><strong>Volume (Å$^3$)</strong></td>
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<td>7667.4(9)</td>
<td>8452.8(5)</td>
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<td>8</td>
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<td><strong>ρ (calcd.) (Mg/m$^3$)</strong></td>
<td>1.307</td>
<td>1.332</td>
<td>1.257</td>
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<td><strong>μ (mm$^{-1}$)</strong></td>
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<td>1.016</td>
<td>0.116</td>
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<td><strong>F(000)</strong></td>
<td>1400</td>
<td>3216</td>
<td>3352</td>
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<td><strong>Radiation</strong></td>
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<td>Cu Kα</td>
<td>Mo Kα</td>
</tr>
<tr>
<td><strong>Theta range (°)</strong></td>
<td>2.048 to 27.877</td>
<td>3.825 to 63.685</td>
<td>1.469 to 27.102</td>
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<td><strong>T (K)</strong></td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td><strong>Reflections Collected</strong></td>
<td>35310</td>
<td>64333</td>
<td>72880</td>
</tr>
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<td><strong>Independent</strong></td>
<td>7284</td>
<td>6294</td>
<td>9329</td>
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<tr>
<td><strong>Reflections</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>R_{int}</strong></td>
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<td>0.0679</td>
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<td><strong>GOF (F$^2$)</strong></td>
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<td>1.028</td>
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<td><strong>R1 indices [I&gt;2σ(I)]</strong></td>
<td>0.0583</td>
<td>0.0669</td>
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<tr>
<td><strong>wR2 indices (all data)</strong></td>
<td>0.1812</td>
<td>0.1862</td>
<td>0.2034</td>
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<tr>
<td><strong>Largest diff. peak and hole (e. Å$^{-3}$)</strong></td>
<td>0.507 &amp; -0.696</td>
<td>0.219 &amp; -0.511</td>
<td>1.384 &amp; -0.930</td>
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<td><strong>CCDC No.</strong></td>
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<td>1937236</td>
<td>1912467</td>
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Table 2.10  X-ray table for 2-27, 2-28, and 2-31.

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<th>Empirical Formula</th>
<th>Ph₂P(PhNNPh) (O₂C₁₂H₆N₂)Bcat (2-27)</th>
<th>Ph₂P(PhNNPh)(NCH₂Ph)Bcat (2-28)</th>
<th>Ph₂N=N(PPh₂)(Bcat) (2-31)</th>
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<td>591.46</td>
<td>498.30</td>
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<td>Triclinic</td>
<td>Monoclinic</td>
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<td>Space Group</td>
<td>P₂₁/n</td>
<td>P̅</td>
<td>P₂₁/c</td>
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<td>25.3105(14)</td>
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<td>b (Å)</td>
<td>28.9949(14)</td>
<td>12.362(3)</td>
<td>13.9331(8)</td>
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<td>c (Å)</td>
<td>13.4925(6)</td>
<td>13.462(4)</td>
<td>15.4998(9)</td>
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<td>α (°)</td>
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<td>90</td>
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<td>β (°)</td>
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<td>86.350(7)</td>
<td>107.602(3)</td>
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<td>γ (°)</td>
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<td>90</td>
</tr>
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<td>Volume (Å³)</td>
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<td>1499.9(6)</td>
<td>5210.1(5)</td>
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<td>Z</td>
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<td>2</td>
<td>8</td>
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<td>ρ (calcd.) (Mg/m³)</td>
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<td>1.310</td>
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<td>μ (mm⁻¹)</td>
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<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>Theta range (°)</td>
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<td>1.544 to 27.527</td>
<td>1.688 to 30.034</td>
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<td>150(2)</td>
<td>150(2)</td>
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<tr>
<td>Reflections Collected</td>
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<td>24953</td>
<td>125585</td>
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<td>Independent</td>
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<td>6893</td>
<td>15233</td>
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<tr>
<td>Reflections</td>
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<td></td>
<td></td>
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<tr>
<td>R(int)</td>
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<td>GOF (F²)</td>
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<td>R1 indices [I&gt;2σ(I)]</td>
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<td>wR2 indices (all data)</td>
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<td>0.1522</td>
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<td>Largest diff. peak and</td>
<td>0.961 &amp; -0.921</td>
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<td>0.367 &amp; -0.491</td>
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<td>hole (e. Å⁻³)</td>
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<td>CCDC No.</td>
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Table 2.11  X-ray table for 2-32 and 2-33.

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<th>Empirical Formula</th>
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<th>[Fluorenyl]N=N(PPh$_2$)(BMes$_2$) (2-33)</th>
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<td>Triclinic</td>
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<td>Space Group</td>
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<td>$P\overline{1}$</td>
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<td>10.9419(8)</td>
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<tr>
<td>$b$ (Å)</td>
<td>12.5079(14)</td>
<td>12.4455(10)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>13.5474(17)</td>
<td>12.8932(9)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>95.608(6)</td>
<td>94.044(4)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
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<td>94.334(4)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
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<td>96.359(4)</td>
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<td>1734.4(2)</td>
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<td>2</td>
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<tr>
<td>$\rho$ (calcd.) (Mg/m$^3$)</td>
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<td>1.200</td>
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<td>$\mu$ (mm$^{-1}$)</td>
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<td>Mo Kα</td>
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<td>1.589 to 28.699</td>
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<td>Independent Reflections</td>
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<td>8963</td>
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<td>$R_{int}$</td>
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<td>GOF (F$^2$)</td>
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<tr>
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<td>wR2 indices (all data)</td>
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<td>0.1334</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e. Å$^{-3}$)</td>
<td>0.818 &amp; -0.568</td>
<td>0.370 &amp; -0.268</td>
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<td>CCDC No.</td>
<td>----</td>
<td>----</td>
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2.14.3 Phosphinoboration of Diazobenzene

2-20 1-(benzo[d][1,3,2]dioxaborol-2-yl)-2-(diphenylphosphanyl)-1,2-diphenylhydrazine (Ph$_2$P(PhNNPh)Bcat)

In a 20 mL vial, a solution of Ph$_2$PBcat (0.34 mmol, 103 mg, 1 eq.) was prepared in DCM (3 mL). A solution of PhN=NPh (0.34 mmol, 61.7 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) to afford a white solid (151 mg, 92% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 6.39 (tt, $J$ = 7, 1 Hz, 1H), 6.50 – 6.53 (m, 2H), 6.65 – 6.70 (m, 1H), 6.72 (dd, $J$ = 6, 3 Hz, 1H), 6.96 – 7.02 (m, 1H), 7.11 – 7.16 (m, 2H), 7.31 (d, $J$ = 7, 1 Hz, 2H), 7.52 – 7.58 (m, 2H), 7.72 – 7.77 (m, 1H), 7.99 – 8.05 (m, 2H) ppm. $^{11}$B{$^1$H} NMR (128 MHz, CDCl$_3$): $\delta$ = 27.6 (s, br) ppm. $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ = 69.4 (s) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ = 112.1, 115.2 (d, $J$ = 9 Hz), 119.8, 120.4, 122.3, 123.1, 123.6, 128.0 (d, $J$ = 6 Hz), 128.1 (d, $J$ = 7 Hz), 128.8, 129.2 (d, $J$ = 4 Hz), 129.8, 133.1 (d, $J$ = 21 Hz), 134.1 (d, $J$ = 23 Hz), 148.3 ppm. HRMS (TOF MS EI+): m/z [M] 486.1666 (calc’d for C$_{30}$H$_{24}$BN$_2$O$_2$P: 486.1668).

2-21 1-(phenanthrol[9,10-d][1,3,2]dioxaborol-2-yl)12-(diphenylphosphanyl)-1,2-diphenylhydrazine (Ph$_2$P(PhNNPh)Bquin)

In a 20 mL vial, a solution of Ph$_2$PBquin (0.06 mmol, 25.2 mg, 1 eq.) was prepared in DCM (3 mL). A solution of PhN=NPh (0.06 mmol, 11.4 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo and washed with cold n-pentane (3 x 2 mL) to afford a white solid (33.3 mg, 91% isolated yield). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ = 6.69 – 6.75 (m, 1H), 6.81 – 6.90 (m, 3H), 6.91 – 6.99 (m, 2H), 6.99 – 7.14 (m, 3H), 7.14 – 7.23 (m, 1H), 7.24 – 7.35 (m, 3H), 7.40 – 7.46 (m, 1H), 7.58 – 7.63 (m, 2H), 7.84 (ddt, $J$ = 8, 6, 1 Hz, 1H), 7.91 – 7.94 (m, 1H), 7.97 – 8.02 (m, 1H), 8.29 (dd, $J$ = 8, 2 Hz, 1H), 8.37 (ddd, $J$ = 8, 1, 1 Hz, 1H) ppm. $^{11}$B{$^1$H} NMR (128 MHz, CDCl$_3$): $\delta$ = 26.3 (s, br) ppm. $^{31}$P{$^1$H} NMR (202
MHz, C₆D₆): δ = 70.9 (s) ppm. $^{13}$C{¹H} NMR (125 MHz, C₆D₆): δ = 112.7, 115.8 (d, J = 8 Hz), 116.7 (d, J = 16 Hz), 117.9, 119.9 (d, J = 1 Hz), 120.8 (t, J = 5 Hz), 123.1 (d, J = 7 Hz), 123.4 – 123.9 (m), 125.3, 127.2, 127.9, 128.4, 128.5, 128.9, 129.1, 129.4, 129.6, 129.8, 129.9, 133.7 (d, J = 21 Hz), 134.2 (d, J = 23 Hz), 136.2 (d, J = 16 Hz), 136.8 (d, J = 20 Hz), 140.1, 140.3, 144.7, 145.2, 147.4, 149.5 (d, J = 11 Hz) ppm. HRMS (DART-TOF): m/z [M-(Bquin)+H] 369.15195 (calc’d for C₂₄H₂₂N₂P: 369.15206). HRMS (DART-TOF): m/z [M-Ph₂P(PhNNPh)-(Bquin)+H] 209.05984 (calc’d for C₁₄H₁₀O₂: 209.06025).

2-22 1-(diphenylphosphanyl)-1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (Ph₂P(PhNNPh)Bpin)

and

2-23 $N,N',P,P$-tetraphenyl-$N'$-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinic hydrazide (Ph₂P(O)(PhNNPh)Bpin)

In a 50 mL Schlenk tube, a solution of Ph₂PBpin (0.34 mmol, 106 mg, 1 eq.) was prepared in DCM (5 mL). A solution of PhN=NP (0.34 mmol, 61.7 mg, 1 eq.) in DCM (5 mL) was added at ambient temperature. The reaction mixture was sealed and heated at 70 °C for 2 days. The solution was then dried in vacuo. Single crystals of 2-23 suitable for X-ray diffraction were grown from n-pentane. HRMS (TOF ESI+) for (7): m/z [M+H] 495.23719 (calc’d for C₃₀H₃₃BN₂O₂P⁺: 495.23727).
2.14.4 Frustrated Lewis Pair Reactivity of R₂P(PhNNPh)BR’₂ Species

2-24 1',2',3',3',4',5'-hexaphenylspiro[benzo[d][1,3,2]dioxaborole-2,6'-[1,2,4,5,3,6]tetrazaphosphaborinan]-3'-ium-2-ide (Ph₂P(PhNNPh)₂Bcat)

In a 20 mL vial, a solution of Ph₂PBcat (0.13 mmol, 1 eq.) was prepared in DCM (3 mL). A solution of PhN=NPh (0.40 mmol, 3 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 48 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) and with cold toluene (3 x 2 mL) to afford a yellow solid (74.7 mg, 86% isolated yield).

1H NMR (500 MHz, DMSO-d₆): δ = 6.41 (dt, J = 7, 1 Hz, 2H), 6.52 – 6.57 (m, 4H), 6.67 – 6.73 (m, 4H), 6.74 (dd, J = 6, 3 Hz, 2H), 6.88 (dd, J = 6, 3 Hz, 2H), 6.98 – 7.05 (m, 2H), 7.14 – 7.18 (m, 4H), 7.34 (dt, J = 7, 1 Hz, 4H), 7.53 – 7.61 (m, 4H), 7.74 – 7.80 (m, 2H), 8.01 – 8.08 (m, 4H) ppm. ¹¹B{¹H} NMR (128 MHz, DMSO-d₆): δ = 11.7 (s) ppm. ³¹P{¹H} NMR (162 MHz, DMSO-d₆): δ = 43.7 (s) ppm. ¹³C{¹H} NMR (125 MHz, DMSO-d₆): δ = 109.3, 114.6, 117.6, 118.5, 118.6, 119.4, 122.0, 125.0, 127.7, 128.8, 129.2 (d, J = 14 Hz), 134.9 (d, J = 11 Hz), 135.1, 141.8, 141.9, 146.7, 151.6 ppm. HRMS (ESI+): m/z [M+H] 668.2617 (calc’d for C₄₂H₃₄BN₄O₂P: 668.2622).

2-25 1',2',3',3',4',5'-hexaphenylspiro[phenanthrol[9,10-d][1,3,2]dioxaborole-2,6'-[1,2,4,5,3,6]tetrazaphosphaborinan]-3'-ium-2-ide (Ph₂P(PhNNPh)₂Bquin)

In a 20 mL vial, a solution of Ph₂PBquin (0.01 mmol, 37.5 mg, 1 eq.) was prepared in toluene (3 mL). A solution of PhN=NPh (0.03 mmol, 50.1 mg, 3 eq.) in toluene (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 48 h. The solution was then reduced in vacuo, the product was precipitated with n-pentane, and washed with n-pentane (3 x 2 mL) to afford a white solid (64.9 mg, 91% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ = 6.40 (t, J = 7 Hz, 2H), 6.70 (dd, J = 9, 7 Hz, 4H), 6.82 (d, J = 8 Hz, 4H), 6.96 (t, J = 7 Hz, 2H), 7.06 (t, J = 8 Hz, 4H), 7.36 (d, J = 8 Hz, 4H), 7.45 – 7.53 (m, 6H), 7.57 – 7.66 (m, 4H), 8.08 – 8.15 (m, 4H), 8.20 (dd, J = 8, 1 Hz, 2H), 8.77 (d, J = 8 Hz, 2H) ppm. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ = 12.6 (s) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 41.8 (s) ppm. ¹³C{¹H}
NMR (100 MHz, CDCl₃): δ = 115.1, 117.8, 120.2, 120.8, 121.3, 122.4, 122.6, 123.0, 123.2, 125.0, 125.1, 125.9, 126.1, 128.1, 128.4, 129.0, 129.2, 129.3, 129.4, 134.8, 134.8, 135.4, 135.5, 141.6, 142.8, 143.0, 147.8 ppm. HRMS (ESI+): m/z [M+H] 768.2933 (calc’d for C₅₀H₃₉BN₄O₂P: 768.2935).

2-26 6',8'-dioxo-1',1',2',3',7'-pentaphenyl-2',3',7',8'-tetrahydro-1'H,6'H-spiro[benzo[d][1,3,2]dioxaborole-2,4'-[1,2,4]triazolo[1,2-
a][1,2,4,5,3,6]tetrazaphosphaborinin]-1'-ium-2-ide (Ph₂P(PhNNPh)(PhN(OCN)₂)Bcat)

In a 20 mL vial, a solution of Ph₂P(PhNNPh)Bcat (0.14 mmol, 1 eq.) was prepared in DCM (3 mL). A solution of 4-phenyl-1,2,4-triazole-3,5-dione (0.14 mmol, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) and with cold toluene (3 x 2 mL) to afford a yellow solid (80.5 mg, 81% isolated yield). ¹H NMR (500 MHz, CDCl₃): δ = 6.47 – 6.62 (m, 3H), 6.66 – 6.89 (m, 5H), 6.95 – 7.33 (m, 8H), 7.34 – 7.48 (m, 2H), 7.49 – 7.61 (m, 2H), 7.64 – 7.71 (m, 3H), 7.80 (s, 2H), 7.86 – 8.00 (m, 1H), 8.45 (s, 2H) ppm. ¹¹B{¹H} NMR 128 MHz, CDCl₃: δ = 13.9 (s) ppm. ³¹P{¹H} NMR 162 MHz, CDCl₃: δ = 42.6 (s) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 109.7 (d, J = 22 Hz), 117.1, 120.3, 125.2, 125.4 (d, J = 2 Hz), 125.5, 127.2, 128.0, 128.4, 128.6, 129.0, 129.2, 129.6, 131.4, 134.0, 134.5, 136.6, 138.0, 139.5 (d, J = 15 Hz), 145.2, 151.3 (d, J = 6 Hz), 153.0 (d, J = 7 Hz) ppm.
2,2',3',4'-tetraphenyl-3',4'-dihydro-2'H-spiro[benzo[d][1,3,2]dioxaborole-
2,5'-[1,6,3,4,5,2]dioxadiazaphosphaborocino[7,8-f][1,10]phenanthrolin]-2'-ium-2-ide
(Ph$_2$P(PhNNPh)(O$_2$C$_{12}$H$_6$N$_2$)Bcat)

In a 20 mL vial, a solution of Ph$_2$P(PhNNPh)Bcat (0.13 mmol, 1 eq.) was prepared in DCM (3 mL). A solution of 1,10-phenanthroline-5,6-dione (0.13 mmol, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) and with cold toluene (3 x 2 mL) to afford a yellow solid (25.3 mg, 28% isolated yield).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 6.64$ (td, $J = 8$, 1 Hz, 1H), 6.68 – 6.76 (m, 2H), 6.87 – 6.92 (m, 1H), 7.05 (t, $J = 5$ Hz, 2H), 7.23 (d, $J = 7$ Hz, 2H), 7.37 (d, $J = 8$ Hz, 2H), 7.42 – 7.52 (m, 4H), 7.59 (td, $J = 8$, 4 Hz, 2H), 7.68 – 7.78 (m, 2H), 8.19 – 8.28 (m, 2H), 8.84 (s, 2H) ppm.

$^{11}$B$^1$H NMR (128 MHz, DMSO-d$_6$): $\delta = 15.2$ (s) ppm.

$^{31}$P$^1$H NMR 162 MHz, DMSO-d$_6$): $\delta = 49.5$ (s) ppm.

$^{13}$C$^1$H NMR (125 MHz, CDCl$_3$): $\delta = 108.7$, 109.7, 118.1 (d, $J = 22$ Hz), 129.0, 129.3, 129.4, 130.1 (d, $J = 15$ Hz), 133.3, 134.0 (d, $J = 13$ Hz), 135.7, 135.8, 136.1 (d, $J = 12$ Hz), 152.0 (d, $J = 52$ Hz) ppm. HRMS (DART-TOF+): m/z [M+H] 696.2211 (calc’d for C$_{42}$H$_{31}$BN$_4$O$_4$P: 696.2207).

2-28 4'-benzyl-1',2',3',3'-tetraphenylspiro[benzo[d][1,3,2]dioxaborole-2,5'-
[1,2,4,3,5]triazaphosphaborolidin]-3'-ium-2-ide (Ph$_2$P(PhNNPh)(NCH$_2$Ph)Bcat)

In a 20 mL vial, a solution of Ph$_2$P(PhNNPh)Bcat (0.15 mmol, 1 eq.) was prepared in DCM (3 mL). A solution of benzyl azide (0.15 mmol, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) and with cold toluene (3 x 2 mL) to afford a yellow solid (64.7 mg, 73% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 4.07$ (d, $J = 19$ Hz, 2H), 6.59 (dd, $J = 7$, 1 Hz, 1H), 6.66 (t, $J = 1$ Hz, 1H), 6.68 (d, $J = 1$ Hz, 1H), 6.69 – 6.79 (m, 2H), 6.82 – 6.88 (m, 1H), 6.88 – 6.96 (m, 2H), 6.97 (t, $J = 2$ Hz, 1H), 6.98 (dd, $J = 4$, 2 Hz, 3H), 6.99 – 7.00 (m, 2H), 7.01 – 7.04 (m, 1H), 7.11 – 7.18 (m,
2H), 7.31 – 7.45 (m, 4H), 7.57 (t, J = 8 Hz, 6H) ppm. $^1$H NMR (128 MHz, CDCl₃): \( \delta = 10.6 \) (s ppm). $^{31}$P$^{(1)}$H NMR (162 MHz, CDCl₃): \( \delta = 50.8 \) (s ppm). $^{13}$C$^{(1)}$H NMR (125 MHz, CDCl₃): \( \delta = 46.5 \) (d, \( J = 2 \) Hz), 109.5, 114.7, 117.9, 118.7, 121.7 (d, \( J = 3 \) Hz), 124.6 (d, \( J = 2 \) Hz), 127.1, 128.2, 128.6, 128.9 (d, \( J = 2 \) Hz), 129.1, 129.2, 134.3, 138.5 (d, \( J = 1 \) Hz), 142.7 (d, \( J = 5 \) Hz), 146.6 (d, \( J = 5 \) Hz), 152.3 ppm. HRMS (DART-TOF+): m/z [M+H] 592.23296 (calc’d for C$_{37}$H$_{32}$BN$_3$O$_2$P: 592.23252).

2-29 2-((2,2-diphenyldiazaineyl)diphenylphosphonio)-1,2-diphenyldiazaineyl)-2-hydroxybenzo[d][1,3,2]dioxaborol-2-ide (Ph$_2$P(Ph$_2$NH)(PhNNPh)(OH)Bcat)

In a 20 mL vial, a solution of Ph$_2$P(Ph$_2$NH)Bcat (0.14 mmol, 1 eq.) was prepared in DCM (3 mL). A solution of N,N-diphenylnitrous amide (0.14 mmol, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried in vacuo, recrystallized by layering with n-pentane and DCM, and washed with cold n-pentane (3 x 2 mL) and with cold toluene (3 x 2 mL) to afford a yellow solid (75.0 mg, 76% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): \( \delta = 5.88 – 5.92 \) (s br, 1H), 6.51 – 6.55 (s br, 1H), 6.70 – 6.79 (m, 5H), 6.94 – 7.00 (m, 2H), 7.00 – 7.09 (m, 4H), 7.12 – 7.20 (m, 3H), 7.32 – 7.42 (m, 10H), 7.42 – 7.53 (m, 4H), 7.83 (ddt, \( J = 12, 7, 1 \) Hz, 6H) ppm. $^{11}$B$^{(1)}$H NMR (128 MHz, CDCl$_3$): \( \delta = 6.6 \) (s ppm). $^{31}$P$^{(1)}$H NMR (162 MHz, CDCl$_3$): \( \delta = 29.5 \) (s ppm). $^{13}$C$^{(1)}$H NMR (125 MHz, CDCl$_3$): \( \delta = 114.0, 121.0, 121.8, 124.7, 128.7, 128.8, 129.3, 129.3, 130.0, 130.6, 131.6, 132.4, 132.4, 132.6, 132.7, 136.1, 146.5, 146.6 \) ppm. HRMS (DART-ESI+): m/z [M+H] 687.27025 (calc’d for C$_{42}$H$_{37}$BN$_4$O$_3$P: 687.26963).
2.14.5 Phosphinoboration of Diazomethane

2-30 2-(diphenylmethylene)-1-(diphenylphosphanyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hydrazine (Ph$_2$C=NN(PPh$_2$)(Bpin))

In a 20 mL vial, a solution of Ph$_2$PBpin (0.1 mmol, 31.2 mg, 1 eq.) was prepared in DCM (3 mL). A solution of diphenyldiazomethane (0.1 mmol, 19.4 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried in vacuo to afford a colourless solid (48.1 mg, 95% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.11 (s, 12H), 6.59 – 6.62 (m, 2H), 7.18 – 7.22 (m, 2H), 7.23 – 7.29 (m, 4H), 7.33 – 7.36 (m, 6H), 7.46 – 7.49 (m, 2H), 7.63 – 7.67 (m, 4H) ppm. $^{11}$B{$^1$H} NMR (128 MHz, CDCl$_3$): $\delta$ = 24.3 (s, br) ppm. $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ = 48.5 (s) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ = 24.5, 83.5, 83.5, 127.4, 127.9, 127.9, 128.1, 128.7, 128.8 (br), 129.0, 129.7, 133.8 (d, br, $J = 21$ Hz), 135.3, 138.3, 138.8 (d, $J = 12$ Hz), 169.2 ppm.

2-31 1-(benzo[d][1,3,2]dioxaborol-2-yl)-2-(diphenylmethylene)-1-(diphenylphosphinyl)hydrazine (Ph$_2$C=NN(PPh$_2$)(Bcat))

In a 20 mL vial, a solution of Ph$_2$PBcat (0.1 mmol, 30.4 mg, 1 eq.) was prepared in DCM (3 mL). A solution of diphenyldiazomethane (0.1 mmol, 19.4 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried in vacuo and recrystallized from Et$_2$O to afford a colourless crystalline solid (45.4 mg, 91% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 6.40 – 6.43 (m, 2H), 6.94 (dd, $J = 6$, 3 Hz, 2H), 7.01 – 7.06 (m, 4H), 7.11 (tt, $J = 8$, 2 Hz, 1H), 7.26 – 7.30 (m, 2H), 7.32 – 7.40 (m, 8H), 7.48 – 7.51 (m, 2H), 7.63 – 7.67 (m, 4H) ppm. $^{11}$B{$^1$H} NMR (128 MHz, CDCl$_3$): $\delta$ = 25.6 (s, br) ppm. $^{31}$P{$^1$H} NMR (202 MHz, CDCl$_3$): $\delta$ = 49.8 (s) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ = 112.0, 122.15, 127.6, 128.1, 128.2, 128.3, 128.5, 128.9, 129.4, 130.5, 133.8, 134.0, 134.7, 137.3, 13.4, 137.7, 148.3, 148.3, 172.0 ppm.
2-32  1-(dimesitylboranyl)-2-(diphenylmethylene)-1- (diphenylphosphinyl)hydrazine (Ph₂C=NN(PPh₂)(BMes₂))

In a 20 mL vial, a solution of Ph₂PBMes₂ (0.1 mmol, 43.4 mg, 1 eq.) was prepared in DCM (3 mL). A solution of diphenylazomethane (0.1 mmol, 19.4 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et₂O to afford a white solid (51.6 mg, 82% isolated yield). 

**¹H NMR (500 MHz, CDCl₃):** δ = 1.17 (s, 3H), 1.99 (s, 3H), 2.18 (s, 3H), 2.24 (s, 3H), 2.28 (s, 3H), 2.52 (s, 3H), 5.72 (dd, J = 8 Hz, 1 Hz, 2H), 6.46 (s, 1H), 6.67 (dd, J = 7 Hz, 1 Hz, 2H), 6.82 (s, 1H), 7.01 (t, J = 8 Hz, 2H), 7.22 (tt, J = 7 Hz, 1 Hz, 1H), 7.25-7.30 (m, 4H), 7.34-7.40 (m, 8H), 7.86 (td, J = 7 Hz, 1 Hz, 2H), 7.93 (td, J = 8 Hz, 1 Hz, 2H) ppm. 

**¹³B{¹H} NMR (128 MHz, CDCl₃):** δ = 45.8 (s, br) ppm. 

**³¹P{¹H} NMR (162 MHz, CDCl₃):** δ = 57.2 (s) ppm. 

**¹³C{¹H} NMR (125 MHz, CDCl₃):** δ = 21.1, 21.3, 22.6, 22.7, 23.6, 25.0 (d, J = 9 Hz), 127.4, 127.5, 127.8 (d, J = 6 Hz), 128.0, 128.0, 128.1, 128.2, 128.4, 128.7 (d, J = 3 Hz), 128.7, 129.8, 130.5, 132.7 (d, J = 22 Hz), 135.1, 136.9, 137.0, 137.0, 137.1, 137.4 (d, J = 5 Hz), 137.6, 138.8, 139.4 (d, J = 20 Hz), 140.6 (d, J = 1 Hz), 141.0, 141.2 (d, J = 3 Hz), 143.2, 165.8 (d, J = 1 Hz) ppm. 

**HRMS (DART-TOF+):** m/z [M+H] 629.32627 (calc’d for C₄₃H₄₅B₁N₂P₁: 629.32569).

2-33  1-(dimesitylboranyl)-1-(diphenylphosphinyl)-2-(9H-fluoren-9- ylidene)hydrazine ([Fluorenyl]N=N(PPh₂)(BMes₂))

In a 20 mL vial, a solution of Ph₂PBMes₂ (0.1 mmol, 45.0 mg, 1 eq.) was prepared in DCM (3 mL). A solution of 9-diazo-fluorene (0.1 mmol, 19.9 mg, 1 eq.) in DCM (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 3 h. The solution was then dried *in vacuo* and recrystallized from a hot solution of Et₂O to afford a yellow solid (61.4 mg, 95% isolated yield). 

**¹H NMR (500 MHz, CDCl₃):** δ = 1.66 (s, 3H), 1.86 (s, 3H), 1.88 (s, 3H), 2.00 (s, 3H), 2.34 (s, 3H), 3.00 (s, 3H), 6.19 (d, J = 10 Hz, 2H), 6.78 (s, 1H), 6.98 (s, 1H), 7.02-7.05 (m, 3H), 7.19 (td, J = 7, 1 Hz, 1H), 7.23 (td, J = 7, 1 Hz, 1H), 7.27-7.33 (m, 4H), 7.28 (ddt, J = 7, 4, 1 Hz, 2H), 7.44-7.47 (m, 2H), 7.49-7.52 (m, 1H), 7.57 (dt, J = 7, 1 Hz, 1H), 7.82 (td, J = 8, 1 Hz, 2H), 8.51
(dt, J = 7, 1 Hz, 1H) ppm. \[^{11}\text{B}\{^{1}\text{H}\} \text{NMR (128 MHz, CDCl}_3\}): \delta = 52.7 \text{ (s, br) ppm.} \[^{31}\text{P}\{^{1}\text{H}\} \text{NMR (162 MHz, CDCl}_3\}): \delta = 64.3 \text{ (s) ppm.} \[^{13}\text{C}\{^{1}\text{H}\} \text{NMR (125 MHz, CDCl}_3\}): \delta = 20.8, 21.4, 22.5, 22.7, 22.9, 25.2 \text{ (d, } J = 11 \text{ Hz)}, 119.3, 119.7, 122.6, 126.7, 127.3, 127.6 \text{ (d, } J = 8 \text{ Hz)}, 127.8 \text{ (d, } J = 2 \text{ Hz)}, 127.8, 127.9, 127.9, 128.2 \text{ (d, } J = 21 \text{ Hz)}, 128.4, 128.8, 129.2, 130.4 \text{ (d, } J = 5 \text{ Hz)}, 130.7, 131.0 \text{ (d, } J = 18 \text{ Hz)}, 131.1, 136.1 \text{ (d, } J = 26 \text{ Hz)}, 137.0, 137.1, 137.2, 137.6 \text{ (d, } J = 1 \text{ Hz)}, 138.3, 138.7 \text{ (d, } J = 13 \text{ Hz)}, 140.2, 140.6 \text{ (d, } J = 3 \text{ Hz)}, 141.0 \text{ (d, } J = 28 \text{ Hz)}, 141.6 \text{ (d, } J = 1 \text{ Hz)}, 142.5, 159.5 \text{ (d, } J = 1 \text{ Hz}) \text{ ppm.} \[^{12}\text{C}\{^{1}\text{H}\} \text{NMR (125 MHz, CDCl}_3\)}.

2.14.6 Computational Details

Calculations were carried out with the Gaussian 16\textsuperscript{92} package. Geometry optimizations and frequency calculations were performed with the BP86\textsuperscript{93, 94} functional and the polarized triple-zeta basis set Def2-TZVP.\textsuperscript{95, 96} Natural bond orbital and natural population analyses were performed on optimized structures using NBO 6.0\textsuperscript{97} at the M06-2X/Def2-TZVP\textsuperscript{98} level of theory. X-ray coordinates were used as the starting geometry for geometry optimizations where possible. The absence of any imaginary frequency with an absolute magnitude greater than 10 cm\textsuperscript{-1} confirmed that each optimized structure was indeed located at a minimum on its potential energy hypersurface. Transition states were confirmed by the existence of only one imaginary frequency with an absolute magnitude greater than 10 cm\textsuperscript{-1}. Frequency calculations were used to provide the thermal corrections of Gibbs free energy. Transition states were submitted to intrinsic reaction coordinate (IRC)\textsuperscript{104, 105} calculations to determine two corresponding minima.

The single-point energy calculations were performed at the BP86/Def2-TZVP level of theory with PCM\textsuperscript{99} solvation modeling (dichloromethane). For comparison, the single-point energies were also evaluated with the inclusion of Grimme’s GD3BJ Empirical Dispersion\textsuperscript{106} method. The gas-phase geometry was used for all solution phase calculations. The Gibbs energy corrections from frequency calculations were added to the single-point energies to obtain the Gibbs free energies in solution and the Gibbs free energies in solution with dispersion.

2.15 References


Chapter 3

Section 3.1 - Electrophilic Phenoxy-substituted Phosphonium Cations

3.1 Highly Electrophilic Phosphonium Cations

The Stephan group became interested in phosphorus-based Lewis acids and, in 2013, synthesized a highly Lewis acidic fluorophosphonium salt \([(C_6F_5)_3PF][B(C_6F_5)_4]\) by treating \((C_6F_5)_3P\) with an equivalent of \(\text{XeF}_2\) to form the difluorophosphorane and subsequently abstracting a fluoride with \([\text{Et}_3\text{Si(Tol)}][\text{B}(C_6F_5)_4]\) (Scheme 3.1).\(^1\) The Lewis acidity of the fluorophosphonium cation, derived from the accessible \(\sigma^*\) orbital located opposite the apical P-F bond (Figure 3.1), was probed experimentally using the Gutmann-Beckett method,\(^2\)\(^3\) resulting in a \(\Delta\delta\) \(^{31}\text{P}\) NMR shift of 40.4 ppm, and computationally using fluoride ion affinity (FIA),\(^4\) which gave a value of 777 kJ/mol. By comparison, \(\text{B}(C_6F_5)_3\), a species commonly used in Lewis acid catalysis, produces a Gutmann-Beckett method \(\Delta\delta\) \(^{31}\text{P}\) NMR shift of 26.6 ppm and has an FIA value of 440 kJ/mol. These results attest to the considerable Lewis acidity of \([(C_6F_5)_3PF][B(C_6F_5)_4]\).

\[
\begin{align*}
\text{C}_6\text{F}_5\text{P} \quad &\xrightarrow{1 \text{ eq } \text{XeF}_2} \quad \text{C}_6\text{F}_5\text{F} \quad &\text{DCM, rt, 8 h} \quad - \text{Xe} \\
\quad &\xrightarrow{\text{Et}_3\text{Si(Tol)}[\text{B}(C_6F_5)_4]} \quad \left[\text{C}_6\text{F}_5\right]^+ \quad &\text{Tol, rt, 1 h} \quad - \text{Et}_3\text{SiF} \\
\end{align*}
\]

Scheme 3.1 Synthesis of \([(C_6F_5)_3PF][B(C_6F_5)_4]\).

Figure 3.1 Surface contour plot (isovalue 0.03) of the LUMO of \([(C_6F_5)_3PF]^+\), featuring significant P-F anti-bonding character. P: orange, C: black, F: pink.
Given the strong Lewis acidity of \([\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\), its competency in Lewis acid catalysis was investigated. Due to its marked fluorophilicity, it was first applied to the hydrodefluorination\(^1\) of alkyl C-F bonds and was subsequently applied to hydroarylation,\(^5\) deoxygenation,\(^6,\) \(^7\) hydrogenation,\(^8\) dehydrocoupling,\(^9\) olefin polymerization,\(^10\) hydrosilylation,\(^10\) C-C cross-coupling,\(^11,\) \(^12\) Diels-Alder reactions,\(^13\) and Nazarov cyclizations\(^13\) (Scheme 3.2, Scheme 3.3).

\[\text{Scheme 3.2} \quad \text{Hydrodefluorination (top left), deoxygenation (top right), dehydrocoupling (bottom left), and hydrosilylation (bottom right) reactions catalyzed by } [(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\].

\[\text{Scheme 3.3} \quad \text{Hydroarylation (top), Diels-Alder (bottom left), and Nazarov cyclization (bottom right) reactions catalyzed by } [(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\].

Despite its breadth of reactivity, the general adoption of \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\] as a Lewis acid catalyst is prevented due in large part to its acute moisture sensitivity which requires that \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\] be handled only in strictly air- and moisture-free conditions. It is therefore desirable to develop more robust systems that maintain high Lewis acidity in less stringent conditions.
conditions. One approach is to vary the equatorial C₆F₅ groups to tune the degree to which they withdraw electrons from the phosphorus centre, thereby changing the accessibility of the σ* orbital (Figure 3.2). The Stephan group has replaced one or more C₆F₅ substituents with alkyl or aryl groups commonly found on phosphines (i.e. tBu, Ph, Mes, 2-Tol, 4-C₆H₄F, 4-C₆F₄H) and found that Lewis acidity significantly decreased according to Gutmann–Beckett method shifts and FIA values. Additionally, the Stephan group has explored C₆Cl₅ analogues, as these also contain electron withdrawing groups necessary to maintain Lewis acidity but offer more steric bulk to protect the Lewis acidic site. Although the resulting electrophilic phosphonium cations (EPCs) were more robust, their Lewis acid reactivity was hindered. Dicationic EPCs have been made bearing cationic N-heterocyclic carbene or N-Me-pyridinium electron withdrawing substituents. In the former case, [(SIMes)Ph₂PF][B(C₆F₅)₄]₂ was shown to be more fluorophilic than [(C₆F₅)₃PF][B(C₆F₅)₄] through a competition experiment wherein [(SIMes)Ph₂PF][B(C₆F₅)₄]₂ was seen to abstract a fluoride from (C₆F₅)₃PF₂. In the latter case, [(2-(N-Mepy))Ph₂PF][B(C₆F₅)₄]₂ demonstrated comparable catalytic activity but poorer stability when compared to [(SIMes)Ph₂PF][B(C₆F₅)₄]₂, as decomposition was observed upon exposure to Et₃SiH. A family of bisfluorophosphonium dications has also been synthesized bearing either a naphthyl linker [(C₁₀H₆)(Ph₂PF₂)][B(C₆F₅)₄]₂ or an alkyl chain linker [(CH₂)ₙ(Ph₂PF₂)][B(C₆F₅)₄]₂, where n = 1-5. Although they were shown to have diminished Lewis acidity compared to [(C₆F₅)₃PF][B(C₆F₅)₄], this was improved by closer proximity of the phosphonium centres.

\[
\begin{align*}
\text{R} = \text{alkyl, aryl} & & \text{X} = \text{H, Cl} \\
\end{align*}
\]

\[
\begin{align*}
2 \text{[(SIMes)Ph₂PF][B(C₆F₅)₄]₂} & & 2 \text{[(C₆F₅)₃PF][B(C₆F₅)₄]₂} & & 2 \text{[(2-(N-Mepy))Ph₂PF][B(C₆F₅)₄]₂} \\
2 \text{[(C₁₀H₆)(Ph₂PF₂)][B(C₆F₅)₄]₂} & & \text{[(CH₂)ₙ(Ph₂PF₂)][B(C₆F₅)₄]₂} & & \text{[(SIMes)Ph₂PF][B(C₆F₅)₄]₂} \\
\end{align*}
\]

Figure 3.2  EPC derivatives with varying equatorial substituents.
Another approach is to vary the apical group. While the apical fluorine (Pauling electronegativity: $\chi_{\text{Pauling}} = 3.98$) substituent imparts significant polarity to the P-F $\sigma$ bond and helps to make the $\sigma^*$ orbital accessible for substrate activation, this bond is readily cleaved by strong nucleophiles including water and alcohols.\textsuperscript{19} It is therefore desirable to replace the apical fluorine with an electron withdrawing substituent that can better stabilize this hypervalent interaction. Apicophilic groups on P(V) species generally have strong electronegativity, small steric size, and good $\pi$-accepting ability, with the following trend having been proposed:\textsuperscript{20-23}

$$\text{F} > \text{H} > \text{CF}_3 > \text{OPh} > \text{Cl} > \text{SMe} > \text{OMe} > \text{NMe}_2 > \text{Me} > \text{Ph}$$

The Stephan group has also synthesized EPCs with various apical groups (Figure 3.3). Apically methyl-substituted ($\chi_{\text{Pauling, carbon}} = 2.55$) EPCs were synthesized by the reaction of phosphines with MeOTf, generating dicationic [((2-(N-Mepy))Ph$_2$PMe][B(C$_6$F$_5$)$_4$]$_2$\textsuperscript{17} as well as tricationic [PhPMe(CH$_2$CH$_2$PMePh$_2$)$_2$][OTf]$_3$\textsuperscript{19} and [MeC(CH$_2$PMePh$_2$)$_3$][OTf]$_3$.\textsuperscript{19} In each case, the resulting EPC is much more stable to moisture but is a significantly less potent Lewis acid compared to its fluorinated alternative. Variations of mono- and dicationic EPCs have also been made to include an apical chlorine ($\chi_{\text{Pauling}} = 3.16$) or bromine ($\chi_{\text{Pauling}} = 2.96$) substituent by the oxidation of phosphines with SO$_2$Cl$_2$ or Br$_2$ and subsequent halide abstraction with [Et$_3$Si(Tol)][B(C$_6$F$_5$)$_4$], generating monocationic [((C$_6$F$_5$)$_3$PCl][B(C$_6$F$_5$)$_4$]\textsuperscript{24} and [((C$_6$F$_5$)$_3$PBr][B(C$_6$F$_5$)$_4$]\textsuperscript{24} and dicationic [[(SIMes)Ph$_2$PCl][B(C$_6$F$_5$)$_4$]]$_2$.\textsuperscript{7} While the monocations were found to be less Lewis acidic than [((C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] from computations, [[(SIMes)Ph$_2$PCl][B(C$_6$F$_5$)$_4$]]$_2$, was found to be competitively reactive with its fluorinated alternative in the hydrodeoxygenation of ketones, with the exception of a sterically encumbered $\alpha$-substituted substrate. More recently, the Ingleson group, in collaboration with the Stephan group, synthesized apically CF$_3$-substituted EPCs [Ph$_2$PCF$_3$][B(C$_6$F$_5$)$_4$] and [Ph$_2$MePCF$_3$][OTf].\textsuperscript{25} These were found to be quite robust to moisture but considerably less Lewis acidic than [((C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$], evidenced by their poorer Lewis acidity as evaluated computationally and from Lewis acid reactivity. More recently, in collaboration with Alcarazo’s group, the Stephan group synthesized dicationic phosphonium salts bearing apical cyclopropenium or pyridinium substituents and found them to be moisture tolerant and to have greater Lewis acidity than [((C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] according to computations,\textsuperscript{26} owing to the addition of a strongly electron withdrawing cationic charge close to the phosphorus centre.
Figure 3.3  EPC derivatives with varying apical substituents.

In the majority of the abovementioned EPCs, the borate anion \([\text{B(C}_6\text{F}_5\text{)}_4]\) is used because its weakly coordinating nature allows for a fuller expression of the phosphonium cation’s Lewis acidity. However, several EPCs were also synthesized with the triflate \([\text{OTf}]^-\) or the tetrafluoroborate \([\text{BF}_4]^-\) anion by using TMSOTf or BF\(_3\) as a halide abstractor, respectively.\(^{17,19,25,26}\) In each case, the EPC’s solubility and Lewis acid reactivity were significantly negatively impacted by the more coordinating anion.

Taking note of the interplay between Lewis acidity and robustness evident from the diverse array of EPCs mentioned above, the incorporation of oxygen-containing yet electron-withdrawing apical groups onto the \((\text{C}_6\text{F}_5)_3\text{P}\) moiety is targeted to maximize both properties. The synthesis of EPCs bearing apical fluorine-substituted phenoxy groups is reported herein. Their moisture tolerances are established with respect to their fluorinated alternative \([(\text{C}_6\text{F}_5)_3\text{PF}]\text{[B(C}_6\text{F}_5\text{)}_4]\). Lewis acidities are explored computationally with fluoride ion affinity and the global electrophilicity index and experimentally with the Gutmann-Beckett test and by evaluation of their reactivities in Lewis acid catalysis.
3.2 Results and Discussion

3.2.1 Synthesis and Characterization

Apical substitutions on \((C_6F_5)_3P\) with fluorine-substituted phenoxy groups were formed from the fluorophosphonium salt \([((C_6F_5)_3PF][B(C_6F_5)_4]\), which was reacted in DCM with an excess of either Et₃SiOPh, Et₃SiO(4-FC₆H₄), or Et₃SiO(2,4-F₂C₆H₃). Upon workup, the phenoxyphosphonium salts \([((C_6F_5)_3P(OPh)][B(C_6F_5)_4]\) (3-1), \([((C_6F_5)_3P(O(4-FC₆H₄)])[B(C_6F_5)_4]\) (3-2), and \([((C_6F_5)_3P(0(2,4-F₂C₆H₃)][B(C_6F_5)_4]\) (3-3) were isolated as white powders in 67%, 94%, and 91% yield, respectively, with concomitant Et₃SiF formation. As the number of fluorines on the phenoxy group increased, the reactions required harsher conditions due to the stronger Si-O bond and the less nucleophilic oxygen centre. While the reaction with Et₃SiOPh required 2 h at ambient temperature, the reactions with Et₃SiO(4-FC₆H₄) required 24 h at 60 °C and Et₃SiO(2,4-F₂C₆H₃) required 48 h at 80 °C (Scheme 3.4). Unfortunately, more heavily fluorinated phenoxyphosphonium salts could not be synthesized by this method or by the reaction of \([((C_6F_5)_3PF][B(C_6F_5)_4]\) with Me₃SiOC₆F₅ or NaOC₆F₅. Finally, the chlorophosphonium salt \([((C_6F_5)_3PCl][B(C_6F_5)_4]\) was reacted with one equivalent of NaOC₆F₅ in DCM for 36 h at ambient temperature to produce, upon workup, \([((C_6F_5)_3P(OC₆F₅)][B(C_6F_5)_4]\) (3-4) as a white powder in 78% yield (Scheme 3.5).

![Scheme 3.4](image-url)  
**Scheme 3.4** Synthesis of phenoxyphosphonium salts 3-1 to 3-3.
Scheme 3.5 Synthesis of phenoxyphosphonium salt 3-4.

The formulations of 3-1 to 3-4 were confirmed by HRMS, elemental analysis, and multinuclear NMR spectroscopy. While $^1$H NMR spectra for 3-1 to 3-3 only showed peaks attributable to protons on the respective phenoxy ring, the $^{31}$P{ $^1$H} NMR spectra only showed a singlet peak at 36.8, 37.7, 42.7, and 47.8 ppm for 3-1 to 3-4, respectively (Figure 3.4, Table 3.1). It is interesting to note that the phosphorus signals shift downfield as the number of fluorines increases on the phenoxy group, consistent with a more deshielded phosphorus centre. Comparing to $[(C_6F_5)_3PF][B(C_6F_5)_4]$, which appears as a doublet centred at 67.8 ppm in $^{31}$P NMR, compounds 3-1 to 3-4 appear upfield by $\Delta \delta = 31.0$, 30.1, 25.1, and 20.0 ppm, respectively, indicating that $[(C_6F_5)_3PF][B(C_6F_5)_4]$ is more deshielded.

Figure 3.4 $^{31}$P{ $^1$H} NMR spectra of 3-1 to 3-4 and $[(C_6F_5)_3PF][B(C_6F_5)_4]$. 
Table 3.1  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>$^{31}$P{\textsuperscript{1}H} NMR signal (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-1</td>
<td>36.8</td>
</tr>
<tr>
<td>2</td>
<td>3-2</td>
<td>37.7</td>
</tr>
<tr>
<td>3</td>
<td>3-3</td>
<td>42.7</td>
</tr>
<tr>
<td>4</td>
<td>3-4</td>
<td>47.8</td>
</tr>
<tr>
<td>5</td>
<td>[(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]</td>
<td>67.8</td>
</tr>
</tbody>
</table>

For all four compounds, the $^{11}$B{\textsuperscript{1}H} NMR spectra show a sharp singlet at -16.7 ppm and the $^{19}$F{\textsuperscript{1}H} NMR spectra show characteristic ortho-, para-, and meta-C\textsubscript{6}F\textsubscript{5} signals at approximately -133.4, 164.0, and -168.0 ppm, respectively, with a meta-para gap of approximately 3.9 ppm. These data are consistent with C\textsubscript{6}F\textsubscript{5} groups on the [B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsuperscript{-} anion. The $^{19}$F{\textsuperscript{1}H} NMR spectra show another set of characteristic ortho-, para-, and meta-C\textsubscript{6}F\textsubscript{5} signals at approximately -125, -126, and -151 ppm, respectively, for 3-1 to 3-3, and at -125.3, -123.7, and -149.8 ppm, respectively, for 3-4, with a meta-para gaps of 24.4, 25.3, 25.2, and 26.1, respectively (Figure 3.5, Table 3.2). These data are consistent with C\textsubscript{6}F\textsubscript{5} groups on positively charged, four-coordinate P(V) centres. Interestingly, the size of this meta-para gap grows when the phenoxy group is substituted with more fluorine atoms, further implying that increased fluorine substitution deshields the phosphorus centre. Comparing these values to [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}], which has a meta-para gap of 27.7 ppm, meta-para gaps of compounds 3-1 to 3-4 are smaller by 3.3, 2.4, 2.5, and 1.6 ppm, respectively, again indicating that [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] is more deshielded. The $^{19}$F{\textsuperscript{1}H} NMR spectra also show the phenoxy fluorines of 3-2 at -109.5 ppm, of 3-3 at -104.5 and -124.4 ppm for para- and ortho-F\textsubscript{2}C\textsubscript{6}H\textsubscript{3}, respectively, and of 3-4 at -148.4, -152, and -155.0 ppm for para-, meta-, and ortho-C\textsubscript{6}F\textsubscript{5}, respectively. Finally, integrations match for a 1:1 ratio of phosphonium cation to borate anion.
Figure 3.5  $^{19}$F{¹H} NMR spectra of 3-1 to 3-4 and [(C₆F₅)₃PF][B(C₆F₅)₄].

Table 3.2  $^{19}$F{¹H} NMR signals of the ortho-, para-, and meta-C₆F₅ fluorines of 3-1 to 3-4 and [(C₆F₅)₃PF][B(C₆F₅)₄].

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>o-C₆F₅ signal (ppm)</th>
<th>p-C₆F₅ signal (ppm)</th>
<th>m-C₆F₅ signal (ppm)</th>
<th>meta-para gap (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-1</td>
<td>-125.5</td>
<td>-126.9</td>
<td>-151.3</td>
<td>24.4</td>
</tr>
<tr>
<td>2</td>
<td>3-2</td>
<td>-125.5</td>
<td>-126.3</td>
<td>-151.0</td>
<td>25.3</td>
</tr>
<tr>
<td>3</td>
<td>3-3</td>
<td>-126.1</td>
<td>-126.6</td>
<td>-151.3</td>
<td>25.2</td>
</tr>
<tr>
<td>4</td>
<td>3-4</td>
<td>-125.3</td>
<td>-123.7</td>
<td>-149.8</td>
<td>26.1</td>
</tr>
<tr>
<td>5</td>
<td>[(C₆F₅)₃PF][B(C₆F₅)₄]</td>
<td>-122.5</td>
<td>-125.3</td>
<td>-150.6</td>
<td>27.7</td>
</tr>
</tbody>
</table>

Single crystals suitable for X-ray diffraction were grown by layering DCM with cyclohexane. Diffraction studies revealed the solid-state structures of 3-1 to 3-4 (Figure 3.6, Figure 3.7), confirming their formulations and demonstrating that the P-O bond lengths, ranging 1.555(2), 1.552(3), and 1.563(3) Å for compounds 3-1 to 3-3, respectively, do not vary significantly as they are all within four standard uncertainty units of each other. Unfortunately, comparisons to 3-4 cannot be made as its solid-state structure displayed heavy disorder, the modelling of which revealed two P-O bond lengths of 1.581(3) and 1.55(1) Å (Table 3.3).

Table 3.3  P-O bond lengths in solid-state structures of 3-1 to 3-4.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>P-O bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-1</td>
<td>1.555(2)</td>
</tr>
<tr>
<td>2</td>
<td>3-2</td>
<td>1.552(3)</td>
</tr>
<tr>
<td>3</td>
<td>3-3</td>
<td>1.563(3)</td>
</tr>
<tr>
<td>4</td>
<td>3-4</td>
<td>1.581(3), 1.55(1)</td>
</tr>
</tbody>
</table>
Figure 3.6  ORTEP depictions of 3-1 (top) and 3-2 (bottom) showing thermal ellipsoids at 50% probability. Hydrogen atoms and counterion omitted. P: orange, O: red, C: black, F: spicy pink.
Figure 3.7 ORTEP depictions of 3-3 (top) and 3-4 (bottom) showing thermal ellipsoids at 50% probability. Hydrogen atoms, counterion, and minor disorder components omitted. P: orange, O: red, C: black, F: spicy pink.
3.2.2 Moisture Tolerance

Having synthesized this new family of phenoxyphosphonium salts, their moisture tolerance was assessed. The air stability of 3-1 to 3-4 and [(C₆F₅)₃PF][B(C₆F₅)₄] was tested by exposing DCM solutions of each salt in NMR tubes to atmosphere for given amounts of time, agitating the solutions, then monitoring them by $^{19}$F{¹H} NMR spectroscopy (Table 3.4). The onset of decomposition was first observed at 1.5 h, 1.5 h, 7 min, and 2 min for 3-1 to 3-4, respectively, with full decomposition observed within 24 h of air exposure in all cases. This trend is consistent with the stability of EPCs decreasing when the strength of electron withdrawing substituents is increased (vide supra). Comparing these to [(C₆F₅)₃PF][B(C₆F₅)₄], for which the onset of decomposition was first observed after 1 min (Table 3.4), compounds 3-1 to 3-4 can be said to be somewhat more robust, although not significantly so, especially in the cases of 3-3 and 3-4.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Onset of Decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-1</td>
<td>1.5 h</td>
</tr>
<tr>
<td>2</td>
<td>3-2</td>
<td>1.5 h</td>
</tr>
<tr>
<td>3</td>
<td>3-3</td>
<td>7 min</td>
</tr>
<tr>
<td>4</td>
<td>3-4</td>
<td>2 min</td>
</tr>
<tr>
<td>5</td>
<td>[(C₆F₅)₃PF][B(C₆F₅)₄]</td>
<td>1 min</td>
</tr>
</tbody>
</table>

Interestingly, 3-1 to 3-4 yield different decomposition products from air exposure than [(C₆F₅)₃PF][B(C₆F₅)₄], which was found to decompose to a mixture of (C₆F₅)₃PF₂ and (C₆F₅)₃PO. As exemplified by the air decomposition of 3-1 (Figure 3.8), the phosphorus-containing decomposition product’s C₆F₅ peaks do not agree with those of (C₆F₅)₃PO. In the case of these phenoxyphosphonium salts, a likely decomposition pathway involves formation of the hydroxyphosphonium salt [(C₆F₅)₃P(OH)][B(C₆F₅)₄] (3-5) with concomitant loss of the respective phenol. Further reaction with moisture would then prompt formation of (C₆F₅)₃PO and [H₃O][B(C₆F₅)₄] (Scheme 3.6).

Scheme 3.6  Moisture decomposition pathway for phenoxyphosphonium salts.
This proposal was investigated by the independent synthesis of 3-5 \textit{in situ} by reacting equimolar amounts of (C₆F₅)₃PO with Jutzi’s acid, [H(OEt₂)₂][B(C₆F₅)₄] in DCM for 10 min at ambient temperature (Scheme 3.7). There is much better agreement when comparing the $^{19}\text{F} \{ ^1\text{H} \}$ NMR spectrum of 3-5 to the decomposition product. Interestingly, when this synthesis was repeated with an extra half equivalent of (C₆F₅)₃PO, only one set of peaks was observed with signals shifted to be in between those of the (C₆F₅)₃PO and 3-5 (Figure 3.9). This demonstrates that an equilibrium exists between (C₆F₅)₃PO and 3-5, with 3-5 dominating in the air decomposition solutions.

Scheme 3.7 Synthesis of 3-5.
Figure 3.9 Stacked $^{19}$F NMR spectra of (top to bottom) $(C_6F_5)_3PO$, 3-5 with 0.5 equivalents of $(C_6F_5)_3PO$, 3-5, and the moisture decomposition product of 3-1.

3.2.3 Lewis Acidity Measurements

Having established the degrees of moisture tolerance of 3-1 to 3-4, their Lewis acid strength was evaluated. The Gutmann-Beckett method was applied, producing minimal $^{31}$P NMR shifts of $\Delta\delta = 0.3$, 1.4, 1.6, and 4.8 ppm for 3-1 to 3-4, respectively. Comparing these values to $[(C_6F_5)_3PF][B(C_6F_5)_4]$ and to $B(C_6F_5)_3$, which give shifts of $\Delta\delta = 40.4$ and 26.6 ppm, respectively, the phenoxyphosphonium salts seem very weakly Lewis acidic (Table 3.5). While, the Gutmann-Beckett method is an indirect measure of Lewis acidity, it is more specifically a measure of oxophilicity. This means that 3-1 to 3-4 could still exhibit interesting reactivity with other nucleophiles, despite their low GB values. Keeping this in mind and not being easily deterred, other measures of Lewis acidity were explored.

Table 3.5 Gutmann-Beckett Test Results.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>G-B test ($\Delta\delta$, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-1</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>3-2</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>3-3</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>3-4</td>
<td>4.8</td>
</tr>
<tr>
<td>5</td>
<td>$[(C_6F_5)_3PF][B(C_6F_5)_4]$</td>
<td>40.4</td>
</tr>
<tr>
<td>6</td>
<td>$B(C_6F_5)_3$</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Computational investigations of the cations of 3-1 to 3-4 were performed using Gaussian 09\textsuperscript{27} at the M11/Def2-TZVP\textsuperscript{28, 29} level of theory. The sites of Lewis acidity of 3-1 to 3-4 were first established. Evaluation of the natural atomic charges indicated that the majority of the cationic
charge was localized on the phosphorus atom (Figure 3.10(a)). Natural population analyses, performed using NBO 6.0,\textsuperscript{30} showed that each cation has a low-lying LUMO with a significant lobe oriented opposite the P-O bond (Figure 3.10(b)). Finally, the $f^\sigma (\rho)$ Fukui function was evaluated using MultiWFN 3.3.8.\textsuperscript{31} The $f^\sigma (\rho)$ Fukui function is a difference electron density map wherein the electron density of the LUMO is subtracted from the LUMO plus one electron. In effect, it shows the electron cloud for an additional electron, simulating a molecule after nucleophilic attack. When applied to the cations of 3-1 to 3-4, the $f^\sigma (\rho)$ Fukui function showed a significant lobe in each in the region oriented opposite the P-O bond (Figure 3.10(c)). Together, these data make a compelling argument that the reactive site on these cations is in fact the phosphorus centre. This is analogous to [(C$_6$F$_5$)$_3$PF]$^+$, wherein the phosphorus centre is the most positively charged atom and the Lewis acidic site is the $\sigma^*$ orbital located opposite the apical P-F bond, as characterized by the LUMO.\textsuperscript{1}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3_10.png}
\caption{Colour-coded natural atomic charges for the cation of 3-1 (left), surface contour plot (isovalue 0.03) of a low-lying LUMO of the cation of 3-1 (middle), and surface contour plot (isovalue 0.0015) of the $f^\sigma (\rho)$ Fukui function of the cation of 3-1 (right). For surface contour plots: P: orange, O: red, C: black, F: pink, H: white.}
\end{figure}

Calculations of the FIA for the cations of 3-1 to 3-4 found values of 703, 712, 718, and 743 kJ/mol, respectively. Consistent with strong electron withdrawing ability, the FIA value increases with increased number of fluorines on the phenoxy ring. The FIA of [(C$_6$F$_5$)$_3$PF]$^+$, calculated at the same level of theory for comparison, revealed a value of 777 kJ/mol and that the phenoxyphosphonium cations have lower values than [(C$_6$F$_5$)$_3$PF]$^+$ by 9.5, 8.4, 7.6, and 4.4% for the cations of 3-1 to 3-4, respectively. Encouragingly however, comparing to B(C$_6$F$_5$)$_3$ (440
kJ/mol), the cations of 3-1 to 3-4 have higher values by 37.4, 38.2, 38.7, and 40.8%, respectively (Table 3.6). Nevertheless, just as the Gutmann-Beckett test is a measure of a Lewis acid’s oxophilicity, FIA is a measure of a Lewis acid’s fluorophilicity and may not be an accurate measure of its Lewis acidity. Given this, an additional measure of Lewis acidity was sought.

The third measure that was chosen was the global electrophilicity index (GEI, $\omega$) of Parr, Szentpály, and Liu. Conceptually, this metric evaluates the capacity for a Lewis acid to receive electrons rather than its interaction with a specific base, as with Et$_3$PO in the Gutmann-Beckett method or with fluoride in the FIA. Consequently, GEI solely evaluates a molecule’s capacity to receive electrons, or its electrophilic power, and does not include any deformation energies associated with geometry changes on binding to a nucleophile. While this precludes directly relating GEI to Lewis acid reactivity, which necessitates coordination to a nucleophile, it does provide a general electrophilicity value. In the derivation of GEI, electrophilicity ($\omega$) is first related to chemical potential ($\chi$) and chemical hardness ($\eta$) according to Equation 3-1.$^2$

$$\omega = \frac{\chi^2}{2\eta}$$  
Eqn 3-1

Using the valence state parabola model, $\chi$ and $\eta$ are then related to ionization energy ($I$) and electron affinity ($A$) according to Equation 3-2.$^2$ Finally, as approximated in Koopmans’ Theorem, the energy of the HOMO was taken as a measure of $I$ and that of the LUMO was taken as a measure of $A$, as also indicated in Equation 3-3.$^3$

$$\omega = \frac{(I+A)^2}{2(I-A)}$$  
Eqn 3-2

$$\omega = \frac{(E_{\text{HOMO}}+E_{\text{LUMO}})^2}{2(E_{\text{HOMO}}-E_{\text{LUMO}})}$$  
Eqn 3-3

According to Equation 3-3, GEI can be calculated directly from the molecular orbital energies obtained from a molecule’s electronic structure calculation. This avoids the need to also calculate the energy of a Lewis acid/base adduct, as is the case with FIA, and is therefore significantly computationally cheaper.
In this first application of the Global Electrophilicity Index to main group Lewis acids, the GEI of the cations of 3-1 to 3-4 gave values of 4.21, 4.30, 4.32, and 4.48 eV, respectively. As expected, the GEI values increase with the number of fluorine atoms on the phenoxy ring. Comparing these to the GEI of [(C₆F₅)₃PF]⁺ (5.04 eV), the cations of 3-1 to 3-4 are less electrophilic by 16.5, 14.7, 14.3, and 11.1%, respectively. Encouragingly however, comparing to B(C₆F₅)₃ (2.10 eV), the cations of 3-1 to 3-4 are more electrophilic by 50.1, 51.2, 51.4, and 53.1%, respectively (Table 3.6). This observed trend mirrors that of FIA quite well. Indeed, when plotting a graph of GEI vs. FIA, very linear correlations can be drawn with an R² value of nearly 0.95 for the set of EPCs or >0.99 for the whole data set (Figure 3.11), which supports the suitability of GEI for this application.

Table 3.6  FIA and GEI values of the cations of 3-1 to 3-4, [(C₆F₅)₃PF]⁺, and B(C₆F₅)₃.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>FIA (kJ mol⁻¹)</th>
<th>GEI (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-1⁺</td>
<td>703</td>
<td>4.21</td>
</tr>
<tr>
<td>2</td>
<td>3-2⁺</td>
<td>712</td>
<td>4.30</td>
</tr>
<tr>
<td>3</td>
<td>3-3⁺</td>
<td>718</td>
<td>4.32</td>
</tr>
<tr>
<td>4</td>
<td>3-4⁺</td>
<td>743</td>
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</tr>
<tr>
<td>5</td>
<td>[(C₆F₅)₃PF]⁺</td>
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</tr>
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<td>6</td>
<td>B(C₆F₅)₃</td>
<td>440</td>
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</table>

Figure 3.11  Graph of FIA vs. GEI for the cations of 3-1 to 3-4, [(C₆F₅)₃PF]⁺, and B(C₆F₅)₃.
3.2.4 Lewis Acid Reactivity

Having established the Lewis acidic site and the magnitude of Lewis acidity for each of 3-1 to 3-4, their competency as Lewis acid catalysts was evaluated in several reactions (Scheme 3.8). In the dimerization of 1,1-diphenylethylene, reactions were carried out with 2 mol% catalyst in DCM for 2.5 hours at ambient temperature, resulting in 27, 50, 54, and 62% yields to the dimer 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene for 3-1 to 3-4, respectively. The hydrodefluorination of 1-fluoroadamantane with a stoichiometric amount of Et₃SiH and 5 mol% catalyst in DCM at ambient temperature produced >99% yield of adamantane with concomitant formation of Et₃SiF for 3-1, 3-2, and 3-4 after 30 min, while 3-3 produced 93% yield after 1 hour due to significant decomposition of 3-3 to (C₆F₅)₃PO and (C₆F₅)₃PF₂ during this reaction. In contrast, none of 3-1 to 3-4 were effective hydrodefluorination catalysts under similar reaction conditions when applied to 1-fluoropentane, a much more challenging substrate to activate. The hydrosilylation of α-methylstyrene with a stoichiometric amount of Et₃SiH and 2 mol% catalyst in DCM at 45 °C for 4 hours produced triethyl(2-phenylpropyl)silane in 23, 28, 33, and 52% yields for 3-1 to 3-4, respectively. The deoxygenation of benzophenone with two equivalents of triethylsilane and 1 mol% catalyst in DCM at ambient temperature for 2 h gave diphenylmethane in 31, 85, >99, and >99% yields for compounds 3-1 to 3-4, respectively. The dehydrocoupling of phenol with an equivalent of Et₃SiH and 2 mol% catalyst in DCM at 50 °C for 48 hours produced Et₃Si(OPh) in 25, 30, 33, and 97% yields with concomitant loss of H₂ for 3-1 to 3-4, respectively. However, [(C₆F₅)₃PF][B(C₆F₅)₄] outperforms 3-1 to 3-4 in each of these reactions, achieving 86% yield in the dimerization reaction in 30 min and 1.5 mol% catalyst at ambient temperature;¹⁰ >99% conversion in the hydrodefluorination of 1-fluoroadamantane and >99% yield in the hydrodefluorination of 1-fluoropentane in 1 and 2 hours, respectively, at ambient temperature with 1 mol% catalyst;¹ >99% yield in the hydrosilylation reaction with 1.5 mol% catalyst in 1 hour at ambient temperature;¹⁰ >99% yield in the deoxygenation reaction with 1 mol% catalyst in 5 hours at ambient temperature;⁷ and >99% yield in the dehydrocoupling reaction with 1.5 mol% catalyst in 2 hours at ambient temperature.⁹ This is unsurprising given that [(C₆F₅)₃PF][B(C₆F₅)₄] is established above to be a stronger Lewis acid than 3-1 to 3-4.
Scheme 3.8  Lewis acid reactions catalyzed by 3-1 to 3-4 and [(C₆F₅)₃PF][B(C₆F₅)₄] continued.
Encouragingly, analysis of the $^{19}\text{F}^{1}\text{H}$ NMR spectra after the reactions demonstrated that 3-1 to 3-4 completely survive the Friedel-Crafts dimerization of 1,1-diphenylethylene, the hydrosilylation of $\alpha$-methylstyrene, the deoxygenation of benzophenone, and the dehydrocoupling reactions, with the exception of 3-4 which shows slight decomposition to (C$_6$F$_5$)$_3$PO in the Friedel-Crafts dimerization and ketone deoxygenation reactions. In the hydrodefluorination reaction, 3-1 to 3-4 were seen to persist in the reaction mixtures post-catalysis, albeit with some decomposition to (C$_6$F$_5$)$_3$PO and (C$_6$F$_5$)$_3$PF$_2$ for 3-1 to 3-4. These catalyst fates are consistent with the phenoxyphosphonium salts acting as active Lewis acid catalysts and not as initiators.

3.3 Conclusion

A family of apically phenoxy-substituted phosphonium salts [(C$_6$F$_5$)$_3$P(OPh)][B(C$_6$F$_5$)$_4$] (3-1), [(C$_6$F$_5$)$_3$P(O(4-FC$_6$H$_4$))][B(C$_6$F$_5$)$_4$] (3-2), [(C$_6$F$_5$)$_3$P(O(2,4-F$_2$C$_6$H$_3$))][B(C$_6$F$_5$)$_4$] (3-3), and [(C$_6$F$_5$)$_3$P(OC$_6$F$_3$)][B(C$_6$F$_5$)$_4$] (3-4) were synthesized with varying amounts of fluorines substituted on the phenoxy ring. They were fully characterized by HRMS, elemental analysis, single crystal X-ray crystallography, and multinuclear NMR spectroscopy. $^{31}\text{P}^{1}\text{H}$ and $^{19}\text{F}^{1}\text{H}$ NMR spectroscopy demonstrated trends indicating that the phosphorus centre became less shielded with an increased number of fluorines substituted on the phenoxy ring. Their robustness was assessed, with the onset of decomposition from exposure to atmospheric moisture decreasing from 1.5 h to 2 min when going from compound 3-1 to 3-4. The phosphorus-containing moisture decomposition product was found to be an equilibrium mixture of (C$_6$F$_5$)$_3$PO and hydroxyphosphonium [(C$_6$F$_5$)$_3$P(OH)][B(C$_6$F$_5$)$_4$] (3-5), with 3-5 dominating in solution. The extent of Lewis acidity of 3-1 to 3-4 was experimentally evaluated by the Gutmann-Beckett method, which found only minimal shifts in the $^{31}\text{P}^{1}\text{H}$ NMR. The site of Lewis acidity was then investigated computationally by evaluating natural atomic charges, LUMOs, and the $f^*(\rho)$ Fukui function, which established that the site of Lewis acidity is the $\sigma^*$ orbital located opposite the P-O bond. Lewis acidity was then computationally evaluated using FIA and GEI, with the latter being applied for the first time in a main group Lewis acidic system. Values were found to increase when going from compound 3-1 to 3-4 and to linearly correlate to each other very well. Finally, 3-1 to 3-4 were applied to the Lewis acid catalyzed reactions of Friedel-Crafts dimerization, C-F hydrodefluorination, alkene hydrosilylation, ketone deoxygenation, and phenol dehydrocoupling reactions and were found to be competent catalysts, with observed reactivity increasing with
increased number of fluorines on the phenoxy substituent. In all, 3-1 to 3-4 were found to be slightly more robust but somewhat less Lewis acidic than [(C₆F₅)₃PF][B(C₆F₅)₄].

3.4 Experimental

3.4.1 General Experimental Methods

All manipulations were performed in a MB Unilab glove box produced by MBraun 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 (dichloromethane, tetrahydrofuran, cyclohexane, and n-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone under inert atmosphere. CD₂Cl₂ (Aldrich) was deoxygenated, distilled over CaH₂, then stored over 3 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. [(C₆H₅₋ₓFₓ)OSiEt₃] (x = 0, 1, 2, 5), [(C₆F₅)₃PF][B(C₆F₅)₄], [(C₆F₅)₃PCl][B(C₆F₅)₄], [H(OEt)₂][B(C₆F₅)₄], (C₆F₅)₃PO, and NaOC₆F₅ were prepared according to literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz or a Varian Mercury-300 MHz spectrometer. ¹H, ¹³C{¹H}, ³¹P{¹H}, ¹⁹F, and ¹¹B{¹H} NMR chemical shifts (δ/ppm) are referenced to Me₄Si, Me₂Si, H₃PO₄, CFCl₃, and BF₃•OEt₂, respectively. Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI), a GCT Premier (EI), 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. In the case of 3-3, repeated attempts to obtain satisfactory C analyses gave consistently low values. This was attributable to incomplete combustion and the formation of boron carbide.

3.4.2 X-Ray Diffraction Studies

Single crystals were coated with Paratone oil, mounted on a CryoLoop, and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved and
refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

### Table 3.7 X-ray table for 3-1 and 3-2.

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<td>C₄₈H₄BF₃6OP</td>
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<td>Triclinic</td>
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<td>P1̅</td>
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<td>Mo Kα</td>
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Table 3.8 X-ray table for 3-3 and 3-4.

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<td>(B(C₆F₅)₄)</td>
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<td>• (CH₂Cl₂)</td>
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3.4.3 Synthesis of Catalysts

3-1 \([(\text{C}_6\text{F}_5)_3\text{P(OPh)}][\text{B(\text{C}_6\text{F}_5)_4}]\)

To a solution of \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B(\text{C}_6\text{F}_5)_4}]\) (74 mg, 0.06 mmol) in DCM (5 mL) was added triethyl(phenoxysilane) (PhOSiEt₃, 63 mg, 0.3 mmol). The reaction mixture was left for 2 h at room temperature, which yielded a tan coloured solution. The solvent was removed in vacuo yielding a tan coloured solid which was then washed with n-pentane (3 x 3 mL). The solid was then re-dissolved in DCM (3 mL), layered with cyclohexane (12 mL), and left overnight to recrystallize. After decanting the supernatant, the solid was dried in vacuo to afford a white powder (49 mg, 67% yield). ¹H NMR (500 MHz, CD₂Cl₂): \(\delta = 7.01 – 7.07\) (m, 2H; m-Ph), 7.46 – 7.50 (m, 3H; o-Ph and p-Ph) ppm. ¹¹B¹H NMR (192 Hz, CD₂Cl₂): \(\delta = 1.67\) ppm (s). ¹⁹F NMR (564 MHz, CD₂Cl₂): \(\delta = –125.5\) (t, \(3 J_{\text{FF}} = 14\) Hz, 6F; P(o-\text{C}_6\text{F}_5)_3), -126.9 (sept, \(3 J_{\text{FF}} = 10\) Hz, 3F; P(p-\text{C}_6\text{F}_5)_3), -133.4 (s(br), 8F; B(o-\text{C}_6\text{F}_5)_4), -151.2 – -151.4 (m, 6F; P(m-\text{C}_6\text{F}_5)_3), -164.0 (t, \(3 J_{\text{FF}} = 20\) Hz, 4F; B(p-\text{C}_6\text{F}_5)_4), -167.8 – -168.0 (m(br), 8F; B(m-\text{C}_6\text{F}_5)_4) ppm. ³¹P¹H NMR (243 MHz, CD₂Cl₂): \(\delta = 36.8\) (s) ppm. ¹³C¹H NMR (125 MHz, CD₂Cl₂): \(\delta = 119.2\) (d, \(3 J_{\text{FC}} = 5\) Hz, 2C; o-Ph), 130.2 (d, \(4 J_{\text{FC}} = 2\) Hz, 2C; p-Ph), 132.4 (d, \(4 J_{\text{FC}} = 2\) Hz, 2C; m-Ph), 136.2 (d(br), \(1 J_{\text{FC}} = 345\) Hz, 8C; B(o-\text{C}_6\text{F}_5)_3), 138.1 (d(br), \(1 J_{\text{FC}} = 345\) Hz, 4C; B(p-\text{C}_6\text{F}_5)_4), 139.0 (d(br), \(1 J_{\text{FC}} = 380\) Hz, 6C; P(o-\text{C}_6\text{F}_5)_3), 148.1 (d(br), \(1 J_{\text{FC}} = 345\) Hz, 8C; B(m-\text{C}_6\text{F}_5)_4), 148.2 (d(br), \(1 J_{\text{FC}} = 380\) Hz, 6C; P(p-\text{C}_6\text{F}_5)_3), 149.6 (d(br), \(1 J_{\text{FC}} = 380\) Hz, 3C; P(p-\text{C}_6\text{F}_5)_3) ppm, resonance for ipso-carbons was not observed. HRMS (EI-TOF+): m/z 624.9815 (calcd for \([(\text{C}_6\text{F}_5)_3\text{P(OPh)}]^+ : 624.9839). EA: calcd (%) for C₄₈H₅₅BF₃₅OP: C, 44.20; H, 0.39; found: C, 42.86; H, 0.38.

3-2 \([(\text{C}_6\text{F}_5)_3\text{P(O(4-FC₆H₄)₃})][\text{B(\text{C}_6\text{F}_5)_4}]\)

To a solution of \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B(\text{C}_6\text{F}_5)_4}]\) (74 mg, 0.06 mmol) in DCM (5 mL) was added triethyl(4-fluorophenoxy)silane Et₃SiO(4-FC₆H₄), 68 mg, 0.3 mmol). The reaction mixture was heated to 60°C for 24 h, which yielded a tan coloured solution. The solvent was removed in vacuo yielding a tan coloured solid which was then washed with n-pentane (3 x 3 mL). The solid was then re-dissolved in DCM (3 mL), layered with cyclohexane (12 mL), and left overnight to recrystallize.
After decanting the supernatant, the solid was dried in vacuo to afford a white powder (69 mg, 94% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.02 – 7.08 (m, 2H; o-C₆H₄F), 7.15 – 7.21 (m, 2H; m-C₆H₄F) ppm. ¹¹B[¹H] NMR (160 MHz, CD₂Cl₂): δ = -16.7 (s) ppm. ¹⁹F NMR (470 MHz, CD₂Cl₂): δ = -109.5 – 109.5 (m, 1F; p-C₆H₄F), -125.5 (t, 3JFF = 14 Hz, 6F; P(o-C₆F₅)), -126.3 (sept, 3JFF = 10 Hz, 3F; P(p-C₆F₅)), -133.4 (s(br), 8F; B(o-C₆F₅)), -150.9 – -151.1 (m, 6F; P(m-C₆F₅)), -163.9 (t, 3JFF = 20 Hz, 4F; B(p-C₆F₅)), -167.8 – -168.0 (m(br), 8F; B(m-C₆F₅)) ppm. ³¹P[¹H] NMR (202 MHz, CD₂Cl₂): δ = 37.7 (s) ppm. ¹³C[¹H] NMR (125 MHz, CD₂Cl₂): δ = 119.3 (d, 3JFC = 25 Hz, 2C; m-C₆H₄F), 121.1 (s(br), 2C; o-C₆H₄F), 136.2 (d(br), 1JFC = 345 Hz, 8C; B(o-C₆F₅)), 148.0 (d(br), 1JFC = 345 Hz, 8C; B(m-C₆F₅)), 148.3 (d(br), 1JFC = 380 Hz, 6C; P(o-C₆F₅)), 149.7 (d(br), 1JFC = 345 Hz, 3C; P(p-C₆F₅)) ppm, resonances for ipso-carbons and p-F₆C₆H₄ carbon were not observed. HRMS (EI-TOF+): m/z 642.9744 (calcd. for [(C₆F₅)₃P(O(4-F₆C₆H₄))]⁺ : 642.9721). HRMS (TOF- MS ESI+) of decomposition product: m/z 54895255 (calcd for [(C₆F₅)₃P(OH)]⁺ : 54895156). EA: calcd (%) for C₄₅H₃BF₅O: C, 43.60; H, 0.30; found: C, 41.58; H, 0.26.

3-3 [(C₆F₅)₃P(O(2,4-F₂C₆H₃))][B(C₆F₅)₄]

To a solution of [(C₆F₅)₃PF][B(C₆F₅)₄] (74 mg, 0.06 mmol) in DCM (8 mL) was added triethyl(2,4-difluorophenoxy)silane Et₃SiO(2,4-F₂C₆H₃), 73 mg, 0.3 mmol). The reaction mixture was transferred into a 50 mL Schlenk flask, attached to a Schlenk line, and heated to 60 °C for 48 h, yielding a tan coloured solution. The reaction vessel was returned dry box and the solution transferred to a 20 mL vial. The solvent was removed in vacuo and the solid residue was washed with n-pentane (3 x 3 mL). The solid was then re-dissolved in DCM (3 mL), layered with cyclohexane (12 mL), and left overnight to recrystallize. After decanting the supernatant, the solid was dried in vacuo to afford a white powder (72 mg, 91% yield). ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.003 – 7.12 (m, 2H; 3-C₆F₂H₃), 7.37 (dddd, 3JFH = 9 Hz, 3JHH = 9 Hz, 4JHH = 5 Hz, 5JFH = 2 Hz; 1H; 6-C₆F₂H₃) ppm. ¹¹B[¹H] NMR (160 MHz, CD₂Cl₂): δ = -16.7 (s) ppm. ¹⁹F NMR (470 MHz, CD₂Cl₂): δ = -104.5 – -104.6 (m, 1F; p-C₆F₂H₃), -124.4 (s(br), 1F; o-C₆F₂H₃), -126.1 (t, 3JFF = 14 Hz, 6F; P(o-C₆F₅)), -126.5 – -126.7 (m, 3F; P(p-C₆F₅)), -133.4 (s(br), 8F; B(o-C₆F₅)), -151.2 – -151.4 (m, 6F; P(m-C₆F₅)), -164.0 (t, 3JFF = 20 Hz, 4F; B(p-C₆F₅)), -168.0 (t(br), 3JFF = 18 Hz,
8 F; B(m-C₆F₅)₄ ppm. ³¹P[¹H] NMR (202 MHz, CD₂Cl₂): δ = 42.7 (s) ppm. ¹³C[¹H] NMR (125 MHz, CD₂Cl₂): δ = 107.2 (t, J.FC = 25 Hz, 1C; 3-C₆F₂H₃), 115.2 (d, J.FC = 25 Hz, 1C; 5-C₆F₂H₃), 123.4 (s(br), 1C; 6-C₆F₂H₃), 136.2 (d(br), J.FC = 345 Hz, 8C; B(o-C₆F₅)₄), 138.0 (d(br), J.FC = 345 Hz, 4C; B(p-C₆F₅)₄), 139.1 (d(br), J.FC = 380 Hz, 6C; P(o-C₆F₅)₃), 148.0 (d(br), J.FC = 345 Hz, 8C; B(m-C₆F₅)₄), 148.2 (d(br), J.FC = 345 Hz, 6C; P(m-C₆F₅)₃), 149.7 (d(br), J.FC = 345 Hz, 3C; P(p-C₆F₅)₃) ppm, resonances for ipso-carbons, p-C₆F₂H₃, and o-C₆F₂H₃ were not observed. HRMS (EI-TOF+): m/z 660.9650 (calcd for [(C₆F₅)₃P(O(2,4-F₂C₆H₃))]⁺: 660.9625). EA: calcd (%) for C₄₈H₃BF₃OP: C, 43.02; H, 0.23; found: C, 42.13; H, 0.25.

3-4

[(C₆F₅)₃P(OC₆F₅)] [B(C₆F₅)₄]

To a solution of [(C₆F₅)₃PCl][B(C₆F₅)₄] (580 mg, 0.47 mmol) in DCM (20 mL) was added sodium pentafluorophenoxide (NaOC₆F₅, 144 mg, 0.7 mmol). The reaction mixture was stirred for 36 h at room temperature, which yielded a white powder and a brown/orange supernatant which was decanted. The powder was washed with a solution of 4:6 DCM: n-pentane (3 x 10 mL) and the washing were added to the supernatant, which was then dried in vacuo, washed with n-pentane (3 x 3 mL), and re-dried in vacuo to afford a white powder (506 mg, 78% yield). ¹¹B[¹H] NMR (160 MHz, CD₂Cl₂): δ = -16.7 (s) ppm. ¹⁹F NMR (470 MHz, CD₂Cl₂): δ = -123.7 (sept, J.FF = 10 Hz, 3F; P(p-C₆F₅)₃), -125.3 (t, J.FF = 14 Hz, 6F; P(o-C₆F₅)₃), -133.3 (s(br), 8F; B(o-C₆F₅)₄), -148.4 (t, J.FF = 22 Hz, J.FF = 4 Hz, 1F; O(p-C₆F₅), -149.7 – -149.8 (m, 6F; P(m-C₆F₅)₃), -152.5 – -152.6 (m, 2F; O(m-C₆F₅), -155.0 – -155.1 (m, 2F; O(o-C₆F₅), -163.9 (t, J.FF = 20 Hz, 4F; B(p-C₆F₅)₄), -167.8 – -168.0 (m(br), 8F; B(m-C₆F₅)₄) ppm. ³¹P[¹H] NMR (202 MHz, CD₂Cl₂): δ = 47.8 (s) ppm. Poor solubility precluded the acquisition of satisfactory ¹³C NMR and ¹⁹F - ¹³C HSQC. HRMS (EI-TOF+): m/z 714.9340 (calcd for [(C₆F₅)₃P(OC₆F₅)]⁺: 714.9367). EA: calcd (%) for C₄₈BF₄₀OP•CH₂Cl₂: C, 39.79; H, 0.147; found: C, 39.39; H, 0.19.
To a solution of [H(OEt)$_2$][B(C$_6$F$_5$)$_4$] (15.4 mg, 0.019 mmol) in DCM (0.6 mL) was added tris(pentafluorophenyl)phosphine oxide ([(C$_6$F$_5$)$_3$PO, 10 mg, 0.019 mmol). The reaction mixture was left at ambient temperature for 10 min. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta = 1.25$ (t, $^3J_{CH} = 7$ Hz, 6H; Et$_2$O-CH$_3$), 3.70 (q, $^3J_{CH} = 7$ Hz, 4H; Et$_2$O-CH$_2$), 6.23 (s(br), 1H; P-OH) ppm. $^{11}$B{$^1$H} NMR (128 MHz, CD$_2$Cl$_2$): $\delta = -16.4$ (s) ppm. $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$): $\delta = -131.7$ – -132.0 (m(br), 6F; P(o-C$_6$F$_5$)$_3$), -133.3 (s(br), 8F; B(o-C$_6$F$_5$)$_4$), -139.6 – -140.0 (m, 3F; P(p-C$_6$F$_5$)$_3$), -157.0 – -157.3 (m, 6F; P(m-C$_6$F$_5$)$_3$), -163.9 (t, $^3J_{FF} = 20$ Hz, 4F; B(p-C$_6$F$_5$)$_4$), -167.7 (t(br), $^1J_{FC} = 20$ Hz, 8F; B(m-C$_6$F$_5$)$_4$) ppm. $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$): $\delta = -3.2$ ppm (s(br)). $^{13}$C{$^1$H} NMR (125 MHz, CD$_2$Cl$_2$): $\delta = 14.5$ (s, 2C; Et$_2$O-CH$_3$), 67.6 (s, 2C; Et$_2$O-CH$_2$), 136.2 (d(br), $^1J_{FC} = 240$ Hz, 8C; B(o-C$_6$F$_5$)$_4$), 138.2 (d(br), $^1J_{FC} = 240$ Hz, 4C; B(p-C$_6$F$_5$)$_4$), 147.0 (d(br), $^1J_{FC} = 260$ Hz, 6C; P(o-C$_6$F$_5$)$_3$), 148.1 (d(br), $^1J_{FC} = 240$ Hz, 8C; B(m-C$_6$F$_5$)$_4$), 146.0 (d(br), $^1J_{FC} = 260$ Hz, 6C; P(p-C$_6$F$_5$)$_3$), 138.3 (d(br), $^1J_{FC} = 260$ Hz, 3C; P(p-C$_6$F$_5$)$_3$) ppm, resonance for ipso-carbons was not observed. HRMS (ESI+): m/z 548.95160 (calcd for [(C$_6$F$_5$)$_3$P(OH)]$^+$: 548.95255).

3.4.4 Air Stability Test

In a 20 mL vial, a solution of the phosphonium catalyst (0.02 mmol) was prepared in 0.6 mL DCM. The solution was transferred to an NMR tube and exposed to atmospheric moisture for specific amounts of time. The decomposition was monitored by $^{19}$F NMR spectroscopy.

3.4.5 Gutmann-Beckett Method

In a 20 mL vial, a solution of the phosphonium catalyst (0.02 mmol) was prepared in 0.6 mL DCM and added to a separate vial containing Et$_3$PO (0.02 mmol). The solution was transferred to an NMR tube and monitored by $^{31}$P and $^{19}$F NMR spectroscopy after 1 h at ambient temperature (unless otherwise specified).
3.4.6 Lewis Acid Catalysis

3.4.6.1 Dimerization of 1,1-diphenylethylene

In a 20 mL vial, a solution of the phosphonium catalyst (2 mol%) was prepared in 1 mL DCM. 1,1-diphenylethylene (0.2 mmol) was added at ambient temperature and the reaction mixture was left to stir for 2.5 h. The solution was then dried in vacuo and re-dissolved in 0.6 mL CDCl₃ affording a pale green solution. Conversions were determined by ¹H NMR spectroscopy. Mesitylene was added as an internal standard. Product ¹H NMR spectra are consistent with reference spectra.³⁵

3.4.6.2 Hydrodefluorination of 1-fluoroadamantane

In a 20 mL vial, a solution of the phosphonium catalyst (5 mol%) was prepared in 0.6 mL DCM. Triethylsilane (Et₃SiH, 0.04 mmol) was added at ambient temperature, the reaction was briefly stirred, and then 1-fluoroadamantane was added (0.04 mmol). The reaction mixture was transferred to an NMR tube and left at ambient temperature for 30 min or 1 h, before being monitored by ¹⁹F NMR spectroscopy. Conversions were determined from the proportion of Si-F bonds formed relative to a fluorobenzene internal standard. Product ¹H NMR spectra are consistent with reference spectra.¹

3.4.6.3 Hydrosilylation of α-methylstyrene

In a 20 mL vial, a solution of the phosphonium catalyst (2 mol%) was prepared in 0.6 mL DCM. Triethylsilane (Et₃SiH, 0.05 mmol) was added at ambient temperature, the reaction mixture was briefly stirred, and then α-methylstyrene (0.05 mmol) was added. The mixture was transferred to an NMR tube and heated at 45 °C for 4 h. The solution was then dried in vacuo and re-dissolved in 0.6 mL CDCl₃ affording a colourless solution. Conversions were determined by ¹H NMR spectroscopy. Mesitylene was added as an internal standard. Product ¹H NMR spectra are consistent with reference spectra.³⁶

3.4.6.4 Dehydrocoupling of phenol with Et₃SiH

In a 20 mL vial, a solution of the phosphonium catalyst (2 mol%) was prepared in 0.6 mL DCM. Triethylsilane (Et₃SiH, 0.05 mmol) was added at ambient temperature, the reaction mixture was briefly stirred, and then added to a vial containing phenol (0.05 mmol). The mixture was
transferred to an NMR tube and heated at 50 °C for 48 h. The solution was then dried in vacuo and re-dissolved in 0.6 mL CDCl₃ affording a colourless solution. Conversions were determined by ¹H NMR spectroscopy. Mesitylene was added as an internal standard. Product ¹H NMR spectra are consistent with reference spectra.³⁷

3.4.6.5 Hydrodeoxygenation of benzophenone

In a 20 mL vial, a solution of the phosphonium catalyst (1 mol%) was prepared in 0.6 mL DCM. Triethylsilane (Et₃SiH, 0.04 mmol) was added at ambient temperature, the reaction was briefly stirred, and then the solution was added to a vial containing benzophenone (0.02 mmol). The reaction mixture was left to stir at ambient temperature for 2 h. The solution was then dried in vacuo and re-dissolved in 0.6 mL CDCl₃ affording a colourless solution. Conversions were determined by ¹H NMR spectroscopy. Mesitylene was added as an internal standard. Product ¹H NMR spectra are consistent with reference spectra.³⁸

3.4.7 Computational Details

Electronic structure calculations, including geometry optimization and frequency calculations, were performed with the Gaussian 09²⁷ package using the range-separated hybrid functional M11 and the polarized triple-zeta basis set Def2-TZVP.²⁸,²⁹ Natural bond orbital and natural population analyses were performed on optimized structures using NBO 6.0.³⁰ The Fukui function was evaluated using MultiWFN 3.3.8.³¹ X-ray coordinates were used as the starting geometry for geometry optimizations. The absence of any imaginary frequency with an absolute magnitude greater than 10 cm⁻¹ confirmed that each optimized structure was indeed located at a minimum on its potential energy hypersurface. The electrophilicity index electrophilicity (ω) is first related to chemical potential (χ) and chemical hardness (η) as in Equation 3-4.²

\[ \omega = \frac{\chi^2}{2\eta} \]  
Eqn 3-4

Using the valence state parabola model, chemical potential and chemical hardness are then related to ionization energy (I) and electron affinity (A) according to Equation 3-5.² Finally, as approximated in Koopmans’ Theorem, the energy of the HOMO was taken as a measure of I and that of the LUMO was taken as a measure of A, as also indicated in Equation 3-6.³
\[ \omega = \frac{(I+A)^2}{2(I-A)} \]  
Eqn 3-5

\[ \omega = \frac{(E_{\text{HOMO}}+E_{\text{LUMO}})^2}{2(E_{\text{HOMO}}-E_{\text{LUMO}})} \]  
Eqn 3-6

### 3.5 References


Section 3.2 - Catalytic Double Hydroarylation of Alkynes to 9,9-disubstituted 9,10-dihydroacridine Derivatives by an Electrophilic Phenoxyphosphonium Dication

3.6 Brief Introduction to Hydroarylation

The alkylation of arenes was first reported by Friedel and Crafts in 1887 when they reacted an alkyl halide with aluminum trichloride (AlCl₃) and benzene to yield the alkylated arene and HCl byproduct (Scheme 3.9).¹,² Shortly after the initial report, several other species were found to be competent catalysts in this reaction, including the Lewis acids BF₃, BeCl₂, TiCl₄, SbCl₅, and SnCl₄ as well as Brønsted acids HF•SbF₅ and HSO₃F•SbF₅.³ Despite being catalytic in Lewis or Brønsted acid, these reactions required a stoichiometric or superstoichiometric amount of catalyst due to catalyst poisoning throughout the reaction. This high catalyst loading, the toxicity of alkyl halides, and the acidic salt byproducts are not ideal for large-scale synthesis as significant costs are incurred in buying, handling, and properly disposing of chemicals. Nevertheless, Friedel and Crafts opened the door for innovation on the Friedel-Crafts reaction (F-C) that remains relevant today.

\[
\begin{align*}
R-\text{Cl} & \quad + \quad \text{AlCl}_3 & \quad \rightleftharpoons & \quad \begin{array}{c}
R-\text{Cl} \\
\text{AlCl}_3
\end{array} \\
\text{H} & \quad + \quad \text{R-CH}_2 & \quad \rightleftharpoons & \quad \text{H} \\
\text{C}_2\text{H}_4 & \quad \rightleftharpoons & \quad \begin{array}{c}
\text{R-CH}_2 \\
\text{AlCl}_4
\end{array}
\end{align*}
\]

**Scheme 3.9** Arene alkylation reaction performed by Friedel and Crafts.

Significant efforts have been made to mitigate the environmental and economic costs of the F-C reaction. In 1986, Uemura’s group reported the first alkylation of arenes with benzyl alcohols catalyzed by TeCl₄ and found that reducing the catalyst loading to substoichiometric amounts gave improved yields (Scheme 3.10).⁴ Although TeCl₄ acts to produce the benzyl chloride as a reaction intermediate, the use of alcohols instead of halides significantly reduces the toxicity associated with F-C reactions as the alkylating agent is significantly less toxic and the reaction’s byproduct is water. For example, benzyl chloride, a useful benzylating reagent in F-C reactions, is extremely irritating, carcinogenic, has an oral LD₅₀ in rats of 560 mg/kg,⁵ and was stated to be intolerable
from a single breath containing 79 ppm.\textsuperscript{6} By contrast, while benzyl alcohol is an irritant, is not a known carcinogen, and has an oral LD50 in rats of 1,620 mg/kg.\textsuperscript{7} While this initial F-C reaction generated an alkyl halide \textit{in situ}, further developments avoid alkyl halides entirely. The use of F-C catalysts that use benzyl alcohols was first expanded to Sc(OTf)\textsubscript{3} by Fukuzawa\textsuperscript{8, 9} and was subsequently extended to include catalysts based on late transition metals,\textsuperscript{10-15} lanthanide triflates,\textsuperscript{16-19} strong Brønsted acids,\textsuperscript{16, 20-22} and main-group Lewis acids.\textsuperscript{17, 23, 24}

\begin{equation}
\begin{array}{c}
\text{PhOH} \quad \text{TeCl}_4 \\
\text{TeCl}_3(\text{OH}) \\
\text{PhCl} \quad \text{TeCl}_4-n(\text{OH})_n
\end{array}
\end{equation}

\textbf{Scheme 3.10} First example of a Friedel-Crafts reaction with 1-phenylethanol.

The F-C reaction took another leap forward in 1997 when Shimizu’s group published the F-C alkylation of arenes with olefins including styrenes and cyclohexenes as alkylating agents (Scheme 3.11)\textsuperscript{15} and subsequently in 2000 when Fujiwara’s group published the first transition-metal catalyzed alkylation of arenes using alkynes as the alkylating agent (Scheme 3.12, top).\textsuperscript{25-27} By having an alkene or alkyne as the alkylating agent, these reactions can be perfectly atom economical as no byproducts are formed.\textsuperscript{28} Instead, the arene ring’s proton transfers to the double or triple bond to give an hydroarylation product (Scheme 3.12, bottom). The quick adoption of alkenes as F-C alkylating reagents has led to the application of catalysts based on transition metals,\textsuperscript{14, 29-34} Brønsted acids,\textsuperscript{33, 35} and main-group Lewis acids.\textsuperscript{36-39} However, fewer catalysts have been applied to alkyne hydroarylation, with late transition metals being particularly effective.\textsuperscript{40-43}

\begin{equation}
\begin{array}{c}
\text{PhCH=CH}_2 + \text{PhO} \\
10 \text{ mol\% Mo(CO)}_6 \\
\text{PhCH(Ph)}_2
\end{array}
\end{equation}

\textbf{Scheme 3.11} First example of a Friedel-Crafts reaction with styrene.
Scheme 3.12 First example of a Friedel-Crafts reaction with alkyne (top) and mechanism of acid catalyzed hydroarylation reactions (bottom).

3.7 Hydroarylation with Electrophilic Phosphonium Salts

Shortly after publishing the family of phenoxyphosphonium salts 3-1 to 3-4, the Stephan group applied the approach of replacing the apical fluoride with an apical phenoxy group towards a dicationic phosphonium salt. In an analogous synthesis, the dicationic fluorophosphonium salt [(2-(N-Mepy))Ph2PF][B(C6F5)4]2 was reacted with 1 equivalent of TMSOPh in DCM for 24 hours at 45 °C (Scheme 3.13). Upon workup, the dicationic phenoxyphosphonium salt [(2-(N-Mepy))Ph2P(OPh)][B(C6F5)4]2 was isolated as a yellow solid in 96% yield. In contrast to the monocationic phenoxyphosphonium salts 3-1 to 3-4, which were found to be only somewhat more robust than their fluorinated analogue, [(2-(N-Mepy))Ph2P(OPh)][B(C6F5)4]2 is considerably moisture tolerant, showing no decomposition after 7 days of air exposure in the solid state. Additionally, computationally determined metrics of Lewis acidity found that [(2-(N-Mepy))Ph2P(OPh)][B(C6F5)4]2 (FIA = 920 kJ/mol, GEI = 6.12 eV) is more Lewis acidic when compared to 3-1 (FIA = 718 kJ/mol, GEI = 2.98 eV) and to B(C6F5)4 (FIA = 452 kJ/mol, GEI = 1.41 eV). Indeed, [(2-(N-Mepy))Ph2P(OPh)][B(C6F5)4]2 was found to be an active Lewis acid catalyst, promoting the F-C dimerization of 1,1-diphenylethylene in 33% yield after 2.5 hours at ambient temperature with 2 mol% catalyst, the hydrodefluorination of 1-fluoropentane with Et3SiH and 5 mol% catalyst in 31% conversion after 1 hour at ambient temperature, the hydrosilylation of α-methylstyrene with Et3SiH and 2 mol% catalyst in 87% yield after 4 hours at 45 °C, the dehydrocoupling of PhOH with Et3SiH and 2 mol% catalyst in >99% yield after 48
hours at 50 °C, and the deoxygenation of benzophenone with Et$_3$SiH and 1 mol% catalyst in >99% yield after 2 hours at ambient temperature.$^{45}$

![Scheme 3.13](image)

**Scheme 3.13** Synthesis of [(2-(N-Mepy))Ph$_2$P(OPh)][B(C$_6$F$_5$)$_4$]$_2$.

Having made a new family of EPCs, new Lewis acid catalyzed reactions were sought in which to apply them. It was noted that the Stephan group has published hydroarylations of alkenes with aryl-substituted amines and with aromatic N-, O-, and S-containing heterocycles catalyzed by [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$]$^{46}$ (Scheme 3.14, top) as well as the hydroamination (addition across N-H bond) of alkynes with aryl-substituted amines catalyzed by B(C$_6$F$_5$)$_3$$^{47}$ (Scheme 3.14, bottom). Although the ability for F-C alkylations of anilines to undergo hydroarylation as well as hydroamination is known,$^{34, 48}$ the difference in products between these two strong Lewis acid catalysts is noteworthy. While biasing the reaction towards hydroarylation to selectively generate the *ortho*-arylated product of anilines with styrenes has been achieved with the Lewis acid TiCl$_4$$^{49}$ and with Brønsted acids [PhNH$_3$][B(C$_6$F$_5$)$_4$]$^{35}$ and TfOH,$^{50}$ it is unclear which reaction would be favoured by EPCs and the intriguing possibility exists for divergent chemistry between EPCs and B(C$_6$F$_5$)$_3$ in their reactivity towards alkynes. In this section, the hydroarylation reaction of alkynes with arylamines is explored using [(2-(N-Mepy))Ph$_2$P(OPh)][B(C$_6$F$_5$)$_4$]$_2$ as a catalyst.

![Scheme 3.14](image)

**Scheme 3.14** Hydroarylation reaction catalyzed by [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] (top) and hydroamination reaction catalyzed by B(C$_6$F$_5$)$_3$ (bottom).
3.8 Results and Discussion

3.8.1 Establishing Hydroarylation Reaction

To assess the viability of EPCs in the F-C hydroarylation of alkynes with arylamines, an initial investigation was performed with [(C₆F₅)₃PF][B(C₆F₅)₄]. Reacting (4-Tol)₂NH with (4-Tol)C≡CH and 5 mol% [(C₆F₅)₃PF][B(C₆F₅)₄] in DCM at ambient temperature overnight gave a fairly clean mixture. Analysis of the product’s mass by gas chromatography-mass spectrometry (GC-MS) was consistent for a 1:1 ratio of starting materials. Given the recognized ability for Lewis acids to undergo hydroarylation and hydroamination chemistry, a number of products were predicted (Scheme 3.15).

Product isolation was performed by flash column chromatography on silica gel using n-pentane with 0-5% ethyl acetate. Analysis of the purified product’s ¹H NMR spectrum (Figure 3.12) showed a broad singlet at 5.46 ppm corresponding to a NH proton, indicating that no hydroamination had occurred. However, this spectrum did not agree with any of the predicted hydroarylation products either as it showed three distinct methyl peaks, one of which represented two degenerate methyl environments, and had five aromatic protons each integrating to 2 hydrogens. Using this information, the GC-MS result, and 2D NMR techniques, the product’s formulation was identified as 2,7,9-trimethyl-9-(4-tolyl)-9,10-dihydroacridine (3-6) (Figure 3.12), resulting from two hydroarylation reactions occurring at an ortho-position on each of the diarylamine’s arene rings. Single crystals suitable for X-ray diffraction were grown from

Scheme 3.15 Initial reaction and several potential products.
$n$-pentane. A diffraction study confirmed the formulation of 3-6 and showed that the tricyclic ring system in 3-6 adopts a puckered boat-like geometry, with the methyl and 4-Tol ring at the 9,9-disubstituted position oriented axially and equatorially, respectively (Figure 3.13).

![Figure 3.12](image1.png) **Figure 3.12** $^1$H NMR (C$_6$D$_6$) of isolated product 3-6 from test reaction.

![Figure 3.13](image2.png) **Figure 3.13** ORTEP depiction of 3-6 showing thermal ellipsoids at 50% probability. Hydrogen atoms and solvent omitted clarity. C: black, N: blue.
This type of molecule is called an acridan or a 9,9-disubstituted 9,10-dihydroacridine and is typically made from Grignard reactions of amine-substituted aryl ketones followed by an acid catalyzed ring closure (Scheme 3.16, top). Molecules bearing this motif have found a variety of uses including the detection of explosives (Scheme 3.16, middle) and as host materials for phosphorescent organic light-emitting diodes (Scheme 3.16, bottom).

Scheme 3.16 Typical synthesis of acridanes (top). Example of acridane use in detection of explosives (middle). Example of an acridane used in organic light emitting diodes (bottom).

Having established that [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] catalyzes this double hydroarylation reaction, other EPCs as well as generic Lewis acids were assessed to find the optimal catalyst with which to develop this reaction (Table 3.9). For the catalyst scope, the reaction conditions used were 0.08 mmol (4-Tol)$_2$NH, 0.08 mmol (4-Tol)C≡CH, and 5 mol% EPC catalyst in 3 mL DCM at ambient temperature for 16 hours, with conversion determined by GC-MS. Under these conditions, the generic Lewis acids FeCl$_3$ and AlCl$_3$ gave 52% and 22% conversion to 3-6, respectively (Table 3.9, entries 7 and 8), while the Brønsted acid (CF$_3$SO$_2$)$_2$NH gave 18% conversion (Table 3.9, entry 9). The Lewis acids Bi(O Tf)$_3$, ZnCl$_2$, and InCl$_3$ were all found to be inactive under these conditions (Table 3.9, entries 10-12). These generic Lewis and Brønsted acids were generally outcompeted...
by \( [(C_6F_5)_3PF][B(C_6F_5)_4] \), which gave 74% conversion (Table 3.9, entry 1), as well as by the monocationic EPCs \( 3-4, 3-1 \), and \( [Ph_3PF][B(C_6F_5)_4] \), which gave 71%, 32%, and 32% conversions, respectively (Table 3.9, entries 2, 5, and 6). The dicationic EPCs \( [SIMesPh_2PF][B(C_6F_5)_4]_2 \) and \( [(2-(N-Mepy))Ph_2P(OPh)][B(C_6F_5)_4]_2 \) also proved effective, giving 69% and 62% conversions, respectively (Table 3.9, entries 3 and 4). While \( [(C_6F_5)_3PF][B(C_6F_5)_4] \) appeared to be the optimal catalyst, catalyst fates were also considered, with the only high-performing catalysts to survive the reaction conditions being \( [(2-(N-Mepy))Ph_2P(OPh)][B(C_6F_5)_4]_2 \) (Table 3.9, entries 1-4). Given that \( [(2-(N-Mepy))Ph_2P(OPh)][B(C_6F_5)_4]_2 \) far outperforms these other two EPCs, it was chosen as the optimal catalyst to develop this reaction. As a control, the reactivity of the phosphine oxide \( [(2-(N-Mepy))Ph_2P(O)][B(C_6F_5)_4]_2 \) was tested and was found to be inactive under these reaction conditions (Table 3.9, entry 13).

Table 3.9 Double hydroarylation reaction catalyst screening.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>Catalyst Fate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( [(C_6F_5)_3PF][B(C_6F_5)_4] )</td>
<td>74</td>
<td>Decomposes</td>
</tr>
<tr>
<td>2</td>
<td>( [(C_6F_5)_3P(OCF_5)][B(C_6F_5)_4] ) (3-4)</td>
<td>71</td>
<td>Decomposes</td>
</tr>
<tr>
<td>3</td>
<td>( [SIMesPh_2PF][B(C_6F_5)_4]_2 )</td>
<td>69</td>
<td>Decomposes</td>
</tr>
<tr>
<td>4</td>
<td>( [(2-(N-Mepy))Ph_2P(OPh)][B(C_6F_5)_4]_2 )</td>
<td>62</td>
<td>Survives</td>
</tr>
<tr>
<td>5</td>
<td>( [Ph_3PF][B(C_6F_5)_4] ), ( FeCl_3 )</td>
<td>32</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>( [(C_6F_5)_3P(OPh)][B(C_6F_5)_4] ) (3-1)</td>
<td>32</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>( AlCl_3 )</td>
<td>52</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>( FeCl_3 )</td>
<td>22</td>
<td>---</td>
</tr>
<tr>
<td>9</td>
<td>( (CF_3SO_2)_2NH )</td>
<td>22</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>( Bi(OTf)_3 )</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>11</td>
<td>( ZnCl_2 )</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>12</td>
<td>( InCl_3 )</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>13</td>
<td>( [(2-(N-Mepy))Ph_3P(O)][B(C_6F_5)_4] )</td>
<td>0</td>
<td>---</td>
</tr>
</tbody>
</table>

Conversions determined by GC-MS.

For ease of analysis moving forward, the diarylamine was changed from \( (4-Tol)_2NH \) to \( (4-Tol)_2NMe \). With this substrate, \(^1\)H NMR analysis of crude reaction mixtures is much simpler as
the sharper N-CH$_3$ protons of the starting material and acridane product are well resolved and integrable, whereas the broad NH protons are not.

Having chosen a catalyst and with this diarylamine adjustment made, reaction conditions were screened (Table 3.10). The starting conditions of 0.12 mmol (4-Tol)$_2$NMe, 0.12 mmol (4-Tol)C≡CH, and 5 mol% catalyst in 9 mL DCM at ambient temperature for 24 hours gave 44% yield of the dihydroacridine product 3-7 (Table 3.10, entry 2). As expected, performing the reaction without catalyst gave no conversion (Table 3.10, entry 1). Changing the solvent from DCM to 1,2-dichloroethane (DCE) increased the conversion to 67% (Table 3.10, entry 3). Raising the temperature with either DCM or DCE solvent to 50 °C gave 71% and 85% for DCM and DCE, respectively (Table 3.10, entries 4 and 5). Further raising the temperature to 80 °C with DCE solvent gave 92% conversion (Table 3.10, entry 6). Using high temperature conditions with DCE at 80 °C, the alkyne loading was increased to 0.18 mmol (1.5 equivalents) to give 97% conversion when 9 mL DCE were used and 95% conversion when 2 mL DCE were used (Table 3.10, entries 7 and 8). Dropping the catalyst loading to 1 mol% and 0 mol% gave 69% and 0% conversions, respectively (Table 3.10, entries 9 and 10). The optimal conditions for were found to be 1.5 equivalents of alkyne, 5 mol% catalyst, and 2 mL DCE at 80 °C for 24 hours (Table 3.10, entry 8). Although the analogous reaction with 9 mL DCE did give a slightly better conversion, avoiding the use of the extra solvent volume was deemed more important.
Table 3.10  Double hydroarylation reaction catalysis condition screening.

![Reaction Scheme](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>[cat] (mol%)</th>
<th>Temperature (°C)</th>
<th>Equivalents of alkyne</th>
<th>Volume (mL)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>0</td>
<td>rt</td>
<td>1.0</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>5</td>
<td>rt</td>
<td>1.0</td>
<td>9</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>5</td>
<td>rt</td>
<td>1.0</td>
<td>9</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>DCM</td>
<td>5</td>
<td>50</td>
<td>1.0</td>
<td>9</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>5</td>
<td>50</td>
<td>1.0</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>5</td>
<td>80</td>
<td>1.0</td>
<td>9</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>5</td>
<td>80</td>
<td>1.5</td>
<td>9</td>
<td>97</td>
</tr>
<tr>
<td>8</td>
<td>DCE</td>
<td><strong>5</strong></td>
<td><strong>80</strong></td>
<td><strong>1.5</strong></td>
<td><strong>2</strong></td>
<td><strong>95</strong></td>
</tr>
<tr>
<td>9</td>
<td>DCE</td>
<td>1</td>
<td>80</td>
<td>1.5</td>
<td>2</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>DCE</td>
<td>0</td>
<td>80</td>
<td>1.5</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

Yields determined by $^1$H NMR spectroscopy.

3.8.2 Substrate Scope

Using the optimized conditions (Table 3.10, entry 8), reaction scope was investigated. First, the alkyne was varied to include electron donating alkyl, aryl, or heteroatom substituents (Table 3.11, Figure 3.14, Figure 3.15). It was found that PhC≡CH, (4-PhC$_6$H$_4$)C≡CH, and (4-MeOC$_6$H$_4$)C≡CH gave 95%, 92%, and 65% yields to the acridan products 3-8, 3-9, and 3-10, respectively (Table 3.11, entries 2-4). The significant drop in conversion with (4-MeOC$_6$H$_4$)C≡CH is likely due to the catalyst coordinating to and being poisoned by the methoxy substituent. Next, the alkyne was varied to include electron withdrawing halogens, with (4-BrC$_6$H$_4$)C≡CH, (2,4-F$_2$C$_6$H$_4$)C≡CH, and (4-CF$_3$C$_6$H$_4$)C≡CH giving 93%, 68%, and 10% yields to 3-11, 3-12, and 3-13, respectively (Table 3.11, entries 5-7). These three examples demonstrate that the arene ring on the alkyne must be electron rich to affect this reaction. Using (3-thienyl)C≡CH as the alkyne gave a yield of 86% to 3-14 (Table 3.11, entry 8), demonstrating that heterocycle-substituted alkynes are tolerated. When 1,4-(HC≡C)$_2$C$_6$H$_4$ was used with an excess of (4-Tol)$_2$NMe, a yield of 80% is observed to the double acridane product 3-15 (Table 3.11, entry 9). Interestingly, the reaction with MesC≡CH undergoes only one of the two hydroarylation events, producing the singly hydroarylated product...
2-(1-mesitylvinyl)-N,4-dimethyl-N-(4-tolyl)aniline (3-16) in 83% conversion (Table 3.11, entry 10). This is likely due to significant steric effects imparted by the mesityl group preventing interaction of the catalyst with the resultant alkene. Unfortunately, this reaction is limited to terminal aryl alkynes, as no conversion is observed when PhC≡CPh, CyC≡CH, or C₆H₁₃C≡CH is used (Table 3.11, entries 11-13).

Table 3.11  Double hydroarylation reaction substrate scope with varying alkynes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R¹</th>
<th>Yield (%)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-Tol</td>
<td>H</td>
<td>95 (76)</td>
<td>3-7</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>H</td>
<td>95 (74)</td>
<td>3-8</td>
</tr>
<tr>
<td>3</td>
<td>4-Biphenyl</td>
<td>H</td>
<td>92 (68)</td>
<td>3-9</td>
</tr>
<tr>
<td>4</td>
<td>4-(MeO)C₆H₄</td>
<td>H</td>
<td>65 (26)</td>
<td>3-10</td>
</tr>
<tr>
<td>5</td>
<td>4-BrC₆H₄</td>
<td>H</td>
<td>93 (65)</td>
<td>3-11</td>
</tr>
<tr>
<td>6</td>
<td>2,4-F₂C₆H₃</td>
<td>H</td>
<td>68 (35)</td>
<td>3-12</td>
</tr>
<tr>
<td>7</td>
<td>4-(CF₃)C₆H₄</td>
<td>H</td>
<td>10</td>
<td>3-13</td>
</tr>
<tr>
<td>8</td>
<td>3-Thiophene-yl</td>
<td>H</td>
<td>86 (63)</td>
<td>3-14</td>
</tr>
<tr>
<td>9</td>
<td>4-(HCC)C₆H₄</td>
<td>H</td>
<td>80 (52)</td>
<td>3-15</td>
</tr>
<tr>
<td>10</td>
<td>2,4,6-(Me)₃C₆H₂</td>
<td>H</td>
<td>83 (66)</td>
<td>3-16</td>
</tr>
<tr>
<td>11</td>
<td>Ph</td>
<td>Ph</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>12</td>
<td>Cy</td>
<td>H</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>13</td>
<td>C₆H₁₃</td>
<td>H</td>
<td>0</td>
<td>---</td>
</tr>
</tbody>
</table>

Reactions were performed with 0.12 mmol of arene and 0.18 mmol of alkyne in 2 mL DCE at 80 °C for 24 h. a Performed with 3 equivalents of diarylamine to one equivalent of alkyne substrate.

Figure 3.14  Substrate scope products 3-7 to 3-9.
Next, the diarylamine was varied under the standard conditions while maintaining the alkyne as (4-Tol)C≡CH (Table 3.12, Figure 3.16). The hydroarylation reaction with Ph₂NMe produced only 55% of the dihydroacridine product 3-17 (Table 3.12, entry 1) due to the accessible para-positions on the amine’s aryl rings which also undergo hydroarylation chemistry to furnish differently substituted products. In contrast to (4-Tol)₂NMe, (4-Tol)₂NH gave only 17% yield to 3-6 under the standard conditions (Table 3.12, entry 2), likely due to catalyst saturation or poisoning from coordination to the amine. However, this conversion was improved to 52% yield when reacted at ambient temperature for 24 hours (Table 3.12, entry 3). Electron poor amines bearing para-bromo substituents were found not to be very amenable to this reaction, with (4-BrC₆H₄)₂NMe giving 23% yield to 3-18 and (4-BrC₆H₄)₂NH showing no reactivity (Table 3.12, entries 4 and 5). At the other end of the electronic spectrum, electron-rich amines bearing para-methoxy substituents demonstrated interesting reactivity. While (4-MeOC₆H₄)₂NMe gave 97% yield to 3-19, (4-MeOC₆H₄)₂NH produced a mixture of products from which the major species, isolated in 33% yield, was found to be the partially dearomatized imine-one 7-methoxy-9-methyl-9-(4-tolyl)acridin-2(9H)-one (3-20) (Table 3.12, entries 6 and 7). These results demonstrate that the reaction benefits from electron rich diarylamines. As a further example of this, the electron poor (4-Tol)₂NTES was found to be unreactive under the standard conditions (Table 3.12, entry 8). Performing the selective hydroarylation of (4-Tol)₃N with one equivalent of (4-Tol)C≡CH gave several products, with the single acridane product between 3-21 predominating in 65% yield.
Attempts to synthesize the double or triple acridane products by reacting (4-Tol)$_3$N with excesses of (4-Tol)C≡CH gave intractable mixtures. Similar to the alkyne scope, the arene scope showed substrate limitations. Although (4-Tol)$_2$O gave 15% yield of 2,7,9-trimethyl-9-(4-tolyl)-9H-xanthene (3-22) under the standard reaction conditions and 21% yield when heated to 100 °C for 16 hours, this was the only non-amine-based arene that gave any reaction, as (4-Tol)SPh, Ph$_3$P(O), furan, and pyrrole were found to be unreactive (Table 3.12, entries 10-12).

**Table 3.12** Double hydroarylation reaction substrate scope with varying arenes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>E</th>
<th>X</th>
<th>Yield (%)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NMe</td>
<td>H</td>
<td>55 (35)</td>
<td>3-17</td>
</tr>
<tr>
<td>2</td>
<td>NH</td>
<td>Me</td>
<td>17</td>
<td>3-6</td>
</tr>
<tr>
<td>3</td>
<td>NH</td>
<td>Me</td>
<td>52 (37)$^a$</td>
<td>3-6</td>
</tr>
<tr>
<td>4</td>
<td>NMe</td>
<td>Br</td>
<td>23 (20)</td>
<td>3-18</td>
</tr>
<tr>
<td>5</td>
<td>NH</td>
<td>Br</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>NMe</td>
<td>MeO</td>
<td>97 (66)</td>
<td>3-19</td>
</tr>
<tr>
<td>7</td>
<td>NH</td>
<td>MeO</td>
<td>(33)$^b$</td>
<td>3-20</td>
</tr>
<tr>
<td>8</td>
<td>NTES</td>
<td>Me</td>
<td>0</td>
<td>----</td>
</tr>
<tr>
<td>9</td>
<td>N(4-Tol)</td>
<td>Me</td>
<td>65</td>
<td>3-21</td>
</tr>
<tr>
<td>10</td>
<td>O</td>
<td>Me</td>
<td>15</td>
<td>3-22</td>
</tr>
<tr>
<td>11</td>
<td>O</td>
<td>Me</td>
<td>21$^c$</td>
<td>3-22</td>
</tr>
<tr>
<td>12</td>
<td>S</td>
<td>H, Me</td>
<td>0</td>
<td>----</td>
</tr>
</tbody>
</table>

Reactions were performed with 0.12 mmol of arene and 0.18 mmol of alkyne in 2 mL DCE at 80 °C for 24 h.$^a$ Performed at ambient temperature for 24 h.$^b$ Isolated from complex mixture of products.$^c$ Performed at 100 °C for 16 h.
Figure 3.16  Substrate scope products 3-6 and 3-17 to 3-22.

Single crystals suitable for X-ray diffraction of 3-7, 3-8, 3-9, 3-11, 3-16 and 3-17 were grown from hot ethanol (Figure 3.17, Figure 3.18, Figure 3.19). Diffraction studies not only confirmed their formulations but revealed that, in the cases of the acridane products, two different conformers exist. Similar to 3-6, the solid-state structures of 3-7, 3-8, and 3-9 show that the methyl and arene ring at the 9,9-disubstituted position are oriented equatorially and axially, respectively. Conversely, the solid-state structures of 3-11 and 3-17 show the opposite conformation, with the methyl and aryl substituents oriented axially and equatorially, respectively. Given that only one set of 9,9-disubstituted methyl and aryl peaks are observed in the $^1$H and $^{13}$C\{H\} NMR of each product, the reaction must either be selective for the given conformer or the conformers must be interconverting in solution. The latter proposal is supported by a study of similar molecules which proposes that both conformers exist in solution with a reasonably small barrier to interconversion and that the observation of only one conformer in the solid-state is likely a packing effect.$^{54}$
Figure 3.17 ORTEP depiction of 3-7 (top) and 3-8 (bottom) showing thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. C: black, N: blue.
Figure 3.18  ORTEP depictions 3-9 (top) and 3-11 (bottom) showing thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. C: black, N: blue, Br: red.
Figure 3.19  ORTEP depictions of 3-16 (top) and 3-17 (bottom) showing thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. C: black, N: blue.
3.8.3 Mechanistic Insights

The mechanism of this reaction is proposed to begin with activation of the alkyne by the phosphonium cation to yield an electrophilic carbon site which then undergoes nucleophilic aromatic substitution at the ortho-carbon of an arene ring on the diarylamine. Proton transfer from the ortho-carbon to the alkyne’s terminal carbon and rearomatization of the aryl group afford the singly hydroarylated alkene intermediate complex which then undergoes a second phosphonium cation-mediated activation and hydroarylation reaction to afford the cyclized 9,9-disubstituted 9,10-dihydroacridine product (Scheme 3.17).

Scheme 3.17 Proposed mechanistic cycle for double hydroarylation reaction.

This proposed mechanism is supported by literature precedents and experimental results. First, the notion of alkyne activation by EPCs is supported by a publication from the Stephan group wherein an analogous interaction is proposed for the catalytic isomerization of alkenes by $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (Scheme 3.18 a)).55 This interaction also supports the alkyne substrate scope, as electron rich aryl-substituted alkynes can stabilize the intermediate’s electrophilic carbon
site and internal alkynes are presumably too sterically inaccessible to become activated by EPC. Second, the diarylamine’s role as a nucleophile is supported by a publication from the Stephan group wherein an analogous interaction is proposed in the mechanism of catalytic hydroarylation of alkenes with amines catalyzed by the \([(C_6F_5)_3PF][B(C_6F_5)_4]\) (Scheme 3.18 b)). This is further supported by the observation that electron poor diarylamines are ineffective in this reaction. Finally, the isolation of 3-16 from the reaction of (4-Tol)_2NMe and MesC≡CH represents the proposed reaction intermediate wherein only one hydroarylation event has occurred, leaving the resulting alkene intact.

It is noteworthy that the EPC-catalyzed reaction of alkynes with amines affords hydroarylation products while similar reactions with B(C_6F_5)_3 afford hydroamination products (vide supra). This could be due to the marked increase in Lewis acidity of EPCs with respect to B(C_6F_5)_3, as EPCs can impart greater polarization to the alkyne and generate a more effective electrophile which
would favour nucleophilic aromatic substitution over interaction with the basic amine. Alternatively, differences in steric about the Lewis acidic sites of EPCs and B(C₆F₅)₃ might account for this observed difference in reactivity.

3.9 Conclusion

The present work demonstrates the double hydroarylation reaction of alkynes with diarylamines catalyzed by [(2-(N-Mepy))Ph₂P(OPh)][B(C₆F₅)₄]₂ to afford acridane or 9,9-disubstituted 9,10-dihydroarcridine derivatives. The reaction scope demonstrates that heteroarenes, bis-alkyne substituted arenes, and electron withdrawing and donating groups are tolerated on the alkyne moiety and that diarylamines bearing N-alkyl or N-aryl substitutions are most effective. Additionally, this reaction was shown to be limited to aryl-substituted alkynes bearing a terminal hydrogen and to electron rich diarylamines. The proposed mechanism of EPC activation of the alkyne followed by nucleophilic aromatic substitution by the arene is supported by literature precedents of EPC behaviour in similar reactions and by the isolation of a proposed intermediate in the form of singly hydroarylated product 3-16. It is noteworthy that similar reactions in the presence of B(C₆F₅)₃ afford hydroamination products, illustrating that EPCs provide alternative catalytic avenues which generate unique products.

3.10 Experimental

3.10.1 General Experimental Methods

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N₂. All glassware was oven- or flame-dried and cooled under vacuum before use. Dry, oxygen-free solvents (dichloromethane and n-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone under inert atmosphere. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals, or Alfa Aesar, and were used without further purification unless indicated otherwise. Phosphonium salts [(C₆F₅)₃PF][B(C₆F₅)₄], [(C₆F₅)₃P(OPh)][B(C₆F₅)₄], [(2-(N-Mepy))Ph₂P(OPh)][B(C₆F₅)₄]₂, [(2-(N-Mepy))Ph₂PF][B(C₆F₅)₄]₂, [Ph₂PF][B(C₆F₅)₄], and starting materials [(2-(N-Mepy))Ph₂PF][B(C₆F₅)₄]₂, Ph₂NMe, (4-Tol)₂NMe, (4-MeOC₆H₄)₂NMe, (4-BrC₆H₄)₂NMe, and (4-Tol)₂NTES were prepared according to literature procedures or modified literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz, or a
Varian Mercury-300 MHz spectrometer. \(^1\)H, \(^{13}\)C, \(^{31}\)P, \(^{19}\)F, and \(^{11}\)B NMR chemical shifts (δ/ppm) are referenced to Me\(_4\)Si, Me\(_4\)Si, H\(_3\)PO\(_4\), CFCl\(_3\), and BF\(_3\)•OEt\(_2\), respectively. Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, \(^1\)H-\(^1\)H–COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer.

### 3.10.2 X-ray Diffraction Studies

Single crystals were coated with Paratone oil, mounted on a CryoLoop, and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-K\(_\alpha\) radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SAINT. An empirical absorption correction was applied using SADABS. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.
Table 3.13  X-ray table for 3-6, 3-7, and 3-8.

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>2,7,9-trimethyl-9-(4-tolyl)-9,10-dihydroacridine (3-6)</th>
<th>2,7,9,10-tetramethyl-9-(4-tolyl)-9,10-dihydroacridine (3-7)</th>
<th>2,7,9,10-tetramethyl-9-phenyl-9,10-dihydroacridine (3-8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{23}H_{22}N • (C_{4.33}H_{11})</td>
<td>C_{24}H_{25}N</td>
<td>C_{23}H_{23}N</td>
<td></td>
</tr>
<tr>
<td>Weight (g/mol)</td>
<td>281.66</td>
<td>327.45</td>
<td>313.42</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Trigonal</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P(\overline{3})</td>
<td>Pna(_2_1)</td>
<td>(I)ba(_2_1)</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>18.322(4)</td>
<td>19.792(5)</td>
<td>18.820(12)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>18.322(4)</td>
<td>12.548(3)</td>
<td>25.412(17)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>10.915(3)</td>
<td>7.5356(16)</td>
<td>7.492(5)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>120</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å(^3))</td>
<td>3173.1(17)</td>
<td>1871.4(7)</td>
<td>3583(4)</td>
</tr>
<tr>
<td>(Z)</td>
<td>6</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>(\rho) (calcd.) (Mg/m(^3))</td>
<td>1.179</td>
<td>1.162</td>
<td>1.162</td>
</tr>
<tr>
<td>(\mu) (mm(^{-1}))</td>
<td>0.067</td>
<td>0.067</td>
<td>0.067</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1224</td>
<td>704</td>
<td>1344</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo K(\alpha)</td>
<td>Mo K(\alpha)</td>
<td>Mo K(\alpha)</td>
</tr>
<tr>
<td>Theta range (°)</td>
<td>1.283 to 25.009</td>
<td>1.922 to 27.497</td>
<td>1.346 to 26.732</td>
</tr>
<tr>
<td>(T) (K)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Reflections Collected</td>
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<td>16099</td>
<td>10931</td>
</tr>
<tr>
<td>Independent Reflections</td>
<td>3739</td>
<td>3871</td>
<td>3308</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.0401</td>
<td>0.0962</td>
<td>0.0546</td>
</tr>
<tr>
<td>GOF ((F^2))</td>
<td>1.052</td>
<td>0.932</td>
<td>1.057</td>
</tr>
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<td>R1 indices ([I&gt;2\sigma(I)])</td>
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<td>0.0601</td>
<td>0.0473</td>
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<td>wR2 indices (all data)</td>
<td>0.3328</td>
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<td>0.1338</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e. Å(^{-3}))</td>
<td>0.919 &amp; -0.650</td>
<td>0.249 &amp; -0.229</td>
<td>0.183 &amp; -0.199</td>
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<tr>
<td>CCDC No.</td>
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<td>1580562</td>
<td>1580560</td>
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Table 3.14  X-ray table for 3-9 and 3-11.

<table>
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<tr>
<th></th>
<th>2,7,9,10-tetramethyl-9-([(1,1'-biphenyl)-4-yl]-9,10-dihydroacridine (3-9)</th>
<th>2,7,9,10-tetramethyl-9-(4-bromophenyl)-9,10-dihydroacridine (3-11)</th>
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</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C_{29}H_{27}N</td>
<td>C_{23}H_{22}BrN</td>
</tr>
<tr>
<td>Weight (g/mol)</td>
<td>389.51</td>
<td>392.32</td>
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<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space Group</td>
<td>C2/c</td>
<td>Iba2</td>
</tr>
<tr>
<td>a (Å)</td>
<td>23.643(4)</td>
<td>20.530(13)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>6.2144(9)</td>
<td>25.541(14)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>29.822(4)</td>
<td>7.450(4)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>105.394(6)</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>4224.5(11)</td>
<td>3906(4)</td>
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<tr>
<td>Z</td>
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<td>8</td>
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<tr>
<td>ρ (calcd.) (Mg/m³)</td>
<td>1.225</td>
<td>1.334</td>
</tr>
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<td>μ (mm⁻¹)</td>
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</tr>
<tr>
<td>F(000)</td>
<td>1664</td>
<td>1616</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>Theta range (°)</td>
<td>1.416 to 27.501</td>
<td>1.595 to 26.828</td>
</tr>
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<td>T (K)</td>
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<td>150(2)</td>
</tr>
<tr>
<td>Reflections Collected</td>
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<td>27208</td>
</tr>
<tr>
<td>Independent Reflections</td>
<td>4838</td>
<td>3953</td>
</tr>
<tr>
<td>Rint</td>
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<td>0.1183</td>
</tr>
<tr>
<td>GOF (F²)</td>
<td>0.992</td>
<td>1.011</td>
</tr>
<tr>
<td>R1 indices [I&gt;2σ(I)]</td>
<td>0.0595</td>
<td>0.0325</td>
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<tr>
<td>wR2 indices (all data)</td>
<td>0.1690</td>
<td>0.0989</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e. Å⁻³)</td>
<td>0.296 &amp; -0.313</td>
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<tr>
<td>CCDC No.</td>
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<td>1580561</td>
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### Table 3.15  X-ray table for 3-16 and 3-17.

<table>
<thead>
<tr>
<th></th>
<th>2-(1-mesitylvinyl)-N,4-dimethyl-N-(4-tolyl)aniline (3-16)</th>
<th>9,10-dimethyl-9-(4-tolyl)-9,10-dihydroacridine (3-17)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C_{26}H_{29}N</td>
<td>C_{22}H_{21}N</td>
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<tr>
<td>Weight (g/mol)</td>
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<td>299.40</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P_{2}1/n</td>
<td>Pnma</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.4056(18)</td>
<td>8.0404(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>25.093(6)</td>
<td>13.3233(17)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.580(3)</td>
<td>15.2895(17)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>103.797(8)</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>Volume (Å³)</td>
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<td>1637.9(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ (calcd.) (Mg/m³)</td>
<td>1.130</td>
<td>1.214</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>0.064</td>
<td>0.070</td>
</tr>
<tr>
<td>F(000)</td>
<td>768</td>
<td>640</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>Theta range (°)</td>
<td>1.623 to 27.544</td>
<td>2.027 to 27.608</td>
</tr>
<tr>
<td>T (K)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Reflections Collected</td>
<td>18636</td>
<td>15803</td>
</tr>
<tr>
<td>Independent Reflections</td>
<td>4787</td>
<td>1980</td>
</tr>
<tr>
<td>R_{int}</td>
<td>0.0580</td>
<td>0.0777</td>
</tr>
<tr>
<td>GOF (F²)</td>
<td>1.106</td>
<td>1.177</td>
</tr>
<tr>
<td>R1 indices [I&gt;2σ(I)]</td>
<td>0.1025</td>
<td>0.0861</td>
</tr>
<tr>
<td>wR2 indices (all data)</td>
<td>0.2932</td>
<td>0.1977</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e. Å⁻³)</td>
<td>0.546 &amp; -0.622</td>
<td>0.388 &amp; -0.326</td>
</tr>
<tr>
<td>CCDC No.</td>
<td>1580563</td>
<td>1580565</td>
</tr>
</tbody>
</table>
3.10.3 Pyridinium Phosphine Oxide Synthesis

\[
[(2-(N-Mepy))\text{Ph}_2\text{PO}][\text{B}(\text{C}_6\text{F}_5)_4]
\]

![structure](image)

A DCM solution of \([(2-(N-Mepy))\text{Ph}_2\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\) was exposed to air for 48 h. The resulting solution was then dried in vacuo and the off-white solid was washed with \(n\)-pentane (3 x 5 mL) to afford an off-white solid. Partial characterization. \(^{19}\text{F}\) NMR (377 MHz, CD\(_2\)Cl\(_2\)): \(\delta = -133.0\) (s(br), 8F; B(o-C\(_6\)F\(_5\))\(_4\)), -163.5 (t, \(^{3}J_{\text{FF}} = 22\) Hz, 4F; B(p-C\(_6\)F\(_5\))\(_4\)), -167.3 (m(br), 8F; B(m-C\(_6\)F\(_5\))\(_4\)) ppm. \(^{31}\text{P}\{^1\text{H}\}\) NMR (162 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 28.7\) (s) ppm.

\[
[(2-(N-Mepy))\text{Ph}_2\text{PO}][\text{OTf}]
\]

![structure](image)

A DCM solution of [P(2-(N-Mepy))\text{Ph}_2\text{PF}][\text{OTf}] was exposed to air for 48 h. The resulting solution was then dried in vacuo and the off-white solid was washed with \(n\)-pentane (3 x 5 mL) to afford an off-white solid. \(^{1}\text{H}\) NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 4.52\) (s, 3H; NCH\(_3\)), 7.61 (m, 5H; phenyl-o-CH, pyridyl-o-CH), 7.73 (m, 6H; phenyl-p-m-CH), 8.23 (m, 1H; pyridyl-p-CH), 8.48 (m, 1H; pyridyl-m-CH), 9.21 (m, 1H; pyridyl-m-CH) ppm. \(^{19}\text{F}\) NMR (377 MHz, CD\(_2\)Cl\(_2\)): \(\delta = -78.4\) (s, 3F; O\(_3\)SCF\(_3\)) ppm. \(^{31}\text{P}\{^1\text{H}\}\) NMR (162 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 28.7\) (s) ppm. \(^{13}\text{C}\{^1\text{H}\}\) NMR (125 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 48.9\) (d, \(^{3}J_{\text{CP}} = 3\) Hz, 1C; NCH\(_3\)), 126.9 (d, \(^{1}J_{\text{CP}} = 111\) Hz, 1C; phenyl-i-C), 130.0 (d, \(^{3}J_{\text{CP}} = 13\) Hz, 4C; phenyl-o-CH), 131.3 (d, \(^{4}J_{\text{CP}} = 2\) Hz, 1C; pyridyl-p-CH), 132.1 (d, \(^{3}J_{\text{CP}} = 11\) Hz, 4C; phenyl-m-CH), 133.9 (d, \(^{3}J_{\text{CP}} = 13\) Hz, 1C; pyridyl-o-CH), 134.5 (d, \(^{3}J_{\text{CP}} = 3\) Hz, 2C; phenyl-p-CH), 145.6 (d, \(^{3}J_{\text{CP}} = 8\) Hz, 1C; pyridyl-m-CH), 149.3 (d, \(^{3}J_{\text{CP}} = 89\) Hz, 1C; pyridyl-i-C), 151.8 (d, \(^{3}J_{\text{CP}} = 4\) Hz, 1C; pyridyl-m-CH) ppm, resonance for the sulfur-bound carbon atom of O\(_3\)SCF\(_3\) anion was not observed. HRMS (ESI-TOF+): m/z [M]\(^{+}\) 294.1045 (calcd for C\(_{18}\)H\(_{17}\)NOP: 294.1042).

3.10.4 Catalyst Screening

In a 20 mL vial, a solution of acid catalyst (0.004 mmol, 0.05 eq.) was prepared in DCM (3 mL). A solution of (4-Tol)\(_2\)NH (16.0 mg, 0.08 mmol, 1.0 eq.) in DCM (3 mL) was added at ambient temperature. The mixture was briefly stirred and then a solution of (4-Tol)C=CH (9.4 mg, 0.08 mmol, 1.0 eq.) in DCM (3 mL) was added. The reaction mixture was stirred at ambient temperature for 16 h. The solution was then dried in vacuo. Acid catalyst was removed by dissolving the residue
in a 2:1 mixture of DCM : n-pentane and filtering over a silica plug. Conversion was determined by GCMS.

3.10.5 Condition Screening

Condition screening reactions for the hydroarylation of diarylamines with alkynes were performed according to a common procedure. A sample procedure is outlined below.

In a 20 mL vial, a solution of [(2-(N-Mepy))Ph2P(OPh)][B(C6F5)4]2 (10.2 mg, 0.006 mmol, 0.05 eq.) was prepared in DCM (3 mL). A solution of (4-Tol)2NMe (25.3 mg, 0.12 mmol, 1.0 eq.), prepared in DCM (3 mL), was added at ambient temperature. The mixture was briefly stirred and then a solution of (4-Tol)C≡CH (13.9 mg, 0.12 mmol, 1.0 eq.), prepared in DCM (3 mL), was added. The reaction mixture was stirred at ambient temperature for 24 h. The solution was then dried in vacuo and re-dissolved in CDCl3 (0.6 mL). Conversion was determined by 1H NMR spectroscopy.

3.10.6 Catalysis Scope

Hydroarylations of diarylamines were performed following a common procedure. A generic procedure is provided below. Reactions with (4-Tol)2NH, (4-MeOC6H4)2NH, and (4-BrC6H4)2NH were carried out at ambient temperature instead of 80 °C. Reaction with 1,4-(HCC)2Ph performed with 1.3 eq. (4-Tol)2NMe. Reaction with (4-Tol)3N performed with 1.0 eq. (4-Tol)C≡CH.

In a Schlenk bomb, a solution of [(2-(N-Mepy))Ph2P(OPh)][B(C6F5)4]2 (10.2 mg, 0.006 mmol, 0.05 eq.) was prepared in DCE (0.66 mL). A solution of (4-R’C6H4)2NMe (0.12 mmol, 1.0 eq.) in DCE (0.66 mL) was added at ambient temperature. The mixture was briefly stirred and then a solution of (R)C≡CH (0.18 mmol, 1.5 eq.) in DCE (0.66 mL) was added. The reaction mixture was sealed and heated at 80 °C for 24 h. The solution was then dried in vacuo and re-dissolved in CDCl3 (0.6 mL). Conversions were determined by 1H NMR spectroscopy. Products were isolated by silica chromatography (0-5 % EtOAc in pentane). Single crystals suitable for X-ray diffraction were obtained by recrystallization from hot ethanol.
3-6 2,7,9-trimethyl-9-(4-tolyl)-9,10-dihydroacridine

Obtained as a light yellow solid (13.9 mg, 37% isolated yield). $^1$H NMR (500 MHz, CD$_2$D$_6$): $\delta$ = 1.86 (s, 3H; 9-CH$_3$), 1.99 (s, 6H; 2,7-CH$_3$), 2.09 (s, 1H; 9-(tolyl-p-CH$_3$)), 5.50 (s, 1H; NH), 6.31 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 4,5-CH), 6.78 (s, 2H; 1,8-CH), 6.83 (dd, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, 2H; 3,6-CH), 6.99 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 9-(tolyl-m-CH$_3$)), 7.39 (dt, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz; 9-(tolyl-o-CH$_3$)) ppm. $^{13}$C$^1$H NMR (125 MHz, CD$_2$D$_6$): $\delta$ = 20.9 (2C; 2,7-CH$_3$), 21.0 (1C; 9-(tolyl-p-CH$_3$)), 31.6 (1C; 9-CH$_3$), 46.0 (1C; 9-C), 113.6 (2C; 4,5-CH), 127.7 (2C; 3,6-CH), 128.9 (2C; 9-(tolyl-m-CH$_3$)), 129.4 (2C; 2,7-C), 129.5 (2C; 9-(tolyl-o-CH$_3$)), 129.7 (2C; 1,8-CH), 129.9 (2C; 12,13-C), 135.5 (1C; 9-(tolyl-p-C)), 136.5 (2C; 11,14-C), 147.5 (1C; 9-(tolyl-i-C)) ppm. HRMS (DART-TOF+): m/z [M+H]$^+$ 314.19074 (calcld for C$_{23}$H$_{24}$N: 319.19087).

3-7 2,7,9,10-tetramethyl-9-(4-tolyl)-9,10-dihydroacridine

Obtained as a white solid (29.9 mg, 76% isolated yield). $^1$H NMR (500 MHz, CDC$_3$): $\delta$ = 1.79 (s, 3H; 9-CH$_3$), 2.22 (s, 6H; 2,7-CH$_3$), 2.33 (s, 3H; 9-(tolyl-p-CH$_3$)), 3.35 (s, 3H; NCH$_3$), 6.75 (d, $^4$J$_{HH}$ = 2 Hz, 2H; 1,8-CH), 6.87 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 4,5-CH), 7.00 (d, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, 2H; 3,6-CH), 7.05 (s, 4H; 9-(tolyl-o,m-CH$_3$)) ppm. $^{13}$C NMR (125 MHz, CDC$_3$): $\delta$ = 20.9 (2C; 2,7-CH$_3$), 21.2 (1C; 9-(tolyl-p-CH$_3$)), 28.5 (1C; 9-CH$_3$), 33.6 (1C; NCH$_3$), 45.8 (1C; 9-C), 111.7 (2C; 4,5-CH), 127.4 (2C; 3,6-CH), 128.0 (2C; 1,8-CH), 128.5 (2C; 9-(tolyl-o-CH$_3$)), 128.6 (2C; 9-(tolyl-o-CH$_3$)), 129.0 (2C; 2,7-C), 132.4 (2C; 12,13-C), 135.4 (1C; 9-(tolyl-p-CH$_3$)), 140.0 (2C; 11,14-C), 145.9 (1C; 9-(tolyl-i-C)) ppm. HRMS (DART-TOF+): m/z [M+H]$^+$ 328.20756 (calcld for C$_{24}$H$_{26}$N: 328.20652).

3-8 2,7,9,10-tetramethyl-9-phenyl-9,10-dihydroacridine

Obtained as a white solid (27.8 mg, 74% isolated yield). $^1$H NMR (500 MHz, CDC$_3$): $\delta$ = 1.81 (s, 3H; 9-CH$_3$), 2.22 (s, 6H; 2,7-CH$_3$), 3.35 (s, 3H; NCH$_3$), 6.74 (d, $^4$J$_{HH}$ = 2 Hz, 2H; 1,8-CH), 6.82 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 4,5-CH), 7.00 (dd, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, 2H; 3,6-CH), 7.22 – 7.24 (m, 5H; 9-(phenyl-o,m,p-CH$_3$)) ppm. $^{13}$C NMR (125 MHz,
\textbf{CDCl}_3): \(\delta = 20.9\) (2C; 2,7-CH\(_3\)), 28.3 (1C; 9-CH\(_3\)), 33.4 (1C; NCH\(_3\)), 46.1 (1C; 9-C), 111.7 (2C; 4,5-CH), 126.0 (1C; 9-(phenyl-\(p\)-CH), 127.4 (1C; 9-(phenyl-\(m\)-CH), 127.7 (2C; 3,6-CH), 127.9 (2C; 1,8-CH), 128.6 (1C; 9-(phenyl-\(o\)-CH), 129.0 (2C; 2,7-C), 132.2 (2C; 12,13-C), 140.0 (2C; 11,14-C), 149.0 (1C; 9-phenyl-C) ppm. \textbf{HRMS (DART-TOF+)}: m/z [M+H]+ 314.19205 (calcd for C\(_{23}\)H\(_{24}\)N: 314.19087).

3-9 \hspace{1cm} 2,7,9,10-tetramethyl-9-\([1,1^\prime\)-biphenyl]-4-yl)-9,10-dihydroacridine

Obtained as a white solid (31.8 mg, 68% isolated yield). \textbf{\(^1\)H NMR (500 MHz, CDCl\(_3\))}: \(\delta = 1.86\) (s, 3H; 9-CH\(_3\)), 2.24 (s, 6H; 2,7-CH\(_3\)), 3.36 (s, 3H; NCH\(_3\)), 6.82 (d, \(^4\)J\(_{\text{HH}}\) = 2 Hz, 2H; 1,8-CH), 6.83 (d, \(^3\)J\(_{\text{HH}}\) = 8 Hz, 2H; 4,5-CH), 7.00 – 7.04 (m, 2H; 3,6-CH), 7.22 (dt, \(^3\)J\(_{\text{HH}}\) = 8 Hz, \(^4\)J\(_{\text{HH}}\) = 2 Hz, 2H; 9-(biphenyl-2,6-CH)), 7.32 (tt, \(^3\)J\(_{\text{HH}}\) = 8 Hz, \(^4\)J\(_{\text{HH}}\) = 1 Hz, 1H; 9-(biphenyl-4'-CH)), 7.42 (t, \(^3\)J\(_{\text{HH}}\) = 8 Hz, \(^4\)J\(_{\text{HH}}\) = 2 Hz, 2H; 9-(biphenyl-3',5'-CH)), 7.49 (dt, \(^3\)J\(_{\text{HH}}\) = 8 Hz, \(^4\)J\(_{\text{HH}}\) = 2 Hz, 2H; 9-(biphenyl-3,5-CH)), 7.59 – 7.62 (m, 2H; 9-(biphenyl-2',6'-CH)) ppm. \textbf{\(^{13}\)C\(^{\text{\scriptsize{[\textbf{\textit{H}}]}}\) NMR (125 MHz, CDCl\(_3\))}: \(\delta = 20.9\) (2C; 2,7-CH\(_3\)), 28.3 (1C; 9-CH\(_3\)), 33.5 (1C; NCH\(_3\)), 45.9 (1C; 9-C), 111.8 (2C; 4,5-CH), 126.4 (2C; 9-(biphenyl-3,5-CH)), 127.1 (2C; 9-(biphenyl-2',6'-CH)), 127.2 (1C; 9-(biphenyl-4'-CH)), 127.5 (2C; 3,6-CH), 127.9 (2C; 1,8-CH), 128.8 (2C; 9-(biphenyl-3',5'-CH)), 129.0 (2C; 9-(biphenyl-2,6-CH)), 129.2 (2C; 2,7-C), 132.1 (2C; 12,13-C), 138.6 (1C; 9-(biphenyl-1-C)), 140.1 (2C; 11,14-C), 141.0 (1C; 9-(biphenyl-1'-C)), 148.2 (1C; 9-(biphenyl-4-C)) ppm. \textbf{HRMS (DART-TOF+)}: m/z [M+H]+ 390.22252 (calcd for C\(_{29}\)H\(_{28}\)N: 390.22217).

3-10 \hspace{1cm} 2,7,9,10-tetramethyl-9-(4-methoxyphenyl)-9,10-dihydroacridine

Obtained as a white solid (10.5 mg, 26% isolated yield). \textbf{\(^1\)H NMR (500 MHz, CDCl\(_3\))}: \(\delta = 1.76\) (s, 3H; 9-CH\(_3\)), 2.21 (s, 6H; 2,7-CH\(_3\)), 3.36 (s, 3H; NCH\(_3\)), 3.81 (s, 3H; 9-(phenyl-\(p\)-OCH\(_3\))), 6.71 (d, \(^4\)J\(_{\text{HH}}\) = 2Hz, 2H; 1,8-CH), 6.79 – 6.82 (m, 4H; 4,5-CH, 9-(phenyl-\(m\)-CH)), 6.98 – 7.01 (m, 2H; 3,6-CH), 7.08 – 7.14 (m, 2H; 9-(phenyl-\(o\)-CH)) ppm. \textbf{\(^{13}\)C NMR (125 MHz, CDCl\(_3\))}: \(\delta = 21.0\) (2C; 2,7-CH\(_3\)), 28.7 (1C; 9-CH\(_3\)), 33.6 (1C; NCH\(_3\)), 45.7 (1C; 9-C), 55.4 (1C; 9-(phenyl-\(p\)-OCH\(_3\))), 111.7 (2C; 9-(phenyl-\(m\)-CH)), 113.2 (2C; 4,5-CH), 127.5 (2C; 3,6-CH), 128.1 (2C; 1,8-CH), 129.1 (2C; 2,7-C), 129.9 (2C; 9-(phenyl-\(o\)-CH)), 132.7 (2C; 12,13-C), 140.0 (2C; 11,14-C), 141.1 (1C; 9-(phenyl-\(i\)-C)).
157.8 (1C; 9-(phenyl-p-C)) ppm. HRMS (DART-TOF+): m/z [M+H]$^+$ 344.20418 (calcd for C$_{24}$H$_{25}$NO: 344.20144).

3-11 2,7,9,10-tetramethyl-9-(4-bromophenyl)-9,10-dihydroacridine

Obtained as a white solid (30.6 mg, 65% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.79 (s, 3H; 9-CH$_3$), 2.24 (s, 6H; 2,7-CH$_3$), 3.33 (s, 3H; NCH$_3$), 6.75 (d, $^4$J$_{HH}$ = 2 Hz, 2H; 1,8-CH), 6.81 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 4,5-CH), 6.98 – 7.04 (m, 4H; 3,6-CH, 9-(phenyl-o-CH)), 7.35 (dt, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, 2H; 9-(phenyl-m-CH)) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 20.9 (2C; 2,7-CH$_3$), 28.1 (1C; 9-CH$_3$), 33.4 (1C; NCH$_3$), 45.8 (1C; 9-C), 111.9 (2C; 4,5-CH), 120.0 (1C; 9-(phenyl-p-CBr)), 127.6 (4C; 1,8-CH, 3,6-CH), 129.3 (2C; 2,7-CH), 130.4 (2C; 9-(phenyl-o-CH)), 130.8 (2C; 9-(phenyl-m-CH)), 131.6 (2C; 12,13-C), 140.1 (2C; 11,14-C), 148.3 (1C; 9-(phenyl-i-C)) ppm. HRMS (DART-TOF+): m/z [M+H]$^+$ 392.10177 (calcd for C$_{23}$H$_{25}$BrN: 392.10139).

3-12 2,7,9,10-tetramethyl-9-(2,4-difluorophenyl)-9,10-dihydroacridine

Obtained as a white solid (14.7 mg, 35% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.73 (s, 3H; 9-CH$_3$), 2.17 (s, 6H; 2,7-CH$_3$), 3.41 (s, 3H; NCH$_3$), 6.50 (d, $^4$J$_{HH}$ = 2 Hz, 2H; 1,8-CH), 6.71 – 6.75 (m, 1H; 9-(phenyl-3-CH)), 6.81 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 5,4-CH), 6.94 – 7.00 (m, 1H; 9-(phenyl-5-CH)), 7.00 – 7.02 (m, 2H; 3,6-CH), 7.49 (dt, $^3$J$_{HH}$ = 8 Hz, $^3$J$_{HF}$ = 6 Hz, 1H; 9-(phenyl-6-CH)) ppm. $^{19}$F($^1$H) NMR (375 MHz, CDCl$_3$): $\delta$ = -99.20 (d, $^3$J$_{FF}$ = 8 Hz, 1F; 9-(phenyl-2-F)), -112.69 (d, $^3$J$_{FF}$ = 8 Hz, 1F; 9-(phenyl-4-F)) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 20.8 (2C; 2,7-CH$_3$), 29.6 (1C; 9-CH$_3$), 33.5 (1C; NCH$_3$), 44.0 (1C; 9-C), 105.5 (1C; 9-(phenyl-3-CH)), 110.1 (1C; 9-(phenyl-5-CH)), 111.8 (2C; 4,5-CH), 126.6 (2C; 1,8-CH), 127.7 (2C; 3,6-CH), 129.1 (2C; 2,7-CH), 129.6 (1C; 9-(phenyl-6-CH)), 131.0 (1C; 9-(phenyl-1-C)), 131.2 (2C; 12,13-C), 138.9 (2C; 11,14-C), 161.2 (1C; 9-(phenyl-4-CF)), 162.4 (1C; 9-(phenyl-2-CH)) ppm. HRMS (DART-TOF+): m/z [M+H]$^+$ 350.17171 (calcd for C$_{23}$H$_{22}$F$_2$N: 350.17203).
3-13 2,7,9,10-tetramethyl-9-(4-trifluoromethylphenyl)-9,10-dihydroacridine

Partial characterization (10% conversion). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.91$ (s, 3H; 9-$C$H$_3$), 2.30 (s, 6H; 2,7-$C$H$_3$), 3.36 (s, 3H; NCH$_3$), 7.25 (d, $^3$J$_{HH} = 8$ Hz, 2H; 9-(phenyl-$CH$), 7.48 (d, $^3$J$_{HH} = 8$ Hz, 2H; 9-(phenyl-$CH$) ppm. $^{19}$F$^1$H NMR (282 MHz, CDCl$_3$): -62.47 (s) ppm. MS (EI$^+$): [m/z, (%)] 366.10 ([M$-$CH$_3$]$^+$, 100), 367.20 (33.6).

3-14 2,7,9,10-tetramethyl-9-(3-thiophenyl)-9,10-dihydroacridine

Obtained as a white solid (24.1 mg, 63% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.72$ (s, 3H; 9-$C$H$_3$), 2.19 (s, 6H; 2,7-$C$H$_3$), 3.40 (s, 3H; NCH$_3$), 6.61 (d, $^4$J$_{HH} = 2$ Hz, 2H; 1,8-$C$H), 6.74 (dd, $^3$J$_{HH} = 8$ Hz, 2H; 4,5-$C$H), 6.99 – 7.01 (m, 2H; 3,6-$C$H), 7.18 (dd, $^3$J$_{HH} = 3$ Hz, $^3$J$_{HH} = 1$Hz, 1H; 9-(thiophenyl-4-$CH$)) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 20.8$ (2C; 2,7-$C$H$_3$), 29.3 (1C; 9-$C$H$_3$), 33.4 (1C; NCH$_3$), 44.3 (1C; 9-$C$), 111.6 (2C; 4,5-$C$H), 121.7 (1C; 9-(thiophenyl-4-$CH$)), 125.2 (1C; 9-(thiophenyl-5-$CH$)), 127.6 (4C; 1,3,6,8-$C$H), 129.2 (2C; 2,7-$C$), 129.6 (1C; 9-(thiophenyl-2-$CH$)), 131.7 (2C; 12,13-$C$), 139.5 (2C; 11,14-$C$), 149.3 (1C; 9-(thiophenyl-3-$C$)) ppm. HRMS (DART-TOF$^+$): m/z [M+H]$^+$ 320.14802 (calcd for C$_{21}$H$_{22}$NS: 320.14729).

3-15 1,4-bis(2,7,9,10-tetramethyl-9,10-dihydroacridin-9-yl)benzene

Obtained as a white solid (16.9 mg, 52% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.78$ (s, 6H; 9,9-$C$H$_3$), 2.22 (s, 12H; 2,2',7,7'-$C$H$_3$), 3.37 (s, 6H; NCH$_3$), 6.70 (d, $^4$J$_{HH} = 2$ Hz, 4H; 1,1',8,8'$-CH$), 6.80 (d, $^3$J$_{HH} = 8$ Hz, 4H; 4,4',5,5'$-CH$), 6.99 – 7.01 (m, 4H; 3,3',6,6'$-CH$), 7.12 (s, 4H; benzene-2,3,5,6-$CH$) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 20.8$ (4C; 2,2',7,7'-$C$H$_3$), 28.4 (2C; 9,9-$C$H$_3$), 33.4 (2C; NCH$_3$), 46.0 (2C; 9-$C$), 111.6 (4C; 4,4',5,5'$-CH$), 127.3 (4C; 3,3',6,6'$-CH$), 128.3 (8C; 1,1',8,8'$-CH$, benzene-2,3,5,6-$CH$), 128.9 (4C; 2,2',7,7'$-C$), 132.7 (4C; 12,12',13,13'$-C$), 139.9 (4C; 11,11',14,14'$-C$), 146.3 (2C;
benzene-1,4-C) ppm. HRMS (DART-TOF+): m/z [M+H]^+ 549.32585 (calcd for C_{40}H_{40}N_{2}: 549.32697).

3-16 2-(1-mesitylviny)-N,4-dimethyl-N-(4-tolyl)aniline

Obtained as a white solid (28.1 mg, 66% isolated yield).

$^1$H NMR (500 MHz, CDCl$_3$): \( \delta = 2.02 \) (s, 6H; mesityl-\( \alpha \)-CH$_3$), 2.25 (s, 3H; tolyl-\( p \)-CH$_3$), 2.29 (s, 3H; mesityl-\( \alpha \)-CH$_3$), 2.32 (s, 3H; aniline-4-CH$_3$), 2.71 (s, 3H; NCH$_3$), 5.14 (d, $^3$J$_{HH} = 2$ Hz, 1H; vinyl-C=CH$_2$), 5.96 (d, $^1$J$_{HH} = 2$ Hz, 1H; C=CH$_2$), 6.38 (dt, $^3$J$_{HH} = 8$ Hz, $^4$J$_{HH} = 2$ Hz, 2H; tolyl-\( \alpha \)-CH), 6.84 (s, 2H; mesityl-\( m \)-CH), 6.96 (d, $^3$J$_{HH} = 8$ Hz, tolyl-\( m \)-CH, aniline-6-CH), 7.08 – 7.11 (m, 2H; aniline-3-CH, aniline-5-CH) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): \( \delta = 20.4 \) (1C; tolyl-\( p \)-CH$_3$), 20.8 (2C; mesityl-\( \alpha \)-CH$_3$), 21.1 (1C; mesityl-\( p \)-CH$_3$), 21.3 (1C; aniline-4-CH$_3$), 38.6 (1C; NCH$_3$), 113.2 (2C; tolyl-\( \alpha \)-CH), 119.7 (1C; vinyl-C=CH$_2$), 125.6 (1C; tolyl-\( p \)-C), 128.3 (2C; mesityl-\( m \)-CH), 129.4 (2C; tolyl-\( m \)-CH), 129.9 (1C; aniline-6-CH), 130.1 (1C; aniline-5-CH), 131.4 (1C; aniline-3-CH), 135.8 (1C; mesityl-\( p \)-C), 136.2 (2C; mesityl-\( \alpha \)-C), 136.5 (1C; aniline-4-C), 139.4 (1C; mesityl-i-C), 139.6 (1C; aniline-2-C), 144.2 (1C; aniline-1-C), 145.7 (1C; vinyl-C=CH$_2$), 148.1 (1C; tolyl-i-C) ppm. HRMS (DART-TOF+): m/z [M+H]^+ 356.23764 (calcd for C$_{26}$H$_{30}$N: 356.23782).

3-17 9,10-dimethyl-9-(4-tolyl)-9,10-dihydroacridine

Obtained as a white yellow solid (12.6 mg, 35% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): \( \delta = 1.82 \) (s, 3H; 9-CH$_3$), 2.34 (s, 3H; 9-(tolyl-\( p \)-CH$_3$)), 3.42 (s, 3H; NCH$_3$), 6.87 – 6.91 (m, 2H; 1,8-CH), 6.93 – 6.98 (m, 4H; 2,3,6,7-CH), 7.08 (s, 4H; 9-(tolyl-\( o,m \)-CH$_3$)), 7.21 – 7.25 (m, 2H; 4,5-CH) ppm. $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): \( \delta = 21.1 \) (1C; 9-(tolyl-\( p \)-CH$_3$)), 28.3 (1C; 9-CH$_3$), 33.5 (1C; NCH$_3$), 45.9 (1C; 9-C), 112.0 (2C; 2,7-CH), 120.3 (2C; 1,8-CH), 126.9 (2C; 4,5-CH), 127.4 (2C; 3,6-CH), 128.5 (2C; 9-(tolyl-\( o \)-CH$_3$)), 128.7 (2C; 9-(tolyl-\( m \)-CH$_3$)), 132.6 (2C; 12,13-C), 135.6 (1C; 9-(tolyl-\( p \)-C)), 141.9 (2C; 11,14-C), 145.8 (1C; 9-(tolyl-i-C)) ppm. HRMS (DART-TOF+): m/z [M+H]^+ 455.99605 (calcd for C$_{22}$H$_{20}$Br$_2$N: 455.99625).
2,7-dibromo-9,10-dimethyl-9-(4-tolyl)-9,10-dihydroacridine

Obtained as a light yellow solid (11.0 mg, 20% isolated yield).

$^{1}H$ NMR (500 MHz, CDCl$_3$): $\delta = 1.77$ (s, 3H; 9-CH$_3$), 2.34 (s, 3H; 9-(tolyl-p-CH$_3$)), 3.35 (s, 3H; NCH$_3$), 6.80 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 4,5-CH$_2$), 7.01 (d, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 1 Hz, 2H; 9-(tolyl-o-CH$_3$)), 7.03 – 7.05 (m, 2H; 1,8-C$_6$H), 7.08 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 9-(tolyl-m-CH$_2$)), 7.30 – 7.34 (m, 2H; 3,6-C$_6$H) ppm.

$^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta = 21.1$ (1C; 9-(tolyl-p-CH$_3$)), 28.2 (1C; 9-CH$_3$), 33.8 (1C; NCH$_3$), 45.9 (1C; 9-C), 113.3 (2C; 2,7-Br), 113.8 (2C; 4,5-CH), 128.3 (2C; 9-(tolyl-o-CH$_3$)), 128.8 (2C; 9-(tolyl-m-CH$_3$)), 129.9 (2C; 3,6-CH), 130.1 (2C; 1,8-CH), 134.4 (2C; 12,13-C), 136.3 (1C; 9-(tolyl-p-CH$_3$)), 140.7 (2C; 11,14-C), 144.0 (1C; 9-(tolyl-i-CH$_3$)) ppm. HRMS (DART-TOF$^+$): m/z [M+H]$^+$ 455.99605 (calcd for C$_{22}$H$_{20}$Br$_2$N: 455.99625).

2,7-dimethoxy-9,10-dimethyl-9-(4-tolyl)-9,10-dihydroacridine

Obtained as a white solid (28.4 mg, 66% isolated yield).

$^{1}H$ NMR (500 MHz, CDCl$_3$): $\delta = 1.81$ (s, 3H; 9-CH$_3$), 2.31 (s, 3H; 9-(tolyl-p-CH$_3$)), 3.33 (s, 3H; NCH$_3$), 3.71 (s, 6H; 2,7-OCH$_3$), 6.61 (d, $^4$J$_{HH}$ = 3 Hz, 2H; 1,8-CH)$_2$, 6.78 (dd, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 3 Hz, 2H; 3,6-CH)$_2$, 6.81 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 4,5-CH), 7.04 (s, 4H; 9-(tolyl-o,m-CH$_3$)) ppm. $^{13}$C{$^1$H} NMR (500 MHz, CDCl$_3$): $\delta = 21.1$ (1C; 9-(tolyl-p-CH$_3$)), 27.7 (1C; 9-CH$_3$), 33.6 (1C; NCH$_3$), 46.4 (1C; 9-C), 55.8 (2C; 2,7-OCH$_3$), 111.3 (2C; 3,6-CH), 112.1 (2C; 4,5-CH), 114.2 (2C; 1,8-CH), 128.4 (2C; 9-(tolyl-o-CH$_3$)), 128.6 (2C; 9-(tolyl-m-CH$_3$)), 133.6 (2C; 12,13-C), 135.6 (1C; 9-(tolyl-p-CH$_3$)), 137.0 (2C; 11,14-C), 144.9 (1C; 9-(tolyl-i-CH$_3$)), 153.7 (2C; 2,7-COCH$_3$) ppm. HRMS (DART-TOF$^+$): m/z [M+H]$^+$ 360.19568 (calcd for C$_{24}$H$_{26}$NO$_2$: 360.1965).
3-20 7-methoxy-9-methyl-9-(4-tolyl)acridin-2(9H)-one

Obtained as a yellow solid (12.7 mg, 33% isolated yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.74 (s, 3H; 9-CH$_3$), 2.33 (s, 3H; 9-(tolyl-p-CH$_3$)), 3.74 (s, 3H; 7-OCH$_3$), 6.09 (d, $^4$J$_{HH}$ = 2 Hz, 1H; 1-CH), 6.44 (d, $^4$J$_{HH}$ = 3 Hz, 1H; 8-CH), 6.57 (dd, $^3$J$_{HH}$ = 10 Hz, $^4$J$_{HH}$ = 2 Hz, 1H; 3-CH), 6.88 (dd, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 3 Hz, 1H; 6-CH), 7.05 – 7.12 (m, 4H; 9-(tolyl-o,m-CH)), 7.41 (d, $^3$J$_{HH}$ = 10 Hz, 1H; 4-CH), 7.67 (d, $^3$J$_{HH}$ = 8 Hz, 1H; 5-CH) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ = 21.1 (1C; 9-(tolyl-p-CH$_3$)), 33.4 (1C; 9-CH$_3$), 47.0 (1C; 9-C), 55.7 (1C; 7-OCH$_3$), 112.9 (1C; 6-CH), 114.9 (1C; 8-CH), 128.2 (2C; 9-(tolyl-o-CH)), 129.5 (2C; 9-(tolyl-m-CH)), 130.2 (1C; 1-CH), 131.4 (1C; 3-CH), 133.6 (1C; 5-CH), 137.0 (1C; 11-C), 137.2 (1C; 9-(tolyl-p-C)), 141.0 (1C; 12-C), 141.5 (1C; 4-CH), 142.5 (1C; 9-(tolyl-i-C)), 149.2 (1C; 13-C), 150.1 (1C; 14-C), 161.9 (1C; 7-C), 187.1 (1C; 2-C) ppm. HRMS (DART-TOF+): m/z [M+H]$^+$ 330.15001 (calcd for C$_{22}$H$_{20}$NO$_2$: 330.14940).

3-21 2,7,9-trimethyl-9,10-(di-4-tolyl)-9,10-dihydroacridine

Product was inseparable from a by-product, putatively with two alkyne additions. Partial characterization (65% conversion). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 1.91 (s, 3H; 9-CH$_3$), 2.12 (s, 6H; 2,7-CH$_3$), 2.38 (s, 3H; 9-(tolyl-p-CH$_3$)), 2.49 (s, 3H; N-(tolyl-p-CH$_3$)), 6.19 (d, $^3$J$_{HH}$ = 8 Hz, 2H; 4,5-CH), 6.60 (d, $^4$J$_{HH}$ = 2 Hz, 2H; 1,8-CH), 6.72 (dd, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, 2H; 3,6-CH), 7.13 – 7.17 (m, 2H; 9-(tolyl-o-CH)), 7.21 (dt, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, 2H; N-(tolyl-o-CH)), 7.32 (dt, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, 2H; 9-(tolyl-m-CH)), 7.40 – 7.43 (m, 2H; N-(tolyl-m-CH)) ppm. $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ = 20.7 (2C; 2,7-CH$_3$), 21.2 (1C; 9-(tolyl-p-CH$_3$)), 21.5 (1C; N-(tolyl-p-CH$_3$)), 32.4 (1C; 9-CH$_3$), 45.3 (1C; 9-C), 113.8 (2C; 4,5-CH), 127.1 (2C; 3,6-CH), 128.6 (2C; 9-(tolyl-o-CH)), 129.0 (2C; 9-(tolyl-m-CH)), 129.3 (2C; 1,8-CH), 130.3 (2C; 12,13-CH), 131.2 (2C; N-(tolyl-o-CH)), 131.6 (2C; N-(tolyl-m-CH)), 135.3 (1C; 9-(tolyl-p-C)), 137.9 (1C; N-(tolyl-p-C)), 138.8 (2C; 11,14-CH), 139.0 (1C; N-(tolyl-i-C)), 147.5 (1C; 9-(tolyl-i-C)) ppm. HRMS (DART-TOF+): m/z [M+H]$^+$ 404.23847 (calcd for C$_{30}$H$_{30}$N: 404.23782). By-product HRMS (DART-TOF+): m/z [M+H]$^+$ 520.30039 (calcd for C$_{39}$H$_{38}$N: 520.30042).
2,7,9-trimethyl-9-(4-tolyl)-9\textit{H}-xanthene

Partial characterization (21% conversion). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): $\delta = 1.92$ (s, 3H; 9-CH\textsubscript{3}), 2.21 (s, 6H; 2,7-CH\textsubscript{3}), 6.64 – 6.68 (m, 2H; 1,8-CH), 6.97 – 7.01 (m, 4H) ppm. MS (EI\textsuperscript{+}): [m/z, (\%)] 313.20 ([M-H]\textsuperscript{+}, 100), 314.30 (23.4), 315.20 (2.5).

### 3.10.7 Numbering Convention

![Numbering Convention Diagram]

### 3.10.8 Computational Details

Electronic structure calculations were performed using Gaussian 09.\textsuperscript{64} Geometry optimizations were carried out at the BP86/Def2-TZVP level and each geometry was confirmed to be a minimum on its potential energy surface by confirming the Hessian to be positive definite with a frequency calculation. Orbital and internal energies needed to calculate global electrophilicity indices (GEIs) and fluoride ion affinities (FIAs) were obtained from MP2/Def2-TZVPP calculations at the BP86/Def2-TZVP geometries. FIA and GEI were calculated as previously described.\textsuperscript{57}

### 3.11 References


Section 3.3 - Probing Steric Influences on Electrophilic Phosphonium Cations: A Comparison of [(3,5-(CF₃)₂C₆H₃)₃PF]⁺ and [(C₆F₅)₃PF]⁺

3.12 Steric Variations of Electrophilic Phosphonium Cations

The Stephan group’s interest in main group Lewis acid catalysis has led to the synthesis of a variety of differently substituted EPCs (see Chapter 3, Section 3.1). The principal goals of these variants were to tune catalyst properties by increasing Lewis acidic character while maintaining robustness. Given that more electron withdrawing substituents are understood to make the Lewis acid’s LUMO more accessible to substrate activation, attention was mainly given to the electronic influence of the substituents, with less attention given to their steric influence. One set of sterically varied EPCs drew inspiration from O’Hare and Ashley’s work on Lewis acidic boranes, wherein the steric influence of the substituents was increased by incorporating C₆Cl₅ groups in place of C₆F₅ groups.¹ This resulted in a more robust, but less active Lewis acid due to greater protection of the borane’s Lewis acidic site, the empty p orbital on the boron centre, by the presence of larger ortho-Cl atoms (van der Waals radius: rᵥ = 1.80 Å) in place of ortho-F atoms (rᵥ = 1.35 Å).² The related fluorophosphonium salts bearing C₆Cl₅ groups were therefore synthesized and were also found to be more robust and less Lewis acidic as the EPCs’ σ* orbital became less accessible to substrate activation (Figure 3.20).³

![Diagram of Lewis acidic boranes and EPCs incorporating C₆Cl₅ substituents.](image)

**Figure 3.20** Lewis acidic boranes and EPCs incorporating C₆Cl₅ substituents.
Another set of sterically unencumbered boranes was reported by the groups of Ashley and Wildgoose. In a study evaluating the Lewis acidities of various boranes, the authors found that B((3,5-CF₃)₂C₆H₃)₃ is more Lewis acidic than B(C₆F₅)₃ by the Gutmann-Beckett method, producing Δδ ³¹P NMR shifts of 28.1 and 26.6 ppm, respectively, but less Lewis acidic by an electrochemical one electron reduction, displaying reduction potentials of -1.61 and -1.52 eV vs [FeCp₂]⁰⁺, respectively (Table 3.16). Since the Gutmann-Beckett method requires adduct formation with Et₃PO but an electrochemical one-electron reduction requires no such adduct formation, it was concluded that B((3,5-CF₃)₂C₆H₃)₃ and B(C₆F₅)₃ are similarly Lewis acidic but that they differ in the steric environment about their Lewis acidic sites. The steric difference is again due to changes about ortho-substitutions on the aryl substituents, with the larger ortho-F atoms (rᵥ = 1.35 Å) offering more steric protection of the Lewis acidic p-orbital on B(C₆F₅)₃ than the ortho-H atoms (rᵥ = 1.20 Å) on B((3,5-CF₃)₂C₆H₃)₃. Similar Lewis acid strength is retained in both boranes. This is explained by the Hammett parameter, which creates a free-energy relationship to correlate the electron withdrawing ability of substituents to reaction rates and equilibrium constants for reactions involving benzoic acids substituted at the meta- and para-positions, designated as σₘ and σₚ, respectively. Similar substituent constants are found when comparing the C₆F₅ group (σₘ = 0.34, σₚ = 0.06) to the (3,5-CF₃)₂C₆H₃ group (σₘ = 0.43, σₚ = 0.54), with the C₆F₅ group presumably dominating when the ortho-fluorines are also considered.

<table>
<thead>
<tr>
<th>Compound</th>
<th>G-B method (Δδ, ppm)</th>
<th>E°/V vs [FeCp₂]⁰⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(C₆F₅)₃</td>
<td>26.6</td>
<td>-1.52</td>
</tr>
<tr>
<td>B((3,5-CF₃)₂C₆H₃)₃</td>
<td>28.1</td>
<td>-1.61</td>
</tr>
</tbody>
</table>

The impact of this steric difference has been demonstrated by comparing the catalytic activities of these two boranes. Uozumi found that B((3,5-CF₃)₂C₆H₃)₃ outperforms B(C₆F₅)₃ in the
hydrogenation of aldehydes (Scheme 3.19, top) while Oestreich and Melen\textsuperscript{9} found that B((3,5-CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3} outperforms B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in the hydroboration of imines (Scheme 3.19, bottom). In both studies, differences in catalytic activity were attributed to differences in steric profile of the boranes’ Lewis acidic sites, with the more sterically accessible B((3,5-CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3} proving beneficial.

\begin{equation}
\text{C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}CHO} + 1.5 \text{ eq EtO} \overset{\text{5 mol\% [cat]}}{\xrightarrow{\text{Tol}, 60^\circ \text{C}, 12 \text{ h}}} \text{C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}CH(OH)H}
\end{equation}

\text{B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} = 28\%}

\text{B((3,5-CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3} = 70\%}

\begin{equation}
\text{PhC\textsubscript{6}H\textsubscript{4}C\textsubscript{\equiv}N} + 1.2 \text{ eq pinBOH} \xrightarrow{\text{2 mol\% [cat]}} \text{PhC\textsubscript{6}H\textsubscript{4}C\textsubscript{\equiv}NPh}
\end{equation}

\text{B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} = 36\%}

\text{B((3,5-CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3} = 100\%}

**Scheme 3.19**  Aldehyde transfer hydrogenation (top) and imine hydroboration (bottom) catalyzed by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and B((3,5-CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3}.

Although a wide variety of EPCs have been synthesized, CF\textsubscript{3}-bearing substituents have largely been avoided due to the propensity for EPCs to activate the C-F bond of the trifluoromethyl groups, as demonstrated in the Friedel-Crafts coupling of aryl-CF\textsubscript{3} substrates (Scheme 3.20, top).\textsuperscript{10} As a result, it was believed that fluorophosphonium salts bearing CF\textsubscript{3} groups would be inherently unstable. However, the Stephan group found that a 1,8-disubstituted naphthyl fluorophosphonium salt was stable, with evidence for a C-F bond interacting with the phosphorus’ Lewis acidic site only at low temperature and in the solid state structure (Scheme 3.20, bottom).\textsuperscript{11} Although this naphthyl-substituted EPC has only two electron withdrawing C\textsubscript{6}F\textsubscript{5} groups and is therefore less Lewis acidic than [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}], it is still a reasonably strong Lewis acid that previously would have been thought to directly activate CF\textsubscript{3}-groups.
Taking note of these advances in borane and EPC chemistry, this section explores the steric and electronic influences of the \((3,5\text{-CF}_3)_2\text{C}_6\text{H}_3\) substituent in the salt \([(3,5\text{-CF}_3)_2\text{C}_6\text{H}_3]\text{PF}[\text{B}(\text{C}_6\text{F}_5)_4]\) (3-24) in comparison to \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\). Lewis acidity is evaluated experimentally and computationally, while steric differences are established through a set of 1D Selective EXchange SpectroscopY (SEXSY) NMR experiments. The catalytic competencies of 3-24 and \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\) are directly compared in a number of Lewis-acid mediated reactions, with 3-24 demonstrating superior activity when intermediates are more sterically demanding.

### 3.13 Results and Discussion

#### 3.13.1 Synthesis and Characterization

Synthesis of a fluorophosphonium salt bearing \((3,5\text{-CF}_3)_2\text{C}_6\text{H}_3\) substituents was performed following a similar procedure to that of \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\). The phosphine \((3,5\text{-CF}_3)_2\text{C}_6\text{H}_3)_3\text{P}\) was synthesized from a literature procedure by reaction of the aryl bromide with magnesium and \(\text{PCl}_3\).\(^{12}\) Subsequent reaction of \((3,5\text{-CF}_3)_2\text{C}_6\text{H}_3)_3\text{P}\) with an equivalent of \(\text{XeF}_2\) in DCM at ambient temperature for 1.5 hours produced the corresponding difluorophosphorane \((3,5\text{-CF}_3)_2\text{C}_6\text{H}_3)_3\text{PF}_2\) (3-23) as a white solid in 80% isolated yield (Scheme 3.21). The \(^{19}\text{F}\{^1\text{H}\}\) NMR spectrum of 3-23
shows a doublet at -43 ppm, with the corresponding triplet in the $^{31}\text{P}$$^{1}\text{H}$ NMR at -64 ppm, both with a $J$-coupling of 715 Hz. The $^{19}\text{F}$$^{1}\text{H}$ NMR shows an additional singlet at -63 ppm corresponding to the CF$_3$ groups. These spectroscopic data are consistent with a difluorophosphorane species.$^{3}$, $^{13-15}$ The $^1\text{H}$ NMR spectrum shows a singlet at 8.13 ppm corresponding to the para-$\text{CH}$ protons and a doublet at 8.50 ppm with $J$-coupling of 15 Hz corresponding to the ortho-$\text{CH}$ protons. Crystals suitable for singe crystal X-ray diffraction were grown from n-pentane solution. The diffraction study confirms the formulation of 3-23 and shows that it has trigonal bipyramidal geometry and sits on a special position with two-fold symmetry. This results in equivalent P-F bond lengths of 1.645(1) Å, P-C bond lengths of 1.815(2) Å and 1.822(3) Å, and a F-P-F bond angle of 179.7(1)° (Figure 3.21).

**Scheme 3.21** Synthesis of 2-24 and 2-25.

![Scheme 3.21](image)

**Figure 3.21** ORTEP depiction of 3-23 showing thermal ellipsoids at 50% probability. Hydrogen atoms and minor disorder components omitted. P: orange, C: black, F: spicy pink.
Fluoride abstraction from the phosphorus centre was achieved by reacting 3-23 with [Et₃Si(Tol)][B(C₆F₅)₄] at ambient temperature in toluene for 30 minutes to give, upon workup, the corresponding fluorophosphonium salt [(3,5-(CF₃)₂C₆H₃)₃PF][B(C₆F₅)₄] (3-24) in 60% yield as a salmon-pink solid (Scheme 3.22). The NMR spectra are characteristic for fluorophosphonium salts,³,¹³⁻¹⁵ with doublets in the ¹⁹F{¹H} NMR and ³¹P{¹H} NMR spectra at -128 and 92 ppm, respectively, both with a J-coupling of 1040 Hz. Like 3-23, the ¹H NMR of 3-24 shows a doublet at 8.32 ppm with a J-coupling of 14 Hz and a singlet at 8.75 ppm corresponding to the ortho- and para-CH protons, respectively. While the ortho-CH protons are shifted slightly upfield by 0.18 ppm, the para-CH proton is shifted downfield by 0.62 ppm. This shift is analogous to that observed by ¹⁹F{¹H} NMR for the C₆F₅ groups in the series of phenoxyphosphonium salts 3-1 to 3-4 and is therefore consistent with the presence of a positive charge on the phosphorus centre. It is noteworthy that no fluoride abstraction from a CF₃ group is apparent, as the only other signals in the ¹⁹F{¹H} NMR correspond to the CF₃ groups and to the [B(C₆F₅)₄]⁻ anion. Recrystallization by layering benzene over a concentrated DCM solution at ambient temperature afforded crystals suitable for single crystal X-ray diffraction (Figure 3.22). The diffraction study confirms the formulation of 3-24 and shows that the asymmetric unit contains three molecular formulae, with each fluorophosphonium cation in a pseudo-tetrahedral geometry having contracted P-F bond lengths of 1.537(7) Å, 1.542(7) Å, and 1.556(9) Å. These data are consistent with the presence of a positive charge on the phosphorus centre.

**Figure 3.22** ORTEP depiction of 3-24 showing thermal ellipsoids at 50% probability. Hydrogen atoms, counterion, solvents, and minor disorder components omitted. P: orange, C: black, F: spicy pink.

### 3.13.2 Moisture Tolerance

To assess robustness, the air stability of 3-24 was evaluated with the same method used for the phenoxyphosphonium salts 3-1 to 3-4. Namely, a solution of the salt in DCM was added to an NMR tube, exposed to air for varying periods of time, and monitored by NMR spectroscopy. The onset of decomposition of 3-24 to a mixture of 3-23 and the phosphine oxide (3,5-(CF₃)₂C₆H₃)₃PO¹⁶ became apparent after only 1 minute of air exposure, with significant decomposition seen after 5 minutes (Figure 3.23). This indicates that 3-24 is no more robust than [(C₆F₅)₃PF][B(C₆F₅)₄]. However, this is expected as moisture decomposition proceeds through water coordination to the Lewis acidic site which is less sterically protected in 3-24 than in [(C₆F₅)₃PF][B(C₆F₅)₄].
Lewis Acidity Measurements

Computations were performed at the MP2/Def2-TZVPP//BP86/Def2-TZVP level of theory to verify that the Lewis acidic site of the cation of 3-24 is analogous to that of \([\text{C}_6\text{F}_5\text{PF}]^+\). By modelling the natural atomic charges, the phosphorus atom was found to carry most of the cationic charge (Figure 3.24, top left). Next, by evaluating natural population analyses, performed using NBO 6.0, the LUMO was seen to display a significant lobe oriented opposite the P-F bond (Figure 3.24, top right). Finally, the \(f^+_{(\rho)}\) Fukui function of the difference between the LUMO and the LUMO plus one electron, evaluated using MultiWFN 3.3.8, depicts the largest lobe oriented opposite the P-F bond (Figure 3.24, bottom). Together, these results strongly indicate that the cation of 3-24 derives its Lewis acidity from the \(\sigma^*\) orbital located opposite the P-F bond in an analogous manner to \([\text{C}_6\text{F}_5\text{PF}]^+\).
Figure 3.24  Colour-coded natural atomic charges for the cation of 3-24 (top left). Surface contour plot (isovalue 0.03) of the LUMO of the cation of 3-24 (top right). Surface contour plot (isovalue 0.0015) of the $f^*(\rho)$ Fukui function of the cation of 3-24 (bottom). Hydrogen atoms omitted for clarity. For surface contour plots: P: orange, O: red, C: black, F: pink.

To investigate steric differences about the Lewis acidic sites, space filling plots of the cation of 3-24 and of [(C$_6$F$_3$)$_3$PF]$^+$ were compared using the van der Waals radii (Figure 3.25). From these, the steric influences of the C$_6$F$_3$ and 3,5-(CF$_3$)$_2$C$_6$H$_3$ substituents are qualitatively apparent, with the former offering significantly more steric protection about the phosphorus centre than the latter.
Next, the Lewis acidity of 3-24 was gauged through the experimental and computational methods outlined in Chapter 2, Section 1. The Gutmann-Beckett method produced only minimal adduct formation as characterized by a resonance at 73.0 ppm. The major species observed were \([\text{Et}_3\text{PF}][\text{B(C}_6\text{F}_5)_4]\) and \((3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)\text{PO}^{16}\) with signals at 147.3 and 21.3 ppm, respectively, consistent with fluoride-oxide exchange (Scheme 3.23, Figure 3.26). Similar results have been
observed for particularly Lewis acidic or oxophilic EPCs including [(SIMes)Ph2PCI][B(C6F5)4]2\textsuperscript{19}
which prompted the use of this EPC as a catalyst in the deoxygenation of ketones,\textsuperscript{20} amides,\textsuperscript{21}
and phosphine oxides.\textsuperscript{22} However, given that the borane analogues B((3,5-CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3} and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}
are similarly strong Lewis acids\textsuperscript{5} and that [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] is amenable to the Gutmann-Beckett method,\textsuperscript{13} it is unlikely that fluoride-oxide exchange of 3-24 is due to a significant increase
in Lewis acidity. Instead, it is likely due to decreased steric protection about the Lewis acidic site
resulting in a much stronger interaction between the phosphorus centre on 3-24 and the oxygen
atom of Et\textsubscript{3}PO. Although some adduct formation is observed, side reactions make the Gutmann-Beckett test an inappropriate measure of Lewis acidity for 3-24.

**Scheme 3.23** Gutmann-Beckett test of 3-24.

**Figure 3.26** \textsuperscript{31}P\textsubscript{1}H NMR spectrum (DCM) of Gutmann-Beckett test with 3-24 showing fluoride-oxide exchange between 3-24 and Et\textsubscript{3}PO.

Turning attention to computational measures of Lewis acidity, the fluoride ion affinity (FIA) and
global electrophilicity index (GEI) of the cation of 3-24 were evaluated using MP2/Def2-TZVPP//BP86/Def2-TZVP, as outlined in a benchmarking study reported by the Stephan group
According to the FIA calculations, the cation of 3-24 and [(C₆F₅)₃PF]⁺ are similarly Lewis acidic, having values of 771 and 779 kJ/mol, respectively. A similar result is observed when evaluating GEI, with the cation of 3-24 and [(C₆F₅)₃PF]⁺ producing values of 3.41 and 3.62 eV, respectively. By comparing to B(C₆F₅)₃ which has FIA and GEI values of 453 kJ/mol and 1.41 eV, respectively, the cation of 3-24 is only slightly less Lewis acidic than [(C₆F₅)₃PF]⁺ but is still significantly more Lewis acidic than B(C₆F₅)₃.

**Table 3.17** Results of Gutmann-Beckett method, fluoride ion affinity, and global electrophilicity index for 3-24 and its cation, [(C₆F₅)₃PF][B(C₆F₅)₄] and its cation, and B(C₆F₅)₃.

<table>
<thead>
<tr>
<th>Compound</th>
<th>G-B test (Δδ, ppm)</th>
<th>FIA (kJ mol⁻¹)</th>
<th>GEI (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-24</td>
<td>F – O exchange</td>
<td>771</td>
<td>3.41</td>
</tr>
<tr>
<td>[(C₆F₅)₃PF][B(C₆F₅)₄]</td>
<td>40.0</td>
<td>779</td>
<td>3.62</td>
</tr>
<tr>
<td>B(C₆F₅)₃</td>
<td>26.6</td>
<td>471</td>
<td>1.36</td>
</tr>
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</table>

Given that the cation of 3-24 and [(C₆F₅)₃PF]⁺ display quite similar Lewis acidities computationally, other means were sought out to establish which is the more Lewis acidic species. One method to determine the relative Lewis acidities of two species is to directly compare them in a competition reaction. For EPCs, competition reactions are performed by mixing the fluorophosphonium salt of one EPC with an equimolar amount of the difluorophosphorane of another EPC.¹⁹,²⁴ At equilibrium, the more Lewis acidic EPC persists as the difluorophosphorane because it binds to a second fluoride more favourably, while the weaker Lewis acid persists as the fluorophosphonium salt. Mixing [(C₆F₅)₃PF][B(C₆F₅)₄] with 3-24 in DCM at ambient temperature, allowing the solution to equilibrate for 24 hours, and monitoring by ¹⁹F{¹H} NMR spectroscopy revealed a 63:37 ratio of (C₆F₅)₃PF₂ / 3-23 according to integrations of the PF₂ signals (Scheme 3.24, top; Figure 3.27). Performing the complimentary experiment with (C₆F₅)₃PF₂ and 3-24 produced a similar ratio of 72:28 of (C₆F₅)₃PF₂ / 3-23 (Scheme 3.24, bottom; Figure 3.27). Although there is a clear thermodynamic bias towards (C₆F₅)₃PF₂ when reaching equilibrium, a significant amount of 3-23 does persist. These data are consistent with the computationally derived FIA and GEI values for the cation of 3-24 and for [(C₆F₅)₃PF]⁺, confirming that 3-24 is in fact slightly less Lewis acidic.
Scheme 3.24  Competition experiments between C₆F₅- (top) and the (3,5-CF₃)₂C₆H₃-substituted (bottom) fluorophosphonium salts and difluorophosphoranes.

Figure 3.27  $^{19}$F [$^1$H] NMR (DCM) spectrum of reaction mixture of [(C₆F₅)₃PF][B(C₆F₅)₄] and 3-23 at equilibrium (top) and 3-24 and (C₆F₅)₃PF₂ at equilibrium (bottom).
Having established the Lewis acidic strength of 3-24, the steric environment about the Lewis acidic site was probed experimentally with a set of self-exchange reactions. In a competition reaction, the fluorophosphonium salt and the difluorophosphorane are differently substituted, so there is a thermodynamic bias to one side of the reaction. By contrast, a self-exchange reaction using a fluorophosphonium salt and a difluorophosphorane with the same substitutions eliminates the thermodynamic difference between starting materials and products. Therefore, a difference in reactivity observed in self-exchange reactions speaks to a kinetic difference – in this case, given the quite similar Lewis acidities established above, a difference would result in large part from differing steric environments around the Lewis acidic sites imparted by the equatorial substituents. Reactivity in this context is assessed by observing the rate of exchange of the second fluoride between a difluorophosphorane and its fluorophosphonium salt. By comparing the rates of exchange of the C₆F₅- with the (3,5-CF₃)₂C₆H₃-substituted system, the steric impacts of C₆F₅ and (3,5-CF₃)₂C₆H₃ groups can be directly compared (Scheme 3.25).

**Scheme 3.25** Self-exchange reactions of the C₆F₅- (top) and the (3,5-CF₃)₂C₆H₃-substituted (bottom) fluorophosphonium salts and difluorophosphoranes.

These rates can be measured experimentally by gathering ¹⁹F-¹⁹F EXchange SpectroscopY (EXSY) NMR data from ¹⁹F-¹⁹F Nuclear Overhauser Effect SpectroscopY (NOESY) NMR spectroscopy. In a 2D ¹⁹F-¹⁹F NOESY experiment, each fluorine signal has a cross peak with itself, forming a diagonal line across the spectrum, with peaks above and below the diagonal line corresponding to other interactions. Peaks shown as blue dots arise from through-space NOESY interactions between fluorines on the same molecule while peaks shown as orange dots arise from
EXSY interactions, wherein the fluorine signals of the fluorophosphonium and the difluorophosphorane interconvert during the mixing time of the NMR experiment. In the 2D $^{19}$F-$^{19}$F NOESY NMR spectrum of an equimolar mixture of [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] and (C$_6$F$_5$)$_3$PF$_2$ (Figure 3.28), blue NOESY cross peaks are observed between the ortho-, meta-, and para-CF signals for the C$_6$F$_5$ rings. Additional orange EXSY cross peaks are observed between the ortho-, meta-, and para-CF signals of the C$_6$F$_5$ rings on [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] and (C$_6$F$_5$)$_3$PF$_2$, arising from the exchange of the second fluoride from the difluorophosphorane to the fluorophosphonium salt. As exemplified in blue and orange boxes, the meta-CF of (C$_6$F$_5$)$_3$PF$_2$ (blue box) becomes the meta-CF of [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] (orange box) and vice versa during the mixing time of this 2D $^{19}$F-$^{19}$F EXSY NMR experiment.

![2D $^{19}$F-$^{19}$F NOESY NMR (DCM) spectrum of an equimolar mixture of [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] and (C$_6$F$_5$)$_3$PF$_2$.](image)

**Figure 3.28** 2D $^{19}$F-$^{19}$F NOESY NMR (DCM) spectrum of an equimolar mixture of [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] and (C$_6$F$_5$)$_3$PF$_2$.

Having shown that these self-exchange reactions function on a suitable timescale for $^{19}$F-$^{19}$F EXSY, the amount of self-exchange could then be quantified. This was done with 1D Selective EXchange SpectroscopY (1D SEXSY) NMR experiments, wherein a signal that displays an
EXSY cross peak is selectively irradiated and its relaxation is measured with different mixing times. By convention, the irradiated peak (AA) and SEXSY interactions of that peak (AB) are negatively-phased while NOESY interactions of that peak are positively-phased. The degree to which the parent signal undergoes exchange is determined by integrating the 1D SEXSY NMR exchange peak relative to the irradiated peak at each mixing time (τ). Integrations and mixing times can then be related to the reaction rate constant by Equation 3-7, which can be simplified under the linear regression approximation to Equation 3-8. A plot of 2τ versus ln(1+(AB/[AA])) gives a straight line, the slope of which is the inverse of the reaction rate constant.

\[
\frac{[AA]}{[AB]} = \frac{(1-2k^2)(1-e^{-2k\tau})}{(2k^2+(1-2k^2)(e^{-2k\tau})} \quad \text{Eqn 3-7}
\]

\[
2\tau = \frac{1}{k} \ln \left( 1 + \left( \frac{[AB]}{[AA]} \right) \right) \quad \text{Eqn 3-8}
\]

A set of 1D $^{19}$F SEXSY NMR spectra were taken probing the meta-CF$_3$ signal of a mixture of 3-23 and 3-24 with mixing times of 0.05 s, 0.1 s, 0.2 s, 0.25 s, 0.3 s, and 0.4 s. Integrations from the resulting spectra (Figure 3.29) were used to plot a graph of 2τ versus ln(1+(AB/[AA])) with a well-modelled linear fit of $R^2 = 0.998$ (Figure 3.30). Taking the inverse of the slope, the rate constant of this self-exchange reaction was found to be 0.18 s$^{-1}$. Performing the same experiment on the meta-CF signal of a mixture of [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] and (C$_6$F$_5$)$_3$PF$_2$ (Figure 3.31) and plotting the data linearly with a fit of $R^2 = 0.986$ (Figure 3.32), the rate constant is found to be 0.0057 s$^{-1}$. These experiments show that the (3,5-CF$_3$)$_2$C$_6$H$_3$-substituted system exchanges a fluoride 32 times faster than the C$_6$F$_5$-substituted system, demonstrating that the Lewis acidic site of 3-24 is significantly more sterically accessible than that of [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$].
Figure 3.29 Stack of 1D $^{19}$F SEXSY NMR (DCM) spectra with varying mixing times for an equimolar mixture of 3-23 and 3-24.

Figure 3.30 Graph of $2\tau$ versus $\ln(1+([AB]/[AA]))$ for an equimolar mixture of 3-23 and 3-24.
Figure 3.31 Stack of 1D $^{19}$F SEXSY NMR (DCM) spectra with varying mixing times for an equimolar mixture of $(C_6F_5)_3PF_2$ and $[(C_6F_5)_3PF][B(C_6F_5)_4]$.

Figure 3.32 Graph of $2\tau$ versus $\ln(1+([AB]/[AA]))$ for an equimolar mixture of $(C_6F_5)_3PF_2$ and $[(C_6F_5)_3PF][B(C_6F_5)_4]$.

3.13.4 Lewis Acid Reactivity

Having established the Lewis acidity and steric accessibility of 3-24 with respect to $[(C_6F_5)_3PF][B(C_6F_5)_4]$, their Lewis acid reactivities were compared. Given that a significant portion of EPC-catalyzed reactions involve $Et_3SiH$, a control reaction was performed with $Et_3SiH$ and a catalytic amount of 3-24. Unfortunately, significant catalyst degradation was observed by $^{19}$F{$^1$H} NMR spectroscopy, as characterized by loss of the P-F doublet signal and
emergence of a singlet at -176 ppm corresponding to Et$_3$SiF. This result of Si-H bond activation prompting P-F bond cleavage is reminiscent of fluoride-oxide exchange observed in the Gutmann-Beckett method and is therefore unsurprising given the significant steric accessibility of the Lewis acidic site on 3-24. While replacing Et$_3$SiH with the more sterically encumbered iPr$_3$SiH showed no immediate decomposition of 3-24, it also proved too encumbered for productive chemistry, as no conversion was observed in the hydrosilylation of benzophenone or of α-methylstyrene, even when heated to 70 °C for 24 hours. Replacing hydridic silane with hydridic borane reagents including HB(C$_6$F$_5$)$_2$, H$_2$B(C$_6$F$_5$)$_3$, 9-BBN, HBcat, or HBpin resulted in decomposition in all cases. As a result, catalysis involving hydridic silane or borane sources was avoided.

The remaining Lewis acid catalysis that has already been established for EPCs was limited to Friedel-Crafts-type reactions. The dimerization of 1,1-diphenylethylene with 1 mol% catalyst in DCM for 30 min at ambient temperature resulted in 78% and 86% conversion to the dimer 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene for 3-24 and [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$], respectively (Scheme 3.26, top). The hydroarylation of Ph$_2$NH with 1,1-diphenylethylene and 1 mol% catalyst in DCM for 6 h at ambient temperature resulted in 84% and >99% conversion to the hydroarylated product 4-(1,1-diphenylethyl)-N-phenylaniline for 3-24 and [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$], respectively (Scheme 3.26, middle). In both of these cases, [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] outperforms 3-24 by a significant margin, likely owing to its greater Lewis acidity. By contrast, the double hydroarylation of (4-Tol)$_2$NH with (4-Tol)C≡CH and 5 mol% catalyst in DCM for 24 h at ambient temperature produced the acridane-type product 3-6 in 91% and 74% conversions for 3-24 and [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$], respectively (Scheme 3.26, bottom).
Revisiting the proposed mechanism for the double hydroarylation reaction (Scheme 3.27), two reaction intermediates stand out as being particularly sterically demanding and are highlighted in red. Indeed, in the investigation of this reaction (see Chapter 3 - Section 3.2), the steric burden of the MesC≡CH substrate resulted in the exclusive production of the singly hydroarylated product. Given this and the evidence for the greater steric accessibility of 3-24 with respect to [(C₆F₅)₃PF][B(C₆F₅)₄], it is reasonable to attribute differences in catalytic activity towards this reaction to differences in steric accessibility of the EPCs’ Lewis acidic sites, despite [(C₆F₅)₃PF][B(C₆F₅)₄] being a stronger Lewis acid.

**Scheme 3.26** Lewis acid reactions catalyzed by [(C₆F₅)₃PF][B(C₆F₅)₄] and 3-24.
Scheme 3.27  Proposed mechanistic cycle for the double hydroarylation reaction with sterically demanding steps denoted in red.

3.14 Conclusion

A sterically unencumbered fluorophosphonium salt \([(3,5-(CF_3)_2C_6H_3)_3PF][B(C_6F_5)_4]\) (3-24) was synthesized and compared to \([(C_6F_5)_3PF][B(C_6F_5)_4]\) using a number of metrics. The moisture tolerance of 3-24 was found to be similar to that of \([(C_6F_5)_3PF][B(C_6F_5)_4]\), as was its site of Lewis acidity. The extent of Lewis acidity of 3-24, evaluated computationally using FIA and GEI and experimentally though competition experiments with the \(C_6F_5\)-substituted analogue, was found to be only slightly weaker than \([C_6F_5]_3PF][B(C_6F_5)_4]\). The Gutmann-Beckett method was also attempted but fluoride-oxide exchange precluded its usefulness in assessing Lewis acid strength. Steric differences between 3-24 and \([C_6F_5]_3PF][B(C_6F_5)_4]\ were assessed qualitatively with space filling models using van der Waals radii of the cation of each EPC and quantitatively using 1D \(^{19}F\) SEXSY NMR spectroscopy, with 3-24 undergoing a significantly faster self-exchange reaction due to decreased sterics about its Lewis acidic site. This steric difference was borne out in the application of both EPCs as Lewis acid catalysts in a sterically demanding reaction.
3.15 Experimental

3.15.1 General Experimental Methods

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N\textsubscript{2}. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (dichloromethane, diethyl ether, and \textit{n}-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone under inert atmosphere. CD\textsubscript{2}Cl\textsubscript{2} (Aldrich) was deoxygenated, distilled over CaH\textsubscript{2}, then stored over 3 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals, or Alfa Aesar, and were used without further purification unless indicated otherwise. \((3,5-\text{(CF}_3\text{)}_2\text{C}_6\text{H}_3)_3\text{P}\)\textsuperscript{12} and \([(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]\)\textsuperscript{13} were prepared according to literature procedures.

NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz or a Varian Mercury-300 MHz spectrometer. \(^1\text{H}, \ ^{13}\text{C}\{^{1}\text{H}\}, \ ^{31}\text{P}\{^{1}\text{H}\}, \ ^{19}\text{F}, \text{ and }^{11}\text{B}\{^{1}\text{H}\} \) NMR chemical shifts (\(\delta/\text{ppm}\)) are referenced to Me\textsubscript{4}Si, Me\textsubscript{4}Si, H\textsubscript{3}PO\textsubscript{4}, CFCl\textsubscript{3}, and BF\textsubscript{3}•OEt\textsubscript{2}, respectively. Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on a GCT Premier (EI), 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.

3.15.2 X-ray Diffraction Studies

Single crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-K\textsubscript{\alpha} radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.
Table 3.18  X-ray table for 3-23 and 3-24.

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3.15.3  Computational Details

Electronic structure calculations were performed using Gaussian 16. Geometry optimizations for were carried out at the BP86/Def2-TZVP level and each geometry was confirmed to be a minimum on its potential energy surface by confirming the Hessian to be positive definite with a frequency calculation. The Cartesian coordinates of the optimized structures are collected in Tables 1-8. Orbital and internal energies needed to calculate global electrophilicity indices (GEIs) and fluoride ion affinities (FIAs) were obtained from MP2/Def2-TZVPP calculations at the BP86/Def2-TZVP geometries. FIA and GEI were calculated as previously described.
3.15.4 Synthesis of 3,5-(CF$_3$)$_2$C$_6$H$_3$-substituted difluorophosphorane and fluorophosphonium salt

(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$PF$_2$

A solution of (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$P (50 mg, 0.075 mmol) in 5 mL of dichloromethane was added to XeF$_2$ (12.7 mg, 0.075 mmol) in 5 mL of dichloromethane. The reaction was allowed to stir for 1.5 hours at ambient temperature. The solvent was removed in vacuo and the resulting solid was recrystallized from cold n-pentane. The colourless crystals were washed with cold n-pentane (3 x 2 mL) and dried in vacuo to afford a white solid (42.3 mg, 80% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 8.13 (s, 3H; p-C$_6$H$_3$), 8.50 (d, $^3$J$_{PH}$ = 15 Hz, 6H; o-C$_6$H$_3$) ppm. $^{19}$F($^1$H) NMR (377 MHz, CDCl$_3$): $\delta$ = -43.3 (d, $^1$J$_{PF}$ = 715 Hz, 2F; PF$_2$), -63.3 (s, 18F; CF$_3$) ppm. $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$): $\delta$ = -63.6 (t, $^1$J$_{PF}$ = 715 Hz) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ = 122.7 (dq, $^1$J$_{FC}$ = 274 Hz, $^4$J$_{PC}$ = 2 Hz, 6C; CF$_3$), 126.9 – 127.1 (m, 3C; p-C$_6$H$_3$), 132.8 (dq, $^2$J$_{PC}$ = 34 Hz, $^3$J$_{PC}$ = 18 Hz, 6C; m-C$_6$H$_3$), 135.0 – 135.4 (m, 6C; o-C$_6$H$_3$), 136.5 (dt, $^1$J$_{PC}$ = 191 Hz, $^2$J$_{FC}$ = 31 Hz, 3C; i-C$_6$H$_3$) ppm. MS (EI-TOF+): m/z 707.0 (calcd for [(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_2$(3,5-(CF$_3$)$_2$C$_6$H$_2$)PF$_2$]+: 707.0). EA: calcd (%) for C$_{24}$H$_9$F$_{20}$P: C, 40.70; H, 1.28; found: C, 39.78; H, 1.20.

[(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$PF][B(C$_6$F$_5$)$_4$]

A solution of (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$PF$_2$ (71 mg, 0.10 mmol) in toluene (3 mL) was added to a slurry of [Et$_3$Si][B(C$_6$F$_5$)$_4$] (84 mg, 0.095 mmol) in toluene (3 mL). The suspension was stirred for 30 min at ambient temperature before n-pentane (10 mL) was added to fully precipitate the product. The supernatant was decanted yielding an orange solid. This was washed with a cold 1:1 mixture of n-pentane : dichloromethane, filtered, and dried in vacuo to afford a pale orange solid (78 mg, 60% yield). Single crystals of X-ray diffraction quality were grown from a concentrated solution in dichloromethane layered with n-pentane. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ = 8.32 (d, $^3$J$_{PH}$ = 14 Hz, 6H; o-C$_6$H$_3$), 8.75 (s, 3H; p-C$_6$H$_3$) ppm. $^{11}$B($^1$H) NMR (128 MHz, CD$_2$Cl$_2$): $\delta$ = -17.0 (s) ppm. $^{19}$F($^1$H) NMR (377 MHz, CD$_2$Cl$_2$): $\delta$ = -63.7 (s, 18F; CF$_3$), -128.4 (d, $^1$J$_{PF}$ = 1025 Hz, 1F;
PF), -133.2 (s(br), 8F; B(o-C₆F₅)₄), -163.9 (t, 3J_FF = 20 Hz, 4F; B(p-C₆F₅)₄), -167.8 (t, 3J_FF = 17 Hz, 8F; B(m-C₆F₅)₄) ppm. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ = 91.6 (d, ¹J_PP = 1025 Hz) ppm.

¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ = 116.7 (dd, ¹J_PC = 113 Hz, ²J_FC = 14 Hz, 3C; i-C₆H₃), 121.7 (dq, ¹J_FC = 275 Hz, ²J_FC = 2 Hz, 6C; CF₃), 134.3 (s(br), 3C; o-C₆H₃), 134.4 (s(br), 3C; o-C₆H₃), 135.0 (s(br), 4J_PC = 2 Hz, 6C; m-C₆H₃), 136.7 (d(br), ¹J_FC = 245 Hz, 8C; B(o-C₆F₅)₄), 138.9 (d(br), ¹J_FC = 245 Hz, 4C; B(p-C₆F₅)₄), 148.4 (d(br), ¹J_FC = 245 Hz, 8C; B(m-C₆F₅)₄) ppm. HRMS (DART-TOF+): m/z 689.01310 (calcd for [(3,5-(CF₃)₂C₆H₅)₃PF][B(C₂H₅)₄]: 689.01385). EA: calcd (%) for C₄₈H₉BF₃9P: C, 42.13; H, 0.66; found: C, 43.03; H, 0.90.

3.15.5 Gutmann-Beckett Test

In a 20 mL vial, a solution of 3-24 (0.02 mmol) was prepared in 0.6 mL DCM and added to a separate vial containing Et₃PO (0.02 mmol). The solution was transferred to an NMR tube and monitored by ³¹P{¹H} and ¹⁹F{¹H} NMR spectroscopy. After 1 h at ambient temperature the spectra indicate some coordination of Et₃PO and fluoride-oxide exchange to form [(C₂H₅)₃PF][B(C₆F₅)₄] and (3,5-(CF₃)₂C₆H₅)₃PO₁⁶.

3.15.6 Air Stability Test

In a 20 mL vial, a solution of 3-24 (0.02 mmol) was prepared in 0.6 mL DCM. The solution was transferred to an NMR tube and exposed to atmospheric moisture for specific amounts of time. The decomposition was monitored by ¹⁹F{¹H} NMR spectroscopy.

3.15.7 Silane and Borane Stability Tests

In a 20 mL vial, a solution of 3-24 (0.02 mmol) and the given silane or borane (0.2 mmol) was prepared in 0.6 mL DCM and the reaction mixture was left to stir for 16 hours. The solution was then transferred to an NMR tube. Stability was monitored by ¹⁹F{¹H} NMR spectroscopy.

3.15.8 Phosphorane/Phosphonium Exchange Experiments

In a 20 mL vial, a solution of phosphonium salt (0.01 mmol, 1 eq.) was prepared in 0.6 mL DCM. A solution of difluorophosphorane (0.01 mmol, 1 eq.) prepared in 0.6 mL DCM was added and the reaction mixture was left to stir for 24 hours. The solution was then transferred to an NMR tube. Conversions were determined by ¹⁹F{¹H} NMR spectroscopy.
3.15.9 Phosphonium/Phosphorane Self-Exchange Experiments

In a 20 mL vial, a solution of phosphonium salt (0.01 mmol, 1 eq.) was prepared in 0.6 mL DCM. A solution of difluorophosphorane (0.01 mmol, 1 eq.) prepared in 0.6 mL DCM was added. The solution was then transferred to an NMR tube. Self-exchange was monitored by $^{19}$F-$^{19}$F NOESY spectroscopy with mixing times ranging from 50 to 400 ms. The data were evaluated using Equation 3-7 which was simplified to the linearized Equation 3-8. Here, $[AA]$ and $[AB]$ are the irradiated peak and cross-peak, respectively, $\tau$ is the mixing time, and $k$ is the rate constant of the exchange reaction.

\[
\frac{[AA]}{[AB]} = \frac{(1-2k^2)(1-e^{-2k\tau})}{2k^2+(1-2k^2)(e^{-2k\tau})} \quad \text{Eqn 3-7}
\]

\[
2\tau = \frac{1}{k}\ln \left(1 + \left(\frac{[AB]}{[AA]}\right)\right) \quad \text{Eqn 3-8}
\]

3.15.10 Lewis Acid Catalysis

3.15.10.1 Dimerization of 1,1-diphenylethylene

In a 20 mL vial, a solution of 3-24 (1 mol%) was prepared in 1 mL DCM. 1,1-diphenylethylene (0.2 mmol) was added at ambient temperature and the reaction mixture was left to stir for 30 min. The solution was then dried in vacuo and re-dissolved in 0.6 mL CDCl$_3$ affording a pale green solution. Conversions were determined by $^1$H NMR spectroscopy. Product $^1$H NMR spectrum is consistent with reference a spectrum.$^{31}$

3.15.11 Hydroarylation of Ph$_2$NH with 1,1'-diphenylethylene

In a 20 mL vial, a solution of 3-24 (1.5 mol%) was prepared in 1 mL DCM. 1,1-diphenylethylene (30.0 mg, 0.17 mmol, 1 eq.) and Ph$_2$NH (29.0 mg, 0.17 mmol, 1 eq.) were added at ambient temperature and the reaction mixture was left to stir for 6 h. The solution was then dried in vacuo and re-dissolved in 0.6 mL CDCl$_3$. Product $^1$H NMR spectrum is consistent with a reference spectrum.$^{32}$

3.15.12 Hydroarylation of (4-Tol)$_2$NH with (4-Tol)C≡CH

In a 20 mL vial, a solution of the phosphonium catalyst (5 mol%) was prepared in DCM (3 mL). A solution of (4-Tol)$_2$NH (16.0 mg, 0.08 mmol, 1.0 eq.) in DCM (3 mL) was added at ambient
temperature. The mixture was briefly stirred and then a solution of (4-Tol)C≡CH (9.4 mg, 0.08 mmol, 1.0 eq.) in DCM (3 mL) was added. The reaction mixture was stirred at ambient temperature for 24 h. The solution was then dried \textit{in vacuo}. Acid catalyst was removed by dissolving the residue in a 2:1 mixture of DCM / \textit{n}-pentane and filtering over a silica plug. Conversion was determined by GC-MS. Product $^1$H NMR spectra are consistent with reference a spectrum.\textsuperscript{33}

3.16 References


Chapter 4
Phosphorus Coordination Chemistry in Catalysis: Air Stable P(III)-Dications as Lewis Acid Catalysts for the Allylation of C-F Bonds

4.1 Main Group Coordination Chemistry

The Stephan group’s interest in the development of new phosphorus-based Lewis acid catalysts for organic transformations initially led to the development of electrophilic phosphonium cations (EPCs) featuring a highly-reactive cationic P(V) centre substituted with electron withdrawing substituents ([R_3PX]⁺).1-4 Substitutional variants of the initial EPCs have now been used to effect catalytic hydrodefluorination,4 hydroarylation,5, 6 hydrogenation,7 dehydrocoupling,8 olefin polymerization,9 hydrosilylation,9 C-C cross-coupling,10,11 Diels-Alder reactions,12 and Nazarov cyclizations.12 Despite their high activity, obstacles such as the need for specialized substituents (e.g. C₆F₅, pyridinium, NHC, etc.) to impart electrophilicity, very strong oxidants (e.g. XeF₂) to access the +5 oxidation state, and a high sensitivity to atmospheric moisture prevent their broader adoption as useful catalysts. Although significant efforts have been made to address the issue of stability (see Chapter 3, Section 3.1), these have been only moderately successful. Attention has recently changed to other Lewis acidic phosphorus-containing motifs.

The Stephan group’s most recent venture into Lewis acidic phosphorus complexes takes inspiration from the decades of research developments and large libraries established for transition-metal catalyst systems. Such coordination-driven chemistry was envisioned to be fruitful in p-block Lewis acid design as it could yield complexes that are not only highly electrophilic but also highly tunable. The use of coordinating ligands and cationic charge, rather than heavily electron withdrawing substituents and high oxidation states, could provide a means of simultaneously increasing electrophilicity and tuning the steric profile of the catalytic site. Coordination chemistry is not entirely new to p-block element-based catalysts, although its applications have thus far been limited (see Chapter 1). Burford has applied coordination chemistry principles to access a broad array of electrophilic polycations by stepwise replacement of anionic substituents on a P(III) centre with neutral ligands.13-20 The operationally simple and versatile methodology of combining a P(III) halide, a ligand, and a halide abstractor such as TMSOTf, AlCl₃, or AgOTf has yielded a diverse family of polycationic coordination complexes.14, 15, 21-23
The synthesis of tricationic P(III) complexes stabilized by bipyridine ligands was recently reported.\textsuperscript{24} Although the high electrophilicity of these species is desirable from the perspective of Lewis acid catalysis, they also proved to be potent oxidants as demonstrated by the oxidation of 1,4-cyclohexadiene or \( \text{H}_2 \) to yield protons, with concomitant ligand loss (Scheme 4.1). Given that such redox chemistry and ligand decomposition might have a deleterious effect on catalysis, less charged, or less reactive, species may be required for well-defined reactivity. Vidović has recently reported carbodicarbene complexes of the [PhP]\(^{2+} \) dication and showed their high electrophilicity in spite of the reduced molecular charge.\textsuperscript{25-27}

![Scheme 4.1](image)

**Scheme 4.1** Decomposition of \([\text{tBu-bpy})_2\text{P}][\text{OTf}]_3\) from oxidation by 1,4-cyclohexadiene.

The Stephan group has opted to modify Burford’s and Vidovic’s approaches to prepare ligand-stabilized complexes of the [PhP]\(^{2+} \) dication. The synthesis of salts \([\text{tBu-bpy})\text{PPh}][\text{X}]_2\) (\( \text{X} = \text{B(C}_6\text{F}_5)_4 \) (4-1) or OTf), and \([(\text{terpy})\text{PPh})][\text{X}]_2\) (\( \text{X} = \text{B(C}_6\text{F}_5)_4 \) (4-2) or OTf) was reported previously from the combination of commercially available \( \text{PhPCl}_2, \text{KB(C}_6\text{F}_5)_4, \text{or TMSOTf} \), and 4,4’-di-\text{tert}-butyl-2,2’-bipyridyl (i.e. \text{tBu-bpy}) or 2,2’:6’,2’’-terpyridine (i.e. terpy), accompanied by structural authentication of the triflate salts (Scheme 4.2).\textsuperscript{28} The cations of 4-1 and 4-2 feature a dicationic P(III) centre supported by a bipyridine or terpyridine ligand. The choice of tridentate pyridinoid ligands was prompted by the greater stability of chelating ligands that is well known from transition metal coordination chemistry. The solid-state structures of both triflate salts show orientation of a triflate oxygen atom towards the phosphorus centre at distances of 3.268(2) and 3.309(2) Å for \([\text{tBu-bpy})\text{PPh}][\text{OTf}]_2\) and \([(\text{terpy})\text{PPh})][\text{OTf}]_2\), respectively, both of which are within the sum of the van der Waals radii for P and O (3.32 Å), implying that the phosphorus is
the site of Lewis acid reactivity. The cations were also investigated computationally with Gaussian 09 at the PBE1PBE/cc-pVTZ level of theory using Grimme’s D3 dispersion correction, which demonstrated that, while ligand coordination necessarily quenches some of the electron deficiency at the phosphorus atom, calculated NBO partial charges of +1.7 and +1.3 electrons for 4-1$^{2+}$ and 4-2$^{2+}$, respectively, indicate that significant electrophilicity is nevertheless retained. The calculated LUMOs for the two species show prominent lobes on the phosphorus atoms, supporting their formulation as highly electrophilic phosphorus centres. Consistently, dication 4-1 exhibits strong Lewis acidity while dication 4-2 exhibits substantially lower Lewis acidity based on their Gutmann-Beckett method $^{35,36}$ $\Delta \delta$ of 32.3 and 2.5 ppm, respectively.

$\textbf{Scheme 4.2}$ Synthesis of 4-1 and [(tBu-bpy)PPh][OTf]$_2$ (top), 4-2 and [(terpy)PPh][OTf]$_2$ (bottom).

Interestingly, although P(III) Lewis acids have been known for several decades, their competency as catalysts for imine, ketone, olefin, diimide, and pyridine reduction has only recently been
reported. The ability of P(III) Lewis acids to stoichiometrically activate C-F bonds at elevated temperatures has also recently been documented. In a recent report from the Stephan group, both 4-1 and 4-2 were found to abstract fluoride ions from fluoroalkanes at ambient temperature and this discovery was harnessed for the development of hydrodefluorination catalysts, representing the first application of P(III) Lewis acids in C-F bond reduction. It was therefore envisioned that this ability to activate C-F σ bonds could be coupled with delivery of nucleophiles in the presence of a fluoride trap to achieve C-nucleophile type products.

4.2 Lewis Acid C-F Bond Activation

The strength and kinetic inertness of C-F σ bonds, the strongest covalent bond to carbon, makes them valuable in applications where a combination of high bond polarity and stability are desirable. These features, however, also mean that it is challenging to modify organofluorine derivatives without using indiscriminate and atom-inefficient reagents such as organometallic bases and metal hydrides. The widespread application of organofluorine compounds in both small molecule and materials chemistry, and their accumulation as harmful substances in the environment, has prompted the search for milder and more efficient catalytic routes for C-F bond functionalization and degradation. Catalytic reduction of C-F bonds to C-H bonds (hydrodefluorination) has drawn a great deal of attention in recent years. A comparatively less developed reduction strategy is carbodefluorination, the addition of mild carbon nucleophiles to C-F bonds, which is valuable as a C-C bond forming reaction that may reveal new strategies for modification of the aliphatic C-F bonds found in numerous pharmaceuticals. In the latter context, development of metal-free catalytic strategies is particularly desirable as it provides an alternative to toxic metals. Metal-free catalytic addition of carbon nucleophiles to C-F bonds is rare (Scheme 4.3). Paquin and Moran have shown that strong Brønsted acids or hydrogen bond donors can mediate catalytic carbodefluorination by addition of nucleophiles to C-F bonds, with elimination of HF. Following Olah’s use of BF$_3$ as a Lewis acid for addition of fluoroalkanes to arenes, Müller showed that in-situ generated silylium ions could also mediate such Friedel-Crafts C-C coupling. The groups of Terao and Kambe revealed the catalyst-free metathesis between C-F and C-Al bonds to yield C-C bonds, while Ozerov used the combination of [R$_2$Al]$^+$ cations and trialkylalanes for catalytic carbodefluorination of CF$_3$ groups. Young reported that Al(C$_6$F$_5$)$_3$ catalyzes the cross-coupling of silylalkynes with aliphatic C-F bonds. The Stephan group has also shown that EPCs are excellent Lewis acid catalysts for the alkylative defluorination of benzyl fluorides using
allylsilanes as carbon nucleophiles and noncorrosive fluoride acceptors.\textsuperscript{10, 11} Despite the high activity of EPCs, their broad utility as catalysts is limited by their limited tunability and stability \textit{(vide supra)}.

\[ R_3C-F + \text{allylsilane} \xrightarrow{[\text{cat}]} R_3C=CH + \text{Si-F} \]

\textbf{Scheme 4.3} Select catalysts for metal-free for the carbodefluorination of C-F bonds.

The synthesis of dicationic [PhP]\textsuperscript{2+} complexes bearing tridentate diiminopyridine ligands is reported herein as well as the carbodefluorination of C-F bonds with allylsilanes catalyzed by these and by 4-1 and 4-2 as the first examples of catalytic C-C coupling using P(III) Lewis acids. This reaction was found to be selective for C-F bonds over C-Cl and C-Br bonds and the air stability of 4-2\textsuperscript{28} allowed carbodefluorination to be performed under ambient benchtop conditions. The reaction mechanism is explored experimentally and computationally, from which the importance of ligand hemilability is established.

\textbf{4.3 Results and Discussion}

\textbf{4.3.1 P(III)-Dication Coordination Complexes}

Following a similar procedure to the previously reported syntheses of pyridinoid-substituted complexes of the [PhP]\textsuperscript{2+} dication \{[(tBu-bpy)PPh][X]\textsubscript{2} (X = B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4} (4-1) or OTf) and [(terpy)PPh][X]\textsubscript{2} (X = B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4} (4-2) or OTf), complexes bearing tridentate diiminopyridine
ligands were prepared. Like the pyridinoid ligands, the choice of tridentate diimino-pyridine ligands was similarly prompted by the greater stability of chelating ligands that is well known in transition metal coordination chemistry. From one-pot reactions, PhPCl$_2$, NaB(C$_6$F$_5$)$_4$ or TMSOTf, and (1$E,1' E$)-1,1’-(pyridine-2,6-diyl)bis(N-mesitylethan-1-imine) (i.e. MesIminopyridine) or (1$E,1' E$)-1,1’-(pyridine-2,6-diyl)bis(N-(2,6-diisopropylphenyl)ethan-1-imine) (i.e. DippIminopyridine) were combined in DCM at ambient temperature for 1 hour to produce complexes [(MesIminopyridine)PPh][X]$_2$ (X = B(C$_6$F$_5$)$_4$ (4-3) or OTf (4-4)) or [(DippIminopyridine)PPh][X]$_2$ (X = B(C$_6$F$_5$)$_4$ (4-5) or OTf (4-6)). Upon workup, 4-4 and 4-6 were isolated as yellow and yellow-orange powders in 76% and 65% yields, respectively (Scheme 4.4). Unfortunately, despite 4-3 and 4-5 being readily prepared, as inferred by NMR, sufficiently pure isolated samples were not obtained. The $^{31}$P{${}^1$H} NMR signals of these complexes attest to the dicationic charge, with 4-3 and 4-4 appearing at 35.3 and 33.5 ppm, respectively, and 4-5 and 4-6 each appearing at 61.2 ppm. Cold $n$-pentane solutions of 4-4 and 4-6 yielded single crystals suitable for X-ray diffraction, unambiguously confirming their formulations (Figure 4.1 and Figure 4.2). The solid-state structure of 4-4 displays a P-C$_{phenyl}$ distance of 1.815(4) Å, a P-N$_{pyridine}$ distance of 1.787(3) Å, and P-N$_{imine}$ distances of 1.960(3) and 1.994(3) Å. The tridentate diimino-pyridine ligand is essentially planar while the phenyl ring is oriented approximately orthogonally to this plane, with C-P-N angles of 93.4(1), 88.7(1), and 106.3(2)$^\circ$. Although similar bond lengths and angles were observed in the solid-state structure of 4-6, disorder in the aryl-N groups precludes a detailed comparison to 4-4. However, these bond lengths and angles are comparable to those observed in the molecular structures of [(tBu-bpy)PPh][OTf]$_2$ and [(terpy)PPh][OTf]$_2$. Another similarity to [(tBu-bpy)PPh][OTf]$_2$ and [(terpy)PPh][OTf]$_2$ is that interionic contacts are observed between the triflate anion’s oxygen atom and the phosphorus centre in 4-4 and 4-6, with a distance of 3.226(3) Å in the former within the sum of the van der Waals radii for P and O (3.32 Å), implying that the Lewis acidic site is indeed at the phosphorus centre.
Scheme 4.4 Synthesis of diimino-pyridine catalysts 4-3 to 4-6.

Figure 4.1 ORTEP depiction of 4-4 showing close contacts and showing thermal ellipsoids at 50% probability. Hydrogen atoms, counterion, and minor disorder components omitted. P: orange, O: red, N: blue, S: yellow, C: black, F: spicy pink.
Taking inspiration from the Stephan group’s recent report of the catalytic hydrodefluorination using 4-1 and 4-2, these catalysts as well as the newly synthesized 4-3 and 4-5 dications were applied towards C-C bond formation from C-F bond activation coupled with delivery of a nucleophile. Only the borate salts were used due to the weaker coordination of the borate anion with respect to the triflate anion. Due to difficulties isolating 4-3 and 4-5, initial reactions were performed with 5 mol% of 4-1, 4-2, 4-3, and 4-5 generated in situ with the subsequent addition of 2-phenyl-benzyl fluoride and an equimolar amount of allyltrichromylsilane (A1) (Scheme 4.5). These screenings proved successful, with generation of the C-C coupled product 4-7 in 59%, 33%, 41%, and 31% conversions for 4-1, 4-2, 4-3, and 4-5, respectively, and with concomitant generation of trimethylsilyl fluoride. Having demonstrated catalytic carbodefluorination competency, even with a sterically encumbered o-substituted substrate, the substrate scope was
explored. Given the difficulty of isolating 4-3 and 4-5, subsequent reactivity was only explored with 4-1 and 4-2, which are isolable on gram scales.

\[ \text{Scheme 4.5} \quad \text{In situ allyldefluorination reactions catalyzed by 4-1, 4-2, 4-3, and 4-5.} \]

### 4.3.2 Reaction Scope

The substrate scope was first assessed for 4-1, using 0.5 to 2.4 mol% catalyst in DCM at ambient temperature for 1 to 4 hours, 1 equivalent of the benzyl fluoride, and 3 equivalents of the allylsilane (Table 4.1, Figure 4.3, Figure 4.4). Under these conditions, the alkylation of 2-phenyl-benzyl fluoride with A1 produced the allylated product 4-7 in >99% yield, while performing this reaction with electron rich methallyltrimethylsilane (A2) produced 4-8 in >99% yield, and using electron-deficient 2-bromoallyltrimethylsilane (A3) or 2-(chloromethyl)allyltrimethylsilane (A4) produced 4-9 or 4-10 in >99% and 83% yields, respectively (Table 4.1, entries 1-4). Applying the series of allylsilanes to 4-phenyl-benzyl fluoride produced 4-11 to 4-14 in >99%, >99%, 98%, and 86% conversions, respectively (Table 4.1, entries 5-8), while the alkylated 4-tertbutyl-benzyl fluoride produced 4-16 to 4-19 in 47%, 72%, >99%, and 86% yields, respectively (Table 4.1, entries 9-12). The electron-deficient 4-fluoro-benzyl fluoride was also amenable to this reaction, albeit with lower yields of 61%, >99%, 67%, and 70% of 4-20 to 4-23 for A1 to A4, respectively (Table 4.1, entries 13-16). Extending the scope to non-benzylic systems, the reaction of 1-fluoroadamantane with A1 produced 4-26 in 82% yield after only 30 minutes while the reaction of A1 with 1-fluoropentane produced a mixture of allylated rearrangement products, represented herein by 4-28, in 25% conversion after 22 hours (Table 4.1, entries 17 and 18). The results for 4-fluoro- benzyl fluoride and 1-fluoropentane are consistent with lower conversions and harsher conditions being required to access less activated C(sp³)-F bonds. Unfortunately, no activation of aromatic C(sp³)-F bonds was observed under the catalytic conditions. The high efficiency (TON up to 500) of 4-1 prompted us to demonstrate its synthetic utility by repeating the syntheses of 4-23 and 4-7.
on a 1 mmol scale, from which 55% and 91% isolated yields were obtained, respectively (Table 4.1, entries 1 and 16). Despite its high efficiency, catalytic runs were performed in rigorously dried and degassed solvents as 4-1 exhibits poor stability under ambient conditions and decomposes in the presence of even trace amounts of water.

**Table 4.1** Catalytic C-C coupling of C-F bonds with allylsilanes by 4-1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Fluoroalkane</th>
<th>R(^1)</th>
<th>[cat] (mol%)</th>
<th>time (h)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>2-PhC(_6)H(_4)CH(_3)F</td>
<td>H</td>
<td>0.4</td>
<td>4</td>
<td>25</td>
<td>&gt;99 (91)</td>
<td>4-7</td>
</tr>
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<td>2-PhC(_6)H(_4)CH(_3)F</td>
<td>Me</td>
<td>0.2</td>
<td>4</td>
<td>25</td>
<td>&gt;99</td>
<td>4-8</td>
</tr>
<tr>
<td>3</td>
<td>2-PhC(_6)H(_4)CH(_3)F</td>
<td>Br</td>
<td>2.0</td>
<td>1</td>
<td>25</td>
<td>&gt;99</td>
<td>4-9</td>
</tr>
<tr>
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<td>1</td>
<td>25</td>
<td>83</td>
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<tr>
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<td>Br</td>
<td>1.5</td>
<td>2</td>
<td>25</td>
<td>&gt;99</td>
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<td>2</td>
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<tr>
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<td>0.5</td>
<td>25</td>
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<tr>
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<td>H</td>
<td>0.2</td>
<td>22</td>
<td>25</td>
<td>25 (9)</td>
<td>4-28</td>
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Yields were determined by \(^1\)H NMR spectroscopy using mesitylene as internal standard. Isolated yield for reaction done on a 1 mmol scale is given in parentheses. Unless otherwise stated, reactions were performed with 0.1 mmol of fluoroalkane and 0.3 mmol of allylsilane. Performed under N\(_2\) atmosphere using dry DCM. \(^a\) Conversion determined by \(^19\)F\({}^1\)H NMR spectroscopy using C\(_8\)F\(_6\) as internal standard.

The reactivity of 4-2 was then assessed and found to catalyze the coupling of benzyl fluorides with allylsilanes, albeit under slightly more forcing conditions (Table 4.2, Figure 4.3, Figure 4.4). Reaction conditions in DCM varied within the ranges of 1.2 to 5.3 mol% 4-2, ambient temperature to 55 °C, and 20 to 40 hours (Table 4.2, entries 1, 4, 6, 9, 10, 13, and 17). Under these conditions, the reaction of 2-phenyl-benzyl fluoride with A1 produced 4-7 in 95% yield while the reaction
with **A3** produced 4-9 in 85% yield. Applying **A2**, **A4**, and 2-(4-fluorophenyl)allyltrimethylsilane (**A5**) to 4-phenyl-benzyl fluoride produced **4-12**, **4-14**, and **4-15** in 89%, 86%, and 91% yields, respectively. The electron deficient 4-fluoro-benzyl fluoride was seen to react with **A2** to produce **4-21** in 89% yield. The scope was successfully extended to non-benzylic systems by the addition of **A2** to 1-fluoroadamantane to produce **4-27** in 86% yield after only 15 minutes at ambient temperature while the addition of **A1** to 1-fluoropentane gave 83% conversion to a mixture of allylated rearrangement products, represented herein with **4-28** after 24 hours at 55 °C. Unsurprisingly, α,α-difluorotoluene and α,α,α-trifluorotoluene proved to be challenging as expected from their very low fluoride donor strength and the lower electrophilicity of **4-2** (Table 4.2, entries 18 and 19). While α,α-difluorotoluene showed conversion to **4-29** with **A1** at 55 °C, no conversion was observed at either ambient temperature or 55 °C for α,α,α-trifluorotoluene. However, upon changing the solvent to 1,2-difluorobenzene, good conversion to the tris-methylallylated species **4-30** was observed at 100 °C over 20 hours without observation of the mono- or bis-methylallylated intermediates.

The air stability of **4-2** was noted from a previously report, with solutions of **4-2** show only 7% decomposition upon exposure to ambient air for 24 hours. As such, several reactions were performed under in air using dried DCM (Table 4.2, entries 2, 7, 12, 15, and 16). Gratifyingly, reactions of 2-phenyl-benzyl fluoride, 4-phenyl-benzyl fluoride, and 4-tertbutyl-benzyl fluoride with **A2** under these conditions produced the coupled products **4-8**, **4-12**, and **4-17** in 96%, 90%, and 91% yields, respectively. Additionally, the coupling of electron deficient 3,4-difluoro-benzyl fluoride with **A3** produced **4-25** in 67% yield after a prolonged reaction time of 64 hours. As further demonstrations of the robustness of **4-2**, several reactions were performed in air using undried benchtop DCM (Table 4.2, entries 3, 5, 8, 11, and 14). The reactions of 2-phenyl-benzyl fluoride, 4-phenyl-benzyl fluoride, and 3,4-difluoro-benzyl fluoride with **A2** produced **4-8**, **4-12**, and **4-24** in 88%, 83%, and 79% yields, respectively while the couplings of 4-phenyl-benzyl fluoride and 4-tertbutyl-benzyl fluoride with **A1** produced **4-11** and **4-16** in 95% and 88% yields, respectively. To demonstrate the synthetic utility of **4-2**, the latter reaction was repeated on a 1 mmol scale to isolate **4-11** in 58% yield (Table 4.2, entry 5). Notably, the excellent yields obtained for reactions assembled and run in undried benchtop DCM under an ambient atmosphere generally required longer reaction times (Table 4.2, compare entries 2 and 3, 6 and 7).
Table 4.2  Catalytic C-C coupling of C-F bonds with allylsilanes by 4-2.

\[
R-F + 3 \text{eq} \begin{array}{c} \text{Si} \\ \text{DCM} - \text{TMSF} \end{array} \xrightarrow{x \text{ mol\% 4-2}} R-\begin{array}{c} \text{Si} \end{array}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Fluoroalkane</th>
<th>R\textsuperscript{1}</th>
<th>[cat] (mol%)</th>
<th>time (h)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Product</th>
</tr>
</thead>
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<td>55</td>
<td>95\textsuperscript{a}</td>
<td>4-7</td>
</tr>
<tr>
<td>2</td>
<td>2-PhC\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}F</td>
<td>Me</td>
<td>1.2</td>
<td>20</td>
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<td>96\textsuperscript{b}</td>
<td>4-8</td>
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<td>2-PhC\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}F</td>
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<td>30</td>
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<td>88\textsuperscript{c}</td>
<td>4-8</td>
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<td>2-PhC\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}F</td>
<td>Br</td>
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<td>30</td>
<td>55</td>
<td>85\textsuperscript{a}</td>
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<td>35</td>
<td>89\textsuperscript{a}</td>
<td>4-12</td>
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<td>Me</td>
<td>2.9</td>
<td>30</td>
<td>55</td>
<td>80\textsuperscript{b}</td>
<td>4-12</td>
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<td>8</td>
<td>4-PhC\textsubscript{6}H\textsubscript{4}CH\textsubscript{2}F</td>
<td>Me</td>
<td>2.9</td>
<td>30</td>
<td>55</td>
<td>83\textsuperscript{c}</td>
<td>4-12</td>
</tr>
<tr>
<td>9</td>
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<td>CH\textsubscript{2}Cl</td>
<td>4.8</td>
<td>30</td>
<td>55</td>
<td>91\textsuperscript{a}</td>
<td>4-14</td>
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<td>10</td>
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<td>4-FC\textsubscript{6}H\textsubscript{4}</td>
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<td>20</td>
<td>55</td>
<td>86\textsuperscript{a}</td>
<td>4-15</td>
</tr>
<tr>
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<td>24</td>
<td>55</td>
<td>95\textsuperscript{c}</td>
<td>4-16</td>
</tr>
<tr>
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<td>Me</td>
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<td>20</td>
<td>25</td>
<td>91\textsuperscript{b}</td>
<td>4-17</td>
</tr>
<tr>
<td>13</td>
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<td>Me</td>
<td>1.2</td>
<td>20</td>
<td>35</td>
<td>89\textsuperscript{a}</td>
<td>4-21</td>
</tr>
<tr>
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<td>Me</td>
<td>3.7</td>
<td>20</td>
<td>55</td>
<td>79\textsuperscript{c}</td>
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</tr>
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<td>Br</td>
<td>3.4</td>
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<td>67\textsuperscript{b}</td>
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<td>0.25</td>
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<td>86\textsuperscript{b}</td>
<td>4-27</td>
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<td>8</td>
<td>24</td>
<td>55</td>
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</tr>
<tr>
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<td>\textsuperscript{a,e}</td>
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<td>2.7</td>
<td>20</td>
<td>100</td>
<td>\textsuperscript{a,e}</td>
<td>4-30</td>
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</table>

Yields were determined by \textsuperscript{1}H NMR spectroscopy using mesitylene as internal standard. Isolated yields for reactions done on a 1 mmol scale are given in parentheses. Unless otherwise stated, reactions were performed with 0.1 mmol of fluoroalkane and 0.3 mmol of allylsilane.

\textsuperscript{a} Performed under N\textsubscript{2} atmosphere using dry DCM. \textsuperscript{b} Performed in air using dry DCM. \textsuperscript{c} Performed in air using undried DCM. \textsuperscript{d} Conversion determined by \textsuperscript{19}F\textsuperscript{1}H NMR spectroscopy using C\textsubscript{6}F\textsubscript{6} as internal standard. \textsuperscript{e} Complete consumption of starting material was observed but accurate yields could not be determined due to purification issues. Products were detected by mass spectrometry.
Figure 4.3  Substrate scope products 4-7 to 4-26.
The functional group tolerance of catalysts 4-1 and 4-2 was assessed by introducing additives to runs involving the catalytic coupling of 4-phenyl-benzyl fluoride with A1. Catalyst 4-1 was severely inhibited by addition of a nitrile, ether, alcohol, or amine, giving 17%, 37%, 13%, or 10% yields, respectively (Table 4.3, entries 1-4), yet was moderately effective in the presence of a ketone or diarylether, giving 60% or 59% yield, respectively (Table 4.3, entries 5, 6). Complete inhibition was observed in the presence of DMF. The experiment involving addition of pyridine revealed the relationship between 4-1 and 4-2. Addition of approximately one equivalent (with respect to the catalyst) of pyridine to an experiment with 4-1 slowed the reaction substantially but did not completely prevent turnover, while addition of excess pyridine prevented turnover altogether and no consumption of the benzyl fluoride was observed. This latter result was mirrored by the observation that addition of just a single equivalent of pyridine to a catalysis run involving 4-2 was sufficient to prevent turnover (Table 4.3, entries 9, 10, and 17). The similar reactivity observed for the 4-1 plus pyridine system and 4-2 suggests that the latter cation models the structure of pyridine-inhibited 4-1.

Catalyst 4-2 generally exhibited better functional group tolerance, as might be expected based on its lower electrophilicity and greater steric protection of the reaction P(III) site. Although catalyst performance was noticeably poorer compared to the additive-free reactions, moderate to good yields were obtained in the presence of a nitrile, ether, alcohol, amine, or ketone, giving 66%, 56%, 50%, 78%, or 84% yield, respectively (Table 4.3, entries 11-15). The lack of turnover observed in the case of DMF (Table 4.3, entry 16) is presumably due to the strongly coordinating nature of the amide, which precludes C-F bond activation by catalyst inhibition.
Table 4.3 Functional group compatibility of catalytic allylations using 4-1 or 4-2. Yields determined by $^1$H NMR spectroscopy.

![Chemical structure]

<table>
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<th>Entry</th>
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<th>[cat] (mol%)</th>
<th>Additive</th>
<th>time (h)</th>
<th>Temp. (°C)</th>
<th>Conv. (%)</th>
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<td>4-F-PhCN</td>
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<td>25</td>
<td>17</td>
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<tr>
<td>2</td>
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<td>H</td>
<td>2</td>
<td>O(CH$_2$Ph)$_2$</td>
<td>1</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>H</td>
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<td>PhOH</td>
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<td>35</td>
<td>89</td>
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</table>

Performed under N$_2$ atmosphere using dry DCM.

The chemoselectivity of 4-1 and 4-2 was probed by comparing their reactivity towards the coupling reactions between 4-phenyl-benzyl fluoride, benzyl chloride, 4-phenyl-benzyl bromide, and 4-bromo-benzyl bromide with A1. No allylation of benzyl chloride or either benzyl bromide was observed at ambient temperature using 4-1, whereas allylation of 4-phenyl-benzyl fluoride readily proceeds under these conditions. Upon heating to 55 °C for 24 hours, only 2%, 24%, and 2% yields were observed for benzyl chloride, 4-phenyl-benzyl bromide, and 4-bromo-benzyl bromide, respectively (Table 4.4, entries 1-3), indicating a strong preference for allyldefluorination over allyldechlorination or allyldebromination for catalyst 4-1. The results for 4-2 show a similar trend of poor conversions of the C-Cl and C-Br substrates under reactions conditions which allow for 4-phenyl-benzyl fluoride allylation. Performed at 55 °C for 24 hours, allylations of benzyl...
chloride, 4-phenyl-benzyl bromide, and 4-bromo-benzyl bromide gave 9%, 19%, and 11% conversions, respectively (Table 4.4, entries 5-7). The high selectivity of C-F bonds over C-Cl and C-Br bonds contrasts starkly with metal-mediated cross coupling reactions which follow the opposite trend.\textsuperscript{71,72} The differing reactivity trends is tentatively ascribed to the greater strength of the Si-F bond relative to Si-Cl and Si-Br bonds.

**Table 4.4** Chemoselectivity of catalytic allylations using 4-1 or 4-2.

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<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>X</th>
<th>R</th>
<th>[cat] (mol%)</th>
<th>time (h)</th>
<th>Temp (°C)</th>
<th>Conv. (%)</th>
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<td>H</td>
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<td>Ph</td>
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<td>35</td>
<td>89</td>
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</tbody>
</table>

Performed under N\textsubscript{2} atmosphere using dry DCM. Yields determined by \textsuperscript{1}H NMR spectroscopy.

**4.3.3 Mechanistic Insights**

The mechanism of catalytic C-C coupling with 4-1 and 4-2 was probed by a series of control experiments. Combination of 4-1 or 4-2 with a stoichiometric amount of 4-phenyl-benzyl fluoride led to immediate reactions as detected by NMR spectroscopy (Scheme 4.6). The \textsuperscript{31}P\{\textsuperscript{1}H\} NMR and \textsuperscript{19}F\{\textsuperscript{1}H\} NMR spectra in both cases showed resonances exhibiting \textsuperscript{1}J\textsubscript{PF} coupling constants in the 1000 Hz range, consistent with P-F connectivity (Figure 4.5, Figure 4.6). These reactions evidence the ability of 4-1 or 4-2 to activate C-F bonds in benzyl fluorides, although isolation of the resulting fluoride adducts was precluded by onward decomposition to PhPF\textsubscript{2} and poly(methylenebiphenylene) via Friedel-Crafts oligomerization.
Scheme 4.6  Stoichiometric reactions between 4-1 and 4-2 with 4-Ph-benzyl fluoride.

Figure 4.5  $^{31}$P$[^1]H$ NMR (top) and $^{19}$F$[^1]H$ NMR (bottom) (DCM) spectrum of the stoichiometric reaction between 4-1 and 4-Ph-benzyl fluoride at ambient temperature for 18 hours.
Further, the equimolar combination of 4-1 with A1 or A2 showed no reaction after several hours at ambient temperature. Similarly, an equimolar mixture of 4-2 with A2 showed no reaction (Scheme 4.7) even upon heating to 55 °C for 2 days. These observations are consistent with a mechanism involving C-F bond activation by coordination of the benzyl fluoride to the phosphorus centre in the two P(III) Lewis acids (Scheme 4.8). The coordination-activated C-F bond is proposed to undergo C-C bond forming nucleophilic attack by the allylsilane, prompting fluoride transfer to the silyl group to regenerate the P(III) dications with concomitant Me₃SiF formation.

Figure 4.6  $^{31}$P{¹H} NMR (top) and $^{19}$F{¹H} NMR (bottom) (DCM) spectrum of the stoichiometric reaction between 4-2 and 4-Ph-benzyl fluoride at ambient temperature for 20 hours.

Scheme 4.7  Stoichiometric reactions between 4-2 or 4-3 with allylsilanes.
Computational chemistry was applied to further study this mechanistic proposal. Given that cation $4-1^{2+}$ is the only catalyst herein with a vacant coordination site, the analogous Lewis acid reactivity of the cations of $4-2$, $4-3$, and $4-5$ must occur by the dissociation of one arm of the tridentate ligand (Scheme 4.9). This proposed hemilability was probed computationally for $4-2^{2+}$ and $4-3^{2+}$. Using Gaussian 09, geometries were optimized with the M06-2X/Def2-SVP method and single-point energies were recalculated with the M06-2X/Def2-TZVP method with DCM solvation using the SMD method. Hemilability of a pyridinoid substituent in $4-2^{2+}$ gave a bidentate pyridinoid-substituted species resembling $4-1^{2+}$ that is 16.6 kcal/mol uphill over a barrier of 18.9 kcal/mol. The analogous dissociation in $4-3^{2+}$ gave a bidentate imine-pyridyl-substituted species that is 21.7 kcal/mol uphill over a barrier of 23.0 kcal/mol (Figure 4.7). These results are consistent with the air-stability of $4-2$ under ambient conditions as well as the ambient temperature and thermally accessible catalytic reactivity of $4-2$ and $4-3$. 

Scheme 4.8 Proposed mechanistic cycle for the allyldefluorination of fluoroalkanes.
Scheme 4.9  Hemilabile dissociation of one ligand arm of 4-2$^{2+}$ (top) and 4-3$^{2+}$ (bottom).

An alternate mechanism involving the role of 4-1 or 4-2 as initiators to generate [Me$_3$Si]$^+$ cations as the true catalyst was also considered. This mechanism predicts consumption of the P(III) cations as part of the initiation process by allyl group abstraction. In contrast, assaying catalysis reaction
mixtures by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy upon full conversion showed resonances for the intact P(III) cations 4-1 or 4-2 as either the major species or the only species by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure 4.8 and Figure 4.9). These findings are inconsistent with the role of 4-1 or 4-2 as stoichiometric initiators to generate silyl cations. Moreover, free silyl cations are expected to have exceedingly short lifetimes in DCM and they are therefore unlikely to be relevant as catalysts in the conditions employed here, particularly for reactions involving 4-2 that were carried out at 55 °C. The possibility of Brønsted acid catalysis involving generation of HF from trace amounts of water in the solvent was also considered. However, this is discounted by the observation that catalytic experiments run in undried DCM required higher catalyst loadings, temperatures, and longer reaction times to reach completion compared to those run in anhydrous DCM.

**Figure 4.8** $^{31}\text{P}\{^1\text{H}\}$ NMR (DCM) of reaction mixtures at the end of catalytic runs with 4-1. The resonance for 4-1 is at 144 ppm. Low signal-to-noise ratio is due to the low catalyst loadings.
Figure 4.9 $^{31}$P{¹H} NMR (DCM) of reaction mixtures at the end catalytic runs with 4-2. The resonance for 4-2 is at 38 ppm. Low signal-to-noise ratio is due to the low catalyst loadings.
4.4 Conclusion

In the present work, tridentate diiminopyridine ligands were used to support trivalent phosphorus Lewis acids 4-3 to 4-6. Along with di- and terpyridine ligated analogues 4-1 and 4-2, 4-3 and 4-5 were shown to catalyze the allyldefluorination of aliphatic C-F bonds. This represents the first application of P(III) Lewis acids in a catalytic C-C coupling reaction. Given that 4-3 and 4-5 were not cleanly isolable, reaction scope was explored with 4-1 and 4-2. The reaction was found to be tolerant of electron rich and electron poor allylsilanes as well as sterically hindered, electron rich, and electron poor benzyl fluorides. More challenging substrates were also amenable to this reaction, with 1-fluoropentane, α,α-difluorotoluene, and α,α,α-trifluorotoluene demonstrating reactivity under forcing conditions. This reaction was shown to be selective for C-F bonds over C-Cl and C-Br bonds for both catalysts. The bipyridine-substituted complex 4-1 is significantly more active than the terpyridine-substituted complex 4-2, however the latter is recognized to have considerable air stability and demonstrated catalytic competency under atmospheric moisture and undried solvent conditions. To assess functional group tolerance, reactions were performed with an equivalent of various functional group-bearing additives, with 4-1 showing greater losses of reactivity than 4-2, consistent with their relative stabilities. Interestingly, 4-1 displayed similar reactivity to 4-2 when a catalytic amount of pyridine additive was present. Investigations into the mechanism support the notion that 4-1 and 4-2 are the active catalytic species, with C-F bond activation occurring at the phosphorus centre. For 4-2\(^{2+}\) and 4-3\(^{2+}\), computations indicate that one arm of the tridentate ligand dissociates to expose a reactive site on the phosphorus centre, providing an analogy between the dissociated 4-2\(^{2+}\) and 4-1\(^{2+}\). This is further attested to by the reaction of 4-1 with a molar equivalent of pyridine inhibitor, as this mixture’s reactivity resembles that of 4-2.

4.5 Experimental

4.5.1 General Experimental Methods

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N\(_2\). All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (dichloromethane, diethyl ether, and n-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone under inert atmosphere. CD\(_2\)Cl\(_2\) (Aldrich) was deoxygenated, distilled over CaH\(_2\), then stored over 3 Å molecular sieves before
Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals, or Alfa Aesar, and were used without further purification unless indicated otherwise. MesIminopyridine (i.e. \((1E,1'E)-1,1'-(\text{pyridine-2,6-diyi})\text{bis}(N\text{-mesitylethan-1-imine})\))\(^{79}\) and DippIminopyridine (i.e. \((1E,1'E)-1,1'-(\text{pyridine-2,6-diyi})\text{bis}(N\text{-}(2,6-diisopropylphenyl)ethan-1-imine})\))\(^{80}\) were prepared according to literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz, or a Varian Mercury-300 MHz spectrometer. \(^1\text{H}, \ ^{13}\text{C}\{^1\text{H}\}, \ ^{31}\text{P}\{^1\text{H}\}, \ ^{19}\text{F}\{^1\text{H}\}, \text{and } ^{11}\text{B}\{^1\text{H}\} \text{ NMR chemical shifts (δ/ppm) are referenced to } \text{Me}_4\text{Si}, \text{Me}_3\text{Si}, \text{H}_3\text{PO}_4, \text{CFCl}_3, \text{and BF}_3\cdot\text{OEt}_2, \text{respectively.}

Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. Mass spectra (MS) were obtained on an Agilent 5975C VL MSD (EI). High-resolution mass spectra (HRMS) were obtained on a GCT Premier (EI), 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. Fourier-transform infrared spectra (FT-IR) were obtained on a Bruker Alpha Platinum ATR infrared spectrophotometer.

4.5.2 X-Ray Diffraction Studies

Single crystals were coated with Paratone oil, mounted on a CryoLoop, and frozen under a stream of cold nitrogen. Data were collected on a Bruker Kappa Apex II X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-K\(\alpha\) radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.
Table 4.5   X-ray table for 4-4 and 4-6.

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4.5.3 Synthesis of Catalysts

4-1  \([((t\text{Bu-bpy})\text{PPh})][\text{B(C}_6\text{F}_5)_4]_2\]

A solution of the 4,4’-di-tert-butyl-2,2’-dipyridyl (i.e. \(t\text{Bu-bpy}\)) (1 mmol, 0.268 g) in 2 mL DCM was added over 1 minute to a white suspension of \(\text{NaB(C}_6\text{F}_5)_4\) (2 mmol, 1.436 g) and \(\text{PhPCl}_2\) (1 mmol, 0.179 g) in 5 mL DCM to immediately obtain a bright yellow suspension. The reaction was allowed to stir for 1 h and then the solids were removed via filtration. The yellow filtrate was concentrated to ca. 1 mL volume and then ca. 10 mL of pentane was added with stirring to precipitate a light-yellow powder. The supernatant above the powder was decanted and the powder washed with an additional 5 mL pentane and dried under vacuum to yield a yellow powder (1.387 g, 81% yield). \(^1\text{H NMR (400 MHz, CD}_2\text{Cl}_2\)): \(\delta = 1.54\) (s, 18H; C7), 7.50 (ddd, \(J = 12, 8, 1\) Hz, 2H; C3), 7.56 – 7.64 (m, 2H; C2), 7.95 (tt, \(J = 6, 2\) Hz, 1H; C1), 8.37 – 8.45 (m, 2H; C5), 8.80 (dd, \(J = 7, 5\) Hz, 2H; C4), 8.94 (d, \(J = 2\) Hz, 2H; C6) ppm. \(^{19}\text{F}\{^1\text{H}\} \text{NMR (377 MHz, CD}_2\text{Cl}_2\}): \(\delta = -133.80, -163.77, -167.75\) ppm. \(^{31}\text{P}\{^1\text{H}\} \text{NMR (162 MHz, CD}_2\text{Cl}_2\): } \(\delta = 144.06\) (s) ppm. \(^{13}\text{C}\{^1\text{H}\} \text{NMR (101 MHz, CD}_2\text{Cl}_2\): } \(\delta = 23.0, 123.5, 130.7, 132.8\) (d, \(J = 11\) Hz), 134.6 (d, \(J = 33\) Hz), 135.6, 141.3, 143.3 (d, \(J = 18\) Hz), 143.6 (d, \(J = 4\) Hz), 147.4, 149.8, 181.1 ppm. \text{FT-IR (ATR): } 450\) (w), 574 (w), 601 (m), 661 (m), 683 (m), 756 (m), 774 (m), 851 (w), 899 (w), 974 (s), 1084 (s), 1273 (m), 1374 (w), 1457 (s), 1513 (m), 1622 (w), 1644 (w), 2814 (w), 2929 (w), 2970 (w). \text{EA: calcd (%) for C}_72\text{H}_{20}\text{B}_2\text{F}_{40}\text{N}_2\text{P: } \text{C}, 49.86; \text{H}, 1.69; \text{N}, 1.62; \text{found: } \text{C}, 49.88; \text{H}, 1.91; \text{N}, 1.57.
A solution of 2,2'-6',2''-terpyridine (i.e. terpy) (1 mmol, 0.233 g) in 2 mL DCM was added over 1 minute to a colourless suspension of NaB(C₆F₅)₄ (2 mmol, 1.436 g) and PhPCl₂ (1 mmol, 0.179 g) in 5 mL DCM to immediately obtain a bright yellow suspension. An NMR assay after 5 minutes showed that the reaction was complete. The reaction stirred for an additional 1 h and then the solids were removed via filtration. Solvent was removed under vacuum to obtain a pale-yellow viscous oil. Washing this oil with pentane (3 x 5 mL) with vigorous stirring and drying under vacuum to yield a fine yellow powder (1.461 g, 86 % yield). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.24 – 7.34 (m, 3H, C3), 7.39 (td, J = 8, 3 Hz, 2H, C2), 7.51 – 7.60 (m, 1H; C1), 8.23 (ddd, J = 8, 6, 1 Hz, 2H; C5), 8.69 (td, J = 8, 1 Hz, 2H; C6), 8.77 – 8.91 (m, 2H; C7), 8.95 – 9.02 (m, 2H; C4), 9.12 (dd, J = 8, 2 Hz, 2H; C8), 9.28 (ddd, J = 9, 8, 2 Hz, 1H; C9) ppm. ¹⁹F{¹H} NMR (377 MHz, CD₂Cl₂): δ = -133.85, -163.79, -167.87 ppm. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ = 37.4 (s) ppm. ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ = 124.1, 125.6 (d, ¹JPC = 40 Hz), 127.2, 131.3, 133.0, 135.6, 137.4, 138.0, 138.8, 139.9, 147.3, 149.8 ppm. FT-IR (ATR): 409 (w), 422 (w), 435 (w), 448 (w), 456 (w), 473 (w), 497 (m), 513 (m), 550 (w), 560 (w), 563 (w), 574 (m), 580 (w), 602 (m), 612 (m), 654 (m), 661 (m), 683 (m), 725 (w), 740 (w), 755 (m), 774 (m), 974 (s), 1024 (w), 1084 (s), 1253 (w), 1273 (m), 1310 (w), 1374 (w), 1457 (s), 1512 (s), 1558 (w), 1610 (w), 1619 (w), 1644 (m), 2299 (w), 2310 (w). EA: calcd (%) for C₆₉H₁₆B₂F₄₀N₃P: C, 48.77; H, 0.95; N, 2.47; found: C, 48.52; H, 1.41; N, 2.50.

[(MesIminopyridine)PPh][B(C₆F₅)₄]₂

PhPCl₂ (1 mmol, 179 mg) and NaB(C₆F₅)₄ (2 mmol, 1.436 g) were combined in ca. 5 mL DCM and to this a solution of (1E,1′E)-1,1′-(pyridine-2,6-diyl)bis(N-mesitylethan-1-imine) (i.e. MesIminopyridine) (1 mmol, 398 mg) was added to obtain a clear light orange solution. ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = -132.42 (s, o-C₆F₅), -162.32 (t, J = 20 Hz,
$p$-C$_6$F$_5$), -166.43 (s, $m$-C$_6$F$_5$) ppm. $^{31}$P$^1$H NMR (162 MHz, CDCl$_3$): $\delta = 61.15$ ppm.

4-4  [(MesIminopyridine)PPh][OTf]$_2$

PhPCl$_2$ (1 mmol, 179 mg) and TMSOTf (2 mmol, 444.4 mg) were combined in ca. 5 mL DCM and to this a solution of (1E,1'E)-(pyridine-2,6-diyl)bis(N-mesitylen-1-imine) (i.e. MesIminopyridine) (1 mmol, 398 mg) was added to obtain a clear light orange solution. After stirring for 1 hour, all volatiles were removed in vacuo and the sticky product was triturated by washing with 3 x 5 mL pentane and dried to yield a yellow-orange powder. Single crystals suitable for diffraction were obtained from a o-difluorobenzene solution layered with pentane at room temperature (613 mg, 76% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.97$ (broad s, 6H; C11 + C11'), 2.28 (s, 1H; C10 + C10'), 2.30 (s, 6H; C9 + C9'), 2.85 (s, 3H; C3'), 2.86 (s, 3H, C3), 6.66 – 6.90 (m, 5H; C4 + C4' + C5 + C5' + C6), 7.35 (t, $J = 8$ Hz, 2H; C8 + C8'), 7.44 – 7.53 (m, 2H; C7 + C7'), 9.35 (m, $J = 9, 7, 4$ Hz, 1H; C1), 9.4 – 9.46 (m, 2H; C2 + C2') ppm. $^{19}$F$^1$H NMR (377 MHz, CDCl$_3$): $\delta = -133.10$ (s, $o$-C$_6$F$_5$), -163.21 (t, $J = 20$ Hz, $p$-C$_6$F$_5$), -167.40 (s, $m$-C$_6$F$_5$) ppm. $^{31}$P$^1$H NMR (162 MHz, CDCl$_3$): $\delta = 61.15$ ppm.

4-5  [(DippIminopyridine)PPh][B(C$_6$F$_5$)$_4$]$_2$

PhPCl$_2$ (1 mmol, 179 mg) and NaB(C$_6$F$_5$)$_4$ (2 mmol, 1.436 g) were combined in ca. 5 mL DCM and to this a solution of (1E,1'E)-(pyridine-2,6-diyl)bis(N-(2,6-diisopropylphenyl)ethan-1-imine) (i.e. DippIminopyridine) (1 mmol, 481 mg) was added to obtain a clear light orange solution. $^{19}$F$^1$H NMR (377 MHz, CDCl$_3$): $\delta = -133.10$ (s, $o$-C$_6$F$_5$), -163.21 (t, $J = 20$ Hz, $p$-C$_6$F$_5$), -167.40 (s, $m$-C$_6$F$_5$) ppm. $^{31}$P$^1$H NMR (162 MHz, CDCl$_3$): $\delta = 61.15$ ppm.
PhPCl₂ (1 mmol, 179 mg) and TMSOTf (2 mmol, 444.4 mg) were combined in ca. 5 mL DCM and to this a solution of (1E,1′E)-1,1′-(pyridine-2,6-diyl)bis(N-(2,6-diisopropylphenyl)ethan-1-imine) (i.e. DippIminopyridine) (1 mmol, 481 mg) was added to obtain a clear yellow solution. After stirring for 1 hour, all volatiles were removed in vacuo and the sticky product was triturated by washing with 5 x 5 mL pentane and dried to yield a yellow powder. Single crystals suitable for diffraction were obtained from a dichloromethane solution layered with pentane at -30 °C. The compound exhibited poor solubility in common solvents (577 mg, 65 % yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.14 (d, J = 7 Hz, 6H; C14), 0.93 (d, J = 7 Hz, 6H; C13), 0.99 (d, J = 7 Hz, 6H; C12), 1.35 (d, J = 7 Hz, 6H; C11), 1.42 (p, J = 7 Hz, 2H; C9), 2.91 (d, J = 6 Hz, 6H; C3), 3.11 (p, J = 7 Hz, 2H; C10), 6.87 – 7.20 (m, 5H; C4 + C5 + C6), 7.33 – 7.53 (m, 6H; C7 + C8), 9.29 (m, 2H; C2), 9.33 (s, 1H; C1) ppm. ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ = -78.44 (anion CF₃) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 61.20 ppm. ¹³C NMR not recorded due to poor solubility.

4.5.4 In Situ Reactions

A solution of 2-phenyl-benzyl fluoride (0.05 mmol), allyltrimethylsilane (A1) (0.05 mmol), PhPCl₂ (5 mol%), and the appropriate ligand (5 mol%) was made in DCM (0.5 mL). This solution was added to an NMR tube pre-charged with NaB(C₆F₅)₄ (10 mol%) and a sealed capillary containing a solution (CDCl₃) of mesitylene and C₆F₆ as ¹H and ¹⁹F NMR integration standards. The tube was inverted several times to obtain a clear solution, which was monitored under various conditions. Conversions were determined by ¹H NMR spectroscopy. Reaction with 4-1 was performed at ambient temperature for 2 hours. Reactions with 4-2, 4-3, and 4-5 were performed at 55 °C for 17 hours.

4.5.5 Allylation of C-F Bonds

The benzyl fluoride (0.1 mmol) and allylsilane (0.3 mmol) were combined in DCM (0.5 mL). This solution was added to an NMR tube pre-charged with the appropriate amount of solid catalyst and a sealed capillary containing a solution (CDCl₃) of mesitylene and C₆F₆ as ¹H and ¹⁹F{¹H} NMR
integration standards. The tube was inverted several times to obtain a clear solution, which was monitored under various conditions (see Table 4.1 and Table 4.2 for conditions).

### 4-7 2-(but-3-en-1-yl)-1,1'-biphenyl

**Scaled up reaction with 0.1 mmol:** Yield 191.0 mg (91%).

**1H NMR (500 MHz, CDCl₃):** δ = 2.27 (dddt, J = 10, 8, 7, 2 Hz, 2H), 2.72 – 2.78 (m, 2H), 4.91 – 5.00 (m, 2H), 5.77 (ddt, J = 17, 10, 7 Hz, 1H), 7.25 – 7.31 (m, 2H), 7.35 (d, J = 2 Hz, 1H), 7.36 (d, J = 4 Hz, 1H), 7.38 (d, J = 2 Hz, 1H), 7.38 – 7.42 (m, 1H), 7.42 – 7.49 (m, 2H) ppm. **13C{1H} NMR (126 MHz, CDCl₃):** δ = 32.7, 35.3, 114.8, 125.9, 126.9, 127.5, 128.2, 129.3, 130.2, 138.2 (d, J = 2.3 Hz), 139.3, 142.0, 142.1 ppm. **HRMS (DART-TOF+):** 209.13276 ([M+1]+, calcd 209.13303).

### 4-8 2-(3-methylbut-3-en-1-yl)-1,1'-biphenyl

**1H NMR (500 MHz, CDCl₃):** δ = 1.60 (s, 3H), 2.15 – 2.19 (m, 2H), 2.73 – 2.76 (m, 2H), 4.57 (s, 1H), 4.65 (s, 1H), 7.23 – 7.26 (m, 2H), 7.27 – 7.30 (m, 1H), 7.33 – 7.38 (m, 4H), 7.41 – 7.44 (m, 2H) ppm. **13C{1H} NMR (126 MHz, CDCl₃):** δ = 22.4, 31.9, 36.6, 110.2, 125.9, 126.9, 127.5, 128.2, 129.3, 130.2, 139.8, 142.0, 142.0, 145.6 ppm. **HRMS (DART-TOF+):** 223.14817 ([M+1]+, calcd 223.14868).

### 4-9 2-(3-bromobut-3-en-1-yl)-1,1'-biphenyl

**1H NMR (500 MHz, CDCl₃):** δ = 2.51 – 2.56 (m, 2H), 2.86 – 2.94 (m, 2H), 5.34 (q, J = 1 Hz, 1H), 5.37 – 5.38 (m, 1H), 7.19 – 7.23 (m, 1H), 7.22 – 7.27 (m, 1H), 7.29 (dd, J = 8, 4 Hz, 1H), 7.31 – 7.34 (m, 2H), 7.34 – 7.36 (m, 1H), 7.36 – 7.41 (m, 1H), 7.42 – 7.48 (m, 2H) ppm. **13C{1H} NMR (126 MHz, CDCl₃):** δ = 33.5, 42.9, 126.4, 127.1, 127.6, 128.3, 129.2, 129.6, 130.3, 131.3, 133.7, 137.9, 141.7, 142.1 ppm. **MS (EI+):** 286.1 ([M]+, calcd 286.19).
2-(3-(chloromethyl)but-3-en-1-yl)-1,1'-biphenyl

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 2.34$ (dd, $J = 10$, 6, 2H), 2.76 – 2.79 (m, 2H), 3.86 (s, 2H), 4.81 (s, 1H), 5.04 (s, 1H), 7.22 – 7.26 (m, 1H), 7.28 (dd, $J = 8$, 4 Hz, 2H), 7.31 – 7.35 (m, 3H), 7.36 – 7.38 (m, 1H), 7.42 – 7.45 (m, 2H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta = 31.7$, 34.8, 48.2, 114.9, 126.2, 127.1, 127.6, 128.3, 129.3, 129.3, 130.3, 139.0, 141.8, 142.1, 144.7 ppm.


4-(but-3-en-1-yl)-1,1'-biphenyl

Scaled up reaction with 0.1 mmol: Yield 120.7 mg (58%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 2.43$ (ddt, $J = 8$, 7, 1 Hz 2H), 2.77 (t, $J = 8$ Hz, 2H), 5.02 (ddq, $J = 10$, 3, 1 Hz, 1H), 5.09 (dq, $J = 17$, 2 Hz, 1H), 5.91 (ddtd, $J = 17$, 10, 7, 1 Hz, 1H), 7.28 (m, 2H), 7.34 (dddd, $J = 9$, 7, 2, 1 Hz, 1H), 7.44 (td, $J = 8$, 1 Hz, 2H), 7.53 (m, 2H), 7.60 (dt, $J = 8$, 1 Hz, 2H) ppm. $^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$): $\delta = 35.2$, 35.6, 115.2, 127.1, 127.1, 127.2, 128.9, 130.0, 138.2, 138.2, 138.9, 141.1, 141.2 ppm. HRMS (DART-TOF+): 209.13347 ([M+1]$^+$, calcd 209.13303).

4-(3-methylbut-3-en-1-yl)-1,1'-biphenyl

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.83$ (s, 3H), 2.38 – 2.42 (m, 2H), 2.82 – 2.86 (m, 2H), 4.78 – 4.79 (m, 1H), 4.80 – 4.81 (m, 1H), 7.28 – 7.33 (m, 2H), 7.34 – 7.37 (m, 1H), 7.46 (t, $J = 8$ Hz, 2H), 7.53 – 7.58 (m, 2H), 7.59 – 7.64 (m, 2H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta = 22.8$, 34.0, 39.7, 110.4, 127.1, 127.1, 127.2, 128.8, 128.9, 138.9, 141.2, 141.5, 145.5 ppm. HRMS (DART-TOF+): 223.14785 ([M+1]$^+$, calcd 223.14868).
4-13  4-(3-bromobut-3-en-1-yl)-1,1'-biphenyl

\[ \text{δ} = 2.77 \text{ (t, } J = 6 \text{ Hz, 2H), } 2.94 \text{ (t, } J = 8 \text{ Hz, 2H), } 5.43 \text{ (s, 1H), } 4.08 \text{ (s, 2H), } 5.56 \text{ (s, 1H), } 7.28 - 7.30 \text{ (m, 2H), } 7.31 - 7.37 \text{ (m, 1H), } 7.45 \text{ (t, } J = 8 \text{ Hz, 2H), } 7.52 - 7.56 \text{ (m, 2H), } 7.59 - 7.61 \text{ (m, 2H) ppm.} \]

HRMS (DART-TOF+): 304.07075 ([M+NH\textsubscript{4}]\textsuperscript{+}, calcd 304.07009).

4-14  4-(3-(chloromethyl)but-3-en-1-yl)-1,1'-biphenyl

\[ \text{δ} = 2.54 - 2.60 \text{ (m, 2H), } 2.84 - 2.90 \text{ (m, 2H), } 4.08 - 4.11 \text{ (m, 2H), } 5.05 \text{ (d, } J = 1 \text{ Hz, 1H), } 5.18 - 5.12 \text{ (m, 1H), } 7.28 - 7.32 \text{ (m, 2H), } 7.32 - 7.38 \text{ (m, 1H), } 7.41 - 7.48 \text{ (m, 2H), } 7.55 \text{ (d, } J = 8 \text{ Hz, 2H), } 7.60 - 7.62 \text{ (m, 1H) ppm.} \]

HRMS (DART-TOF+): 274.13694 ([M+NH\textsubscript{4}]\textsuperscript{+}, calcd 274.13625).

4-15  4-(2-(4-fluorophenyl)but-3-en-1-yl)-1,1'-biphenyl

\[ \text{δ} = 1.71 \text{ (d, } J = 7 \text{ Hz, 2H), } 3.09 \text{ (ddd, } J = 46, 13, 8 \text{ Hz, 1H), } 3.66 \text{ (q, } J = 7 \text{ Hz, 1H), } 5.05 \text{ (dt, } J = 17, 1 \text{ Hz, 1H), } 5.12 \text{ (dt, } J = 10, 1 \text{ Hz, 1H), } 6.09 \text{ (ddd, } J = 17, 10, 7 \text{ Hz, 1H), } 7.13 - 7.19 \text{ (m, 2H), } 7.28 - 7.30 \text{ (m, 2H), } 7.35 - 7.39 \text{ (m, 1H), } 7.45 - 7.49 \text{ (m, 3H), } 7.50 - 7.53 \text{ (m, 2H), } 7.61 - 7.64 \text{ (m, 2H) ppm.} \]

\[ \text{δ} = -117.52 - -117.60 \text{ ppm (m).} \]

HRMS (DART-TOF+): 303.15470 ([M+H]\textsuperscript{+}, calcd 303.1549).
4-16  1-(but-3-en-1-yl)-4-(tert-butyl)benzene

\[
\begin{align*}
\text{\[^1H\, NMR}\,(500\, MHz, \, \text{CDCl}_3):} & \quad \delta = 1.36 \,(s, \, 9H), \, 2.42 \,(dtt, \, J = 9, \, 7, \, 2\, Hz, \, 2H), \\
& \quad 2.71 - 2.76 \,(m, \, 2H), \, 5.03 \,(dtt, \, J = 10, \, 2, \, 1\, Hz, \, 1H), \, 5.11 \,(dtt, \, J = 17, \, 2, \, 2\, Hz, \, 1H), \, 5.92 \,(dtt, \, J = 17, \, 10, \, 7\, Hz, \, 1H), \, 7.16 - 7.20 \,(m, \, 2H), \, 7.33 - 7.37 \,(m, \, 2H) \,ppm. \\
\text{\[^{13}C\{^1H\}, NMR\,(126\, MHz, \, \text{CDCl}_3):} & \quad \delta = 31.6, \, 34.5, \, 35.0, \, 35.6, \, 114.9 \,(d, \, J = 2\, Hz), \, 125.3, \, 128.2, \, 138.5, \, 139.0, \, 148.7 \,ppm. \\
\text{MS (EI\(+\))}: & \quad 188.2 \,([M]^{+}, \, \text{calcd} \, 188.3). 
\end{align*}
\]

4-17  1-(tert-butyl)-4-(3-methylbut-3-en-1-yl)benzene

\[
\begin{align*}
\text{\[^1H\, NMR\,(400\, MHz, \, \text{CH}_2\text{Cl}_2):} & \quad \delta = 1.31 \,(s, \, 9H), \, 1.55 \,(s, \, 3H), \, 2.29 - 2.35 \,(m, \, 2H), \, 2.68 - 2.77 \,(m, \, 2H), \, 4.74 - 4.77 \,(m, \, 2H), \, 7.10 - 7.18 \,(m, \, 2H), \\
& \quad 7.27 - 7.35 \,(m, \, 2H) \,ppm. \, \text{HRMS (DART-TOF\(+\))}: \quad 220.20618 \,([M+NH_4]^+, \, \text{calcd} \, 220.20652). 
\end{align*}
\]

4-18  1-(3-bromobut-3-en-1-yl)-4-(tert-butyl)benzene

\[
\begin{align*}
\text{\[^1H\, NMR\,(500\, MHz, \, \text{CDCl}_3):} & \quad \delta = 1.33 \,(m, \, 9H), \, 2.73 \,(t, \, J = 8\, Hz, \, 2H), \\
& \quad 2.87 \,(t, \, J = 8\, Hz, \, 2H), \, 5.42 \,(m, \, 1H), \, 5.56 \,(m, \, 1H), \, 7.16 \,(dd, \, J = 8, \, 2\, Hz, \, 2H), \, 7.33 \,(dd, \, J = 8, \, 2\, Hz, \, 2H) \,ppm. \, \text{\[^{13}C\{^1H\}, NMR\,(126\, MHz, \, \text{CDCl}_3):} \\
& \quad \delta = 31.5, \, 34.0, \, 34.5, \, 43.4, \, 117.1, \, 125.4, \, 128.2, \, 133.9, \, 137.5, \, 149.1 \,ppm. \\
\text{HRMS (EI-TOF\(+\))}: & \quad 251.0436 \,([M-\text{CH}_3]^+, \, \text{calcd} \, 251.0435). 
\end{align*}
\]

4-19  1-(tert-butyl)-4-(3-(chloromethyl)but-3-en-1-yl)benzene

\[
\begin{align*}
\text{\[^1H\, NMR\,(500\, MHz, \, \text{CDCl}_3):} & \quad \delta = 1.34 \,(m, \, 9H), \, 2.52 \,(t, \, J = 8\, Hz, \, 2H), \\
& \quad 2.80 \,(dt, \, J = 8, \, 2\, Hz, \, 2H), \, 4.08 \,(m, \, 2H), \, 5.02 \,(m, \, 1H), \, 5.19 \,(m, \, 1H), \, 7.17 \,(dd, \, J = 8, \, 2\, Hz, \, 2H), \, 7.34 - 7.36 \,(m, \, 2H) \,ppm. \, \text{\[^{13}C\{^1H\}, NMR\,(126\, MHz, \, \text{CDCl}_3):} \\
& \quad \delta = 31.6, \, 33.5, \, 34.5, \, 43.8, \, 48.6, \, 114.8, \, 125.4, \, 128.1, \, 138.5, \, 145.0, \, 149.0 \,ppm. \, \text{HRMS (EI-TOF\(+\))}: \quad 221.1102 \,([M-\text{CH}_3]^+, \, \text{calcd} \, 221.1097). 
\end{align*}
\]
4-20 1-(but-3-en-1-yl)-4-fluorobenzene

$^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 2.35 (ddt, $J =$ 9, 7, 1 Hz, 2H), 2.68 (t, $J =$ 8 Hz, 2H), 4.98 (ddt, $J =$ 10, 2, 1 Hz, 1H), 5.03 (dq, $J =$ 17, 2 Hz, 1H), 5.84 (ddt, $J =$ 17, 10, 7 Hz, 1H), 6.94 – 6.99 (mf, 2H), 7.12 – 7.15 (m, 2H) ppm. $^{19}$F$^1$H NMR (377 MHz, CDCl$_3$): $\delta =$ -117.9 ppm. $^{13}$C$^1$H NMR (126 MHz, CDCl$_3$): $\delta =$ 34.4, 35.8, 115.1 (d, $J =$ 21 Hz), 115.3, 129.9 (d, $J =$ 8 Hz), 137.6 (d, $J =$ 3 Hz), 137.9, 161.4 (d, $J =$ 243 Hz) ppm. HRMS (DART-TOF+): 149.07664 ([M-H]$^+$, calcd 149.07665).

4-21 1-fluoro-4-(3-methylbut-3-en-1-yl)benzene

$^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 1.77 (s, 3H), 2.30 (t, $J =$ 8 Hz, 2H), 2.73 (t, $J =$ 8 Hz, 2H), 4.70 (s, 1H), 4.75 (s, 1H), 6.95 – 6.99 (m, 2H), 7.12 – 7.16 (m, 2H) ppm. $^{19}$F$^1$H NMR (377 MHz, CH$_2$Cl$_2$): $\delta =$ -117.9 ppm. $^{13}$C$^1$H NMR (126 MHz, CDCl$_3$): $\delta =$ 22.7, 33.5, 39.8, 110.6, 115.1 (d, $J =$ 21 Hz), 129.8 (d, $J =$ 8 Hz), 137.9 (d, $J =$ 3 Hz), 145.2, 161.4 (d, $J =$ 243 Hz) ppm. HRMS (DART-TOF+): 163.09254 ([M-H]$^+$, calcd 163.09230).

4-22 1-(3-bromobut-3-en-1-yl)-4-fluorobenzene

$^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 2.69 (t, $J =$ 8 Hz, 2H), 2.86 (t, $J =$ 8 Hz, 2H), 5.38 (d, $J =$ 2 Hz, 1H), 5.48 (s, 2H), 6.97 (t, $J =$ 9 Hz, 2H), 7.14 – 7.16 (m, 2H) ppm. $^{19}$F$^1$H NMR (377 MHz, CDCl$_3$): $\delta =$ -117.9 ppm. $^{13}$C$^1$H NMR (126 MHz, CDCl$_3$): $\delta =$ 33.6, 43.5, 115.3 (d, $J =$ 21 Hz), 117.6, 130.0 (d, $J =$ 8 Hz), 133.3, 136.1 (d, $J =$ 3 Hz), 161.6 (d, $J =$ 244 Hz) ppm. HRMS (EI-TOF+): 227.9955 ([M+1]$^+$, calcd 227.9955).

4-23 1-(3-(chloromethyl)but-3-en-1-yl)-4-fluorobenzene

Scaled up reaction with 0.1 mmol: Yield 112.6 mg (55%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 2.48 (d, 8 Hz, 2H), 2.78 (t, $J =$ 8 Hz, 2H), 4.05 (d, $J =$ 1 Hz, 2H), 4.98 (q, $J =$ 1 Hz, 1H), 5.16 (q, $J =$ 1 Hz, 1H), 6.98 (tt, $J =$ 9, 2 Hz, 2H), 7.14 – 7.18 (m, 2H) ppm. $^{19}$F$^1$H NMR (377 MHz, CDCl$_3$): $\delta =$ -177.4 ppm. $^{13}$C$^1$H NMR (126 MHz, CDCl$_3$): $\delta =$ 33.2, 34.9, 48.5, 115.2, 115.3 (d, $J =$ 21 Hz),
129.8 (d, $J = 8$ Hz), 137.1 (d, $J = 3$ Hz), 144.5, 161.5 (d, $J = 244$ Hz) ppm. HRMS (EI-TOF+): 198.0619 ([M+1]$^+$, calcd 198.0612).

### 4-24 1,2-difluoro-4-(3-methylbut-3-en-1-yl)benzene

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.76$ (s, 3H), 2.25 – 2.32 (m, 2H), 2.71 (dd, $J = 9$, 7 Hz, 2H), 4.68 (td, $J = 1$, 1 Hz, 1H), 4.75 (tt, $J = 1$, 1 Hz, 1H), 6.84 – 6.91 (m, 1H), 6.98 (dddd, $J = 11$, 8, 5, 2 Hz, 1H), 7.01 – 7.08 (m, 1H) ppm. $^{19}$F$^{[1]}$H NMR (377 MHz, CH$_2$Cl$_2$): $\delta = -140.3$ (ddd, $J = 21$, 12, 8 Hz), -143.4 – -143.7 ppm (m). $^{13}$C$^{[1]}$H NMR (126 MHz, CDCl$_3$): $\delta = 22.7$, 33.5, 39.4, 110.9, 117.1 (t, $J = 17$ Hz), 124.2 (dd, $J = 6$, 4 Hz), 144.7, 147.8 (d, $J = 13$ Hz), 149.5 (dd, $J = 55$, 9 Hz) ppm. MS (EI+): 182.1 ([M]$^+$, calcd 182.21).

### 4-25 4-(3-bromobut-3-en-1-yl)-1,2-difluorobenzene

![Chemical structure](image)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.68$ (tt, $J = 8$, 1 Hz, 2H), 2.84 (dd, $J = 8$, 7 Hz, 2H), 5.39 (d, $J = 2$ Hz, 1H), 5.48 (dt, $J = 2$, 1 Hz, 1H), 6.86 – 6.93 (m, 1H), 7.00 (ddd, $J = 11$, 8, 2 Hz, 1H), 7.06 (dt, $J = 10$, 8 Hz, 1H) ppm. $^{19}$F$^{[1]}$H NMR (377 MHz, CDCl$_3$): $\delta = -139.3$ (ddd, $J = 21$, 12, 8 Hz), -142.7 ppm (ddd, $J = 22$, 11, 8, 4 Hz). $^{13}$C$^{[1]}$H NMR (126 MHz, CDCl$_3$): $\delta = 33.6$ (d, $J = 1$ Hz), 43.1 (d, $J = 1$ Hz), 117.2 (dd, $J = 17$, 1 Hz), 117.4 (d, $J = 17$ Hz), 117.9, 124.5 (dd, $J = 6$, 4 Hz), 132.9, 137.3 (dd, $J = 6$, 4 Hz), 148.7 (dd, $J = 147$, 13 Hz), 150.7 (dd, $J = 148$, 13 Hz) ppm. MS (EI+): 247.9 ([M]$^+$, calcd 247.1).

### 4-26 3-(1-adamantyl)-propene

![Chemical structure](image)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.47 – 1.48$ (m, 6H), 1.60 – 1.68 (m, 6H), 1.82 (d, $J = 8$ Hz, 2H), 1.94 (m, 3H), 4.96 (ddt, $J = 17$, 3, 1 Hz, 1H), 5.00 (ddt, $J = 10$, 3, 1 Hz, 1H), 5.83 (ddt, $J = 17$, 10, 8 Hz, 1H) ppm. $^{13}$C$^{[1]}$H NMR (126 MHz, CDCl$_3$): $\delta = 28.9$, 32.8, 37.3, 42.6, 49.2, 116.6, 135.1 ppm. HRMS (DART-TOF+): 177.16504 ([M+1]$^+$, calcd 177.16433).
3-(1-adamantyl)-2-methyl-propene

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.48 – 1.52$ (m, 6H), $1.58 – 1.68$ (m, 6H), $1.78$ (s, 3H), $1.8$ (s, 2H), $1.90 – 1.97$ (m, 3H), $4.58$ (dt, $J = 3$, 1 Hz, 1H), $4.84$ (dt, $J = 3$, 1 Hz, 1H) ppm. $^{13}$C$^1$H NMR (126 MHz, CDCl$_3$): $\delta = 26.0$, $29.0$, $31.6$, $37.3$, $43.1$, $45.0$, $113.7$, $128.1$ ppm. MS (EI+): 189.1 ([M]+, calcd 189.32).

oct-1-ene and mixture of allylated rearrangement products

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 0.85$ (t, $J = 7$ Hz, 3H), $1.24 – 1.34$ (m, 6H), $1.35 – 1.37$ (m, 2H), $2.02$ (m, 2H), $4.79 – 4.85$ (m, 2H), $4.92$ (ddd, $J = 10$, 2, 1 Hz, 1H), $5.0$ (m, 1H), $5.79$ (ddt, $J = 17$, 10, 7 Hz, 1H) ppm. $^{13}$C$^1$H NMR (126 MHz, CD$_2$Cl$_2$): $\delta = 14.5$, $22.8$, $25.7$, $28.5$, $33.0$, $37.7$, $115.5$, $138.3$ ppm. MS (EI+): 112.2 ([M]+, calcd 113.0).

(2,6-dimethylhepta-1,6-dien-4-yl)benzene

The desired product was detected by mass spectroscopy, but additional decomposition, presumably via Lewis acid catalyzed polymerization, was also observed. HRMS (DART-TOF+): 201.16400 ([M+1]+, calcd 201.16433).

(2,6-dimethyl-4-(2-methylallyl)hepta-1,6-dien-4-yl)benzene:

The desired product was detected by mass spectroscopy, but additional decomposition, presumably via Lewis acid catalyzed polymerization, was also observed. MS (EI+): 254.2 ([M]+, calcd 254.42).

4.5.6 Allylation of C-X Bonds

The benzyl halide (0.1 mmol) and allyltrimethylsilane (A1) (0.3 mmol) were combined in DCM (0.5 mL). This solution was added to an NMR tube pre-charged with the appropriate amount of solid catalyst and a sealed capillary containing a solution (CDCl$_3$) of mesitylene and C$_6$F$_6$ as $^1$H
and $^{19}$F{$^1$H} NMR integration standards. The tube was inverted several times to obtain a clear solution, which was monitored under various conditions.

4.5.7 Functional Group Tolerance

The appropriate functionalized additive (0.1 mmol), 4-phenyl-benzyl fluoride (0.1 mmol), and allyltrimethylsilane (A1) (0.3 mmol) were combined in DCM (0.5 mL). This solution was added to an NMR tube pre-charged with the appropriate amount of solid catalyst and a sealed capillary containing a solution (CDCl$_3$) of mesitylene and C$_6$F$_6$ as $^1$H and $^{19}$F{$^1$H} NMR integration standards. The tube was inverted several times to obtain a clear solution, which was monitored under various conditions.

4.5.8 Control Reactions

4.5.8.1 Catalytic Reactions with Allylsilanes

A solution of the allylsilane (0.1 mmol) in DCM (0.5 mL) was added to an NMR tube pre-charged with the appropriate amount of solid catalyst (5 mol%). The tube was inverted several times to obtain a clear solution, which was monitored under various conditions.

4.5.8.2 Stoichiometric Reactions with Benzyl Fluorides

A solution of the 4-phenyl-benzyl fluoride (0.01 mmol) in DCM (0.5 mL) was added to an NMR tube pre-charged with the appropriate amount of solid catalyst (0.01 mmol). The tube was inverted several times to obtain a clear solution, which was monitored under various conditions.

4.5.9 Computational Details

Calculations were carried out with the Gaussian 09 package.$^{73}$ Geometry optimizations were performed with the M06-2X functional.$^{74}$ The Def2-SVP basis set was used for all the atoms. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy. Transition states were submitted to intrinsic reaction coordinate (IRC) calculations to determine two corresponding minima.

The single-point energy calculations were performed with the M06-2X/Def2-TZVP method for solution-phase (dichloromethane). The gas-phase geometry was used for all the solution phase
calculations. The SMD method was used, while Bondi radii were chosen as the atomic radii to define the molecular cavity. The Gibbs energy corrections from frequency calculations were added to the single-point energies to obtain the Gibbs free energies in solution. All the solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298K.

4.6 References


Chapter 5

Conclusion

5.1 Summary

The work presented in this thesis explored the synthesis and reactivity of organophosphorus species in the context of phosphinoboranes and phosphorus-based Lewis acids. In Chapter 2, Section 2.1, a series of phosphinoboranes 2-2 to 2-6 were synthesized and their P-B bond character was analyzed from crystallographic and computational data with comparisons to Ph2PBpin, Ph2PBcat, Ph2PBMes2, and Mes2PB(C6F5)2. The reactivity of many of these phosphinoboranes was explored with benzylic chloride, producing acyl phosphines 2-7 to 2-9 and the respective chloroboranes. Additionally, with Ph2PBpin and Ph2PBcat were shown to undergo subsequent addition across the carbonyl group of the diphenylphosphine-substituted acyl phosphate 2-7 to yield 2-10 and 2-11, respectively.

In Chapter 2, Section 2.2, these phosphinoboranes were applied in reactions with carbon dioxide. While Mes2PB(C6F5)2 showed no reactivity, reactions with 2-2, 2-3, Ph2PBpin, and Ph2PBMes2 produced 1,2-addition products across one carbonyl group of carbon dioxide. Phosphinoboranes bearing a Bcat group were shown to produce diphospha-ureas 2-17 to 2-19 with concomitant O(Bcat)2 production. The mechanisms of reactions with Ph2PBpin, Ph2PBcat, and 2-4 were explored computationally. Reactions of Ph2PBpin and Ph2PBcat were found to proceed via two consecutive phosphinoboration reactions of carbon dioxide, while in the case of 2-4, computations support a different mechanism where phosphinoboration of one carbonyl group is followed by P-B/C-O bond metathesis. These insights are supported by a higher activation energy required for the reaction of Ph2PBpin, consistent with the experimentally observed single addition product 2-13. In further support of this computed mechanism, the computed reaction intermediate 2-13 was identified from a single crystal X-ray diffraction study, although its acute instability precluded full characterization.

In Chapter 2, Section 3, reactions of Ph2PBcat and 2-6 with diazobenzene were found to produce the 1,2-addition products 2-20 and 2-21, respectively. Efforts to extend this chemistry to Ph2PBpin required elevated temperatures and gave multiple products while Ph2PBMes2 showed no reactivity even at elevated temperatures. The mechanisms of the addition reactions of Ph2PBcat, Ph2PBpin,
and Ph₂PBMes₂ were probed computationally and found to proceed via B-N adduct formation followed by concerted migration of the phosphorus centre to the other nitrogen atom. This study showed a somewhat higher energy barrier for Ph₂PBpin than for Ph₂PBcat, consistent with the need to heat the reaction mixture, and a significantly higher energy barrier for Ph₂PBMes₂, consistent with the lack of observed reactivity. Despite the weak Lewis acidity of the boron centre in 2-20, as determined computationally by evaluation of the frontier orbitals, intramolecular frustrated Lewis pair reactivity was observed for 2-20 and 2-21 with strongly basic substrates, yielding unique five-, six-, and eight-membered rings 2-24 to 2-28 as well as a hydrolysis product 2-29. Phosphinoboration reactions of diazomethanes were also explored, with 2-30 and 2-31 being isolated. Although quite robust, 2-30 and 2-31 were found not to behave as intramolecular FLPs, instead giving no reaction or decomposition. In targeting other phosphinoborane-derived intramolecular FLPs, the CN-linked 9-PPh₂-10-Bpin-dihydroacridine was prepared and investigated. However, reactions resulted in decomposition via rearomatization of the acridine linker.

In Chapter 3, Section 3.1, a family of apically phenoxy-substituted phosphonium salts 3-1 to 3-4 was synthesized with varying amounts of fluorines on the phenoxy ring. These phosphonium salts were found to be somewhat more robust to atmospheric moisture than the fluorophosphonium analogue [(C₆F₅)₃PF][B(C₆F₅)₄] in the order of increasing stability of 3-4 to 3-1. Evaluations of their Lewis acidities by ³¹P{¹H} and ¹⁹F{¹H} NMR shifts, the Gutmann-Beckett method, fluoride ion affinity (FIA), and the global electrophilicity index (GEI) found the phenoxyphosphonium salts to be somewhat less Lewis acidic than [(C₆F₅)₃PF][B(C₆F₅)₄] in the order of increasing reactivity of 3-1 to 3-4. In this first application of GEI to strong main group Lewis acids, GEI was found to correlate well with the already established FIA. This trend in Lewis acidity was borne out in the productivities of these Lewis acids in Lewis acid catalyzed reactions.

In Chapter 3, Section 3.2, the double hydroarylation of diarylamines with alkynes was discovered, producing acridane or 9,9-disubstituted 9,10-dihydroacridine derivatives. Various Lewis acids were screened and a dicaticonic phenoxyphosphonium salt was chosen for its balance of reactivity and stability. The reaction scope was found to tolerate variants of arene-substituted alkynes bearing heteroarenes, electron donating groups, and electron withdrawing groups, while the use of an arene bearing two alkyne groups was found to yield the double acridane product. The scope of diarylamines was also limited to electron rich diarylamines, with N-alkylated derivatives proving
most productive. However, no reaction was observed for aliphatic or internal alkynes and for electron deficient diarylamines or diaryl groups with other heteroatom linkers (i.e. O, S, P). The proposed mechanism of alkyne activation by the phosphonium salt followed by nucleophilic aromatic substitution by the diarylamine is supported by similar reactions reported for phosphonium salts. Additionally, application of the sterically challenging mesitylacetylene yielded the singly hydroarylated product 3-16, representing the proposed reaction intermediate.

In Chapter 3, Section 3.3, the sterics and electronics imposed by the 3,5-(CF$_3$)$_2$C$_6$H$_3$ substituent of 3-24 were evaluated in comparison to [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$]. The stability of 3-24 was found to be poorer than [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] with respect to moisture, Et$_3$PO, and hydride donors including silanes and boranes, consistent with the decreased sterics at the phosphorus centre. The Lewis acidity of 3-24 was found to be only slightly less than [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] according to FIA and GEI, consistent with competition experiments between 3-23 and [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] and between 3-24 and (C$_6$F$_5$)$_3$PF$_2$. Self-exchange reactions of both Lewis acids were probed with 1D SEXSY which demonstrated that 3-24 underwent self-exchange significantly faster than [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$], consistent with decreased sterics allowing for greater access around the phosphorus centre. This balance of sterics and Lewis acidity was borne out in comparisons of Lewis acid catalysis, with 3-24 outperforming [(C$_6$F$_5$)$_3$PF][B(C$_6$F$_5$)$_4$] only in a sterically demanding reaction.

In Chapter 4, tridentate diiminopyridine ligands were used to stabilize dicationic phosphorus-based Lewis acids 4-3 to 4-6. Along with the bi- and terpyridine ligated analogues 4-1 and 4-2, respectively, 4-3 and 4-5 were found to be active catalysts in the allyldefluorination of aliphatic C-F bonds. This reaction was only developed for 4-1 and 4-2, as 4-3 and 4-5 could not be isolated purely. The scope of this reaction was found to tolerate electron rich and electron deficient allylsilanes, a variety of sterically encumbered, electron rich, and electron deficient benzyl fluorides as well as 1-fluoropentane, α,α-difluorotoluene, and α,α,α-trifluorotoluene, albeit under forcing conditions. Given the recognized air stability of 4-2, reactions were successfully performed in ambient atmosphere and with undried benchtop solvent. Additionally, 4-1 and 4-2 were found to be selective for C-F bond activation over C-Cl or C-Br. Reactions performed in the presence of functional group-bearing additives demonstrated the better functional group tolerance of 4-2 than 4-1, consistent with its improved stability. While investigations into the mechanism support the first step being C-F activation by the Lewis acid catalyst, computations indicate that the active
sites are exposed from hemilability of one of the tridentate ligand arms in 4-2⁺ or 4-3⁺. Therefore, 4-1 effectively models the active catalyst of 4-2. This is the first demonstration of a carbon-carbon coupling reaction catalyzed by trivalent phosphorus Lewis acids.

5.2 Future Work

The reactions of phosphinoboranes with various unsaturated substrates were often found to be clean and facile. Given this and similar reported reactions,¹⁻⁵ a cornucopia of phosphinoboration chemistry likely remains to be discovered. Target substrates for addition chemistry should either contain reactive bonds or sites of unsaturation. Particularly interesting substrates might include those with multiple reactive sites as multiple phosphinoboration events could occur to give surprising and potentially otherwise synthetically challenging products. Additionally, products of phosphinoborane addition reactions could find use as sterically and electronically tunable ligands in metal chemistry with a range of denticities depending on the addition product.⁶⁻⁸

While the phosphinoboration products 2-20 and 2-21 displayed intramolecular frustrated Lewis pair chemistry, similar reactivity was not observed for products with a facile route to decomposition or where the Lewis acidic and basic sites are held closely. Investigations of the intramolecular FLP chemistry of other products of phosphinoboration reactions remain interesting, provided that the systems are chosen carefully. Systems that avoid the pitfalls found herein include those with two or more linker atoms between the Lewis acidic and basic sites and those without a facile route to decomposition (i.e. rearomatization of the linker). Many suitable options exist given the variety of known phosphinoboration products. It would be particularly interesting to compare the steric and electronic influences of aldehyde-, ketone-, and imine-based intramolecular FLP linkers in this context.²⁻⁴

Although the use of phenoxy groups with various degrees of fluorination improved the stability of 3-1 to 3-4 with respect to [(C₆F₅)₃PF][B(C₆F₅)₄], the effect was minor and came at the cost of Lewis acid reactivity. Nevertheless, this strategy was successfully applied to a pyridinium-substituted dicationic phosphonium salt that displayed significantly improved stability while maintaining Lewis acid reactivity. As such, applying this approach to other strong Lewis acids might provide similar results, with a NHC-substituted dicationic phenoxyphosphonium salt being a reasonable target.⁹ Furthermore, with respect to the global electrophilicity index first used to
assess phenoxy-substituted phosphonium salts, the Stephan group has expanded and refined the method to include other Lewis acids.\textsuperscript{10, 11}

The phosphonium salt catalyzed double hydroarylation reaction of diarylamines with alkynes is was shown to produce the double acridane-type product when a 1,4-diethynylbenzene was used. Presumably, the reaction of an alkyl-linked tetraaryldiamine would also produce a double acridane-type product. As such, the combination of these approaches could be used to synthesize acridane-containing polymers. Additionally, the sterically demanding intermediate(s) of this reaction’s catalytic cycle produced a noticeable difference in the catalytic yields of 3-24 and [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] due to differences in stericities around their Lewis acidic sites. Therefore, this reaction could also find use as a test for steric differences between electrophilic phosphonium salts.

When quantifying the electronic and steric differences imparted by fluorinated arene rings around the phosphorus centres of 3-24 and [(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}PF][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}], self-exchange reactions and metrics of Lewis acidity were used to great effect. Results from these experiments were used to predict and rationalize subsequent Lewis acid reactivity. It would be interesting to apply these methodologies to the systematic study of electronic and steric influences imparted by other substituents, as this could be used to inform catalyst design for specific reactions. The natural extension is to study phosphonium salts, but this methodology is likely applicable to other Lewis acidic species including the more commonly used boranes.\textsuperscript{12} However, significantly reduced stericities around the Lewis acidic sites of boranes might result in very fast self-exchange rates or adduct formation, in which case 1D SEXSY\textsuperscript{13} would not be applicable. Instead, variable temperature NMR would provide a suitable replacement.

The isolation of dicationic phosphorus species bearing polydentate ligands was found to be facile for bi- and tridentate pyridyl ligands (4-1 and 4-2) but not for tridentate diiminopyridine ligands (4-3 and 4-5). However, both ligand sets were shown to produce interesting C-F reactivity. As such, a clear extension of this work is to apply these species towards other Lewis acid catalyzed reactions. To date, the Stephan group has reported the use of 4-2 as catalysts in hydrosilylations and deoxygenations,\textsuperscript{14} however Diels-Alder cycloadditions, C-C cross couplings, and Friedel-Crafts alkylations are also under investigation. Another extension is to continue to draw from transition metal ligand libraries to develop dicationic phosphorus species with tunable stability, selectivity, and reactivity. Both bi- and tridentate ligands bound by a number of heteroatoms are
available, including ones that impose chirality at the Lewis acidic site. The Stephan group is currently exploring the synthesis of such derivatives and their use in asymmetric catalysis.

5.3 References


