2008

'Frustrated' Lewis pairs: From Lewis acid -base adducts to the reversible, metal-free activation of hydrogen

Gregory Charles Welch
University of Windsor

'Frustrated' Lewis Pairs: From Lewis Acid-Base Adducts to the Reversible, Metal-Free Activation of Hydrogen

By

Gregory Charles Welch

A Dissertation

Submitted to the Faculty of Graduate Studies

Through the Department of Chemistry and Biochemistry

In Partial Fulfillment of the Requirements for

The Degree of Doctor of Philosophy

At the University of Windsor

Windsor, Ontario, Canada

2008

Your file Votre référence
ISBN: 978-0-494-47110-4
Our file Notre référence
ISBN: 978-0-494-47110-4

Declaration of Co-Authorship/Previous Publication

I. Co-Authorship Declaration

I hereby declare that this thesis incorporates material that is result of joint research, as follows:

This thesis incorporates the outcome of research undertaken with the assistance of the following summer students: Ronan San Juan, Tori Piga, Roberto Prieto, Thorsten Holtrichter-Roessmann, and graduate students: Jason Masuda, Kory Conroy, Lourdes Cabrera, Shamola Labodean, and Emily Hollink under the supervision of professor Douglas W. Stephan. In all cases, the key ideas, primary contributions, experimental designs, data analysis and interpretation, were performed by the author, and the contribution of co-authors was primarily through the provision of guided synthesis and assistance with X-ray data acquisition.

I am aware of the University of Windsor Senate Policy on Authorship and I certify that I have properly acknowledged the contribution of other researchers to my thesis, and have obtained written permission from each of the co-author(s) to include the above material(s) in my thesis.

I certify that, with the above qualification, this thesis, and the research to which it refers, is the product of my own work.

II. Declaration of Previous Publication

This thesis includes 5 original papers that have been previously published in peer reviewed journals, as follows:

Thesis Chapter	Publication title/full citation	Publication status*
Chapter 2	**Welch, G. C.**; Holtrichter-Roessmann, T.; Stephan, D. W. Thermal Rearrangement of Phosphine-$B(C_6F_5)_3$ Adducts. *Inorg. Chem.* 2008, 47, 1904-1906.	*Published*
Chapter 2 and Chapter 3	**Welch, G. C.**; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. Tuning Lewis Acidity Using The Reactivity of "Frustrated Lewis Pairs": Facile Formation of Phosphine-boranes and Cationic Phosphonium-boranes. *Dalton Trans.* 2007, 31, 3407-3414.	*Published*
Chapter 4	**Welch, G. C.**; Masuda, J. D.; Stephan, D. W. Phosphonium-Borate Zwitterions, Anionic Phosphines, and Dianionic Phosphonium-Dialkoxides via Tetrahydrofuran Ring-Opening Reactions. *Inorg. Chem.* 2006, 45, 478-480.	*Published*
Chapter 5	**Welch, G. C.**; Stephan, D. W. Facile Heterolytic Cleavage of Dihydrogen by Phosphines and Boranes. *J. Am. Chem. Soc.* 2007, 129, 1880-1881.	*Published*
Chapter 5	**Welch, G. C.**; San Juan, R.; Masuda, J. D.; Stephan, D. W. Reversible, Metal Free Hydrogen Activation. *Science* 2006, 314, 1124-1126.	*Published*

I certify that I have obtained a written permission from the copyright owner(s) to include the above published material(s) in my thesis. I certify that the above material describes work completed during my registration as graduate student at the University of Windsor.

I declare that, to the best of my knowledge, my thesis does not infringe upon anyone's copyright nor violate any proprietary rights and that any ideas, techniques, quotations, or any other material from the work of other people included in my thesis,

published or otherwise, are fully acknowledged in accordance with the standard referencing practices. Furthermore, to the extent that I have included copyrighted material that surpasses the bounds of fair dealing within the meaning of the Canada Copyright Act, I certify that I have obtained a written permission from the copyright owner(s) to include such material(s) in my thesis.

I declare that this is a true copy of my thesis, including any final revisions, as approved by my thesis committee and the Graduate Studies office, and that this thesis has not been submitted for a higher degree to any other University of Institution.

Abstract

The concept of 'frustrated' Lewis pairs involves donor and acceptor sites in which steric congestion precludes Lewis acid–base adduct formation. In the case of sterically demanding phosphines and some boranes, this lack of active site-quenching prompts nucleophilic attack by P at a carbon *para* to B of $B(C_6F_5)_3$ followed by fluoride transfer, which affords zwitterionic phosphonium borates of the form $[R_3P(C_6F_4)BF(C_6F_5)_2]$ and $[R_2PH(C_6F_4)BF(C_6F_5)_2]$, where R = aryl, alkyl. Additionally, a series of tertiary and secondary phosphine-$B(C_6F_5)_3$ adducts are shown to undergo facile, thermal-induced rearrangement to give analogous zwitterionic species of the form $[R_3P(C_6F_4)BF(C_6F_5)_2]$ and $[R_2PH(C_6F_4)BF(C_6F_5)_2]$, respectively, where R = aryl, alkyl.

These species can be easily transformed into anionic phosphine-borates $[R_2P(C_6F_4)BF(C_6F_5)_2]^-$, cationic phosphonium-boranes $[R_3P(C_6F_4)B(C_6F_5)_2]^+$ and $[R_2PH(C_6F_4)B(C_6F_5)_2]^+$ or the charge neutral phosphino-boranes $R_2P(C_6F_4)B(C_6F_5)_2$. This new reactivity provides a modular route to a family of boranes in which the steric features about the Lewis acidic boron center remain constant and yet the variation in substitution at phosphorus provides a facile avenue for the tuning of the Lewis acidity. Employing the Gutmann–Beckett and Childs methods for determining Lewis acid strength, it was demonstrated that the cationic boranes are more Lewis acidic than $B(C_6F_5)_3$, while the acidity of the phosphino-boranes is diminished.

Sterically demanding tertiary and secondary phosphines, as well as secondary phosphides, have been shown to react with $(THF)B(C_6F_5)_3$ (THF = tetrahydrofuran) to give the THF ring-opened compounds $[R_3P(C_4H_8O)B(C_6F_5)_3]$, $[R_2PH(C_4H_8O)B(C_6F_5)_3]$ and $[R_2P(C_4H_8O)B(C_6F_5)_3Li(THF)_2]$ (R = aryl, alkyl). With appropriate stoichiometry,

these reactions also occur consecutively to give the double THF ring-opened compounds $[Mes_2P(C_4H_8OB(C_6F_5)_3)_2][Li(THF)_4]$ and $[^tBu_2P(C_4H_8OB(C_6F_5)_3)_2][Li]$.

Finally, it has been reported that the compounds $R_2PH(C_6F_4)BH(C_6F_5)_2$ (R = aryl or alkyl), cleanly liberate H_2 at temperatures above 100 °C to give the dehydrogenated products $R_2P(C_6F_4)B(C_6F_5)_2$, which are stable and react with 1 atmosphere of H_2 at 25 °C to reform the starting complex. Combinations of sterically demanding phosphines R_3P and $B(C_6F_5)_3$ also uptake H_2 at ambient temperature and pressure. H_2 liberation from the series of compounds can be facilitated using a weak Lewis base. Preliminary kinetic and deuterium labelling experiments indicate that the reversible activation of H_2 follows an intermolecular mechanism.

Dedication

I dedicate this thesis to Jack and Megan Welch

Acknowledgements

I would like to thank the following people for help during my 4+ years studying at the University of Windsor. First, I would like to thank Jenny McCahill, the entire Welch, McCahill, and Ochej family for all their support along the way. Second, I would like to thank Steve Geier, Dr. Preston Chase and Dr. Jason Masuda for all their help in analyzing, discussing, and editing my work. Special thanks to Mike Fuerth for all his help, time, and patience with all NMR spectroscopic analysis. Next, I would like to thank Prof. Robert Schurko, Prof. Charles Macdonald, Prof. Samuel Johnson, Prof. James Gauld, and Joe Lichaa for all their technical help. I would like to thank Dr. Alan Lough (University of Toronto) for help with X-ray crystallography. Next, I would like to thank the following fellow students and former undergraduates who contributed to work in this thesis: Ronan San Juan (kinetics), Kory Conroy (DOSY NMR), Lourdes Cabrera (synthesis), Roberto Prieto (synthesis), Thorsten Holtrichter-Roessmann (synthesis), Shamola Labodean (synthesis), Tori Piga (synthesis), Emily Hollink (synthesis), and Kelsey Dewar (synthesis). I would like to thank all the staff and faculty at the University of Windsor who have aided in the completion of all of my PhD requirements, especially Marlene Bezaire and Kimberly Kickham. I would like to thank all of my committee members for taking the time to help me out and all the past and present Stephan group members who I have overlapped with. Finally, I would like to thank my supervisor Prof. Douglas W. Stephan for all his guidance, enthusiasm, encouragement, and financial support over the course of the last 4+ years. Thanks to everyone.

Scope and Significance

There is a growing emphasis on 'green chemistry', which entails the development of novel compounds and process to carry out chemical reactions and/or transformations in a way that is efficient, cost effective, and environmentally friendly. Specifically, the ability to activate, store, and deliver or transfer hydrogen to another molecule or system in a 'green' fashion is important to both the hydrogen fuel economy and the catalytic hydrogenation of unsaturated molecules. Eliminating metals from such process reduces costs and environmentally unfriendly waste and, in the case of hydrogen storage, increases the weight % of available H_2. While great strides have been made in the development of metal-free systems capable of delivering or transferring hydrogen, little headway has been made in the metal-free uptake of hydrogen. By challenging the basic assumption that Lewis acids and bases must form donor-acceptor adducts, we have discovered that sterically demanding phosphines and boranes can yield complexes that reversibly activate hydrogen. These complexes represent the first metal-free systems capable of such reactivity. They have been found to be effective hydrogenation catalysts using H_2 as the hydrogen source, which eliminates the need for expensive metals and the use of stoichiometric reducing agents such as BH_4^-. The synthesis, characterization, and reactivity of these complexes is described is this thesis.

The work presented in this thesis has had a profound impact on the scientific community. At the time of writing five publications have directly resulted from this work, and have appeared in the scientific journals Science,[1] Journal of the American Chemical Society,[2] Dalton Transactions[3] and Inorganic Chemistry (2).[4, 5] Additionally, aspects of the work described in this thesis have been patented. Seven publications have resulted

from very closely related chemistry carried out in the Stephan research group and have appeared in the scientific journals Angewandte Chemie International Edition (3),[6-8] Chemical Communications (2),[9, 10] Journal of the American Chemical Society[11] and Inorganica Chimica Acta.[12] The work discussed in this thesis has also inspired several other independent research groups to investigate related chemistry with publications appearing in the scientific journals Science,[13] Angewandte Chemie International Edition (4),[14-17] Chemical Communications (3),[18-20] Inorganic Chemistry[21] and European Journal of Inorganic Chemistry.[22] Concept (Organic and Biomolecuar Chemistry),[23] highlight (Angewandte Chemie International Edition),[24] and perspective (Science)[25] articles have also been published that include work presented in this thesis. This is a high volume of high impact publications considering the first work was published in 2006. The initial publication in Science describing the first literature example of reversible, metal-free hydrogen activation also garnered international attention being featured in Chemical & Engineering News, several CANWEST media outlets, and numerous scientific related websites. The work reported in this publication was also listed as one of NSERCs top 50 discoveries of 2006. Additionally this publication has been cited 53 times at the time of printing this thesis.

Table of Contents

List of Figures

List of Tables

List of Schemes and Equations

List of Abbreviations, Nomenclature and Symbols

Å	angstrom
Abs coeff	absorption coefficient
ArF	fluorylaryl ring
br	broad
BBN	9-borabicyclo[3.3.1]nonanyl, $C_8H_{14}B$
Bu	*n*-butyl, C_4H_9
^{t}Bu	*t*-butyl, C_4H_9
calcd	calculated
CCD	charge coupled device
COD	cyclooctadiene C_8H_{12}
COSY	correlation spectroscopy
Cp	cyclopentyl C_5H_9
Cy	cyclohexyl C_6H_{11}
°C	degrees Celsius
D_{calc}	calculated density
d	doublet
DOSY	diffusion ordered spectroscopy
DEPT	distortionless enhancement by polarization transfer
eq	equivalents
Et	ethyl C_2H_5
Eu	entropy units

FLP	'frustrated' Lewis pair
g	grams
GOF	goodness of fit
h	hours
Hz	hertz
HOESY	heteronuclear Overhauser enhancement spectroscopy
HMQC	heteronuclear multiple quantum correlation
HSQC	heteronuclear single quantum correlation
^{i}Pr	*iso*-propyl, C_3H_7
IR	infrared
J	coupling constant
k	overall rate constant
kcal	kilocalories
kJ	kilojoules
L	liter
m	multiplet
M	mol L^{-1}
m	*meta*
Me	methyl CH_3
Mes	mesityl ($C_6H_2Me_3$-2,4,6)
MesCN	mesitylnitrile
mg	milligram
MHz	megahertz
min	minute

mL	milliliter
mmol	millimole
NAS	nucleophilic aromatic substitution
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
o	*ortho*
p	*para*
PGSE	pulse gradient spin echo
Ph	phenyl, C_6H_5
POV-ray	Persistence of Vision Raytracer
ppm	parts per million
Proton Sponge	1,8-Bis(dimethylamino)naphthalene $C_{10}H_6(NMe_2)_2$
R	residual
R_w	weighted residual
RT	room temperature
s	singlet, seconds
t	triplet
^{t}Bu	tert-butyl $C(CH_3)_3$
THF	tetrahydrofuran C_4H_8O
TMS	trimethylsilyl
wt %	weight percent
μmol	micromole

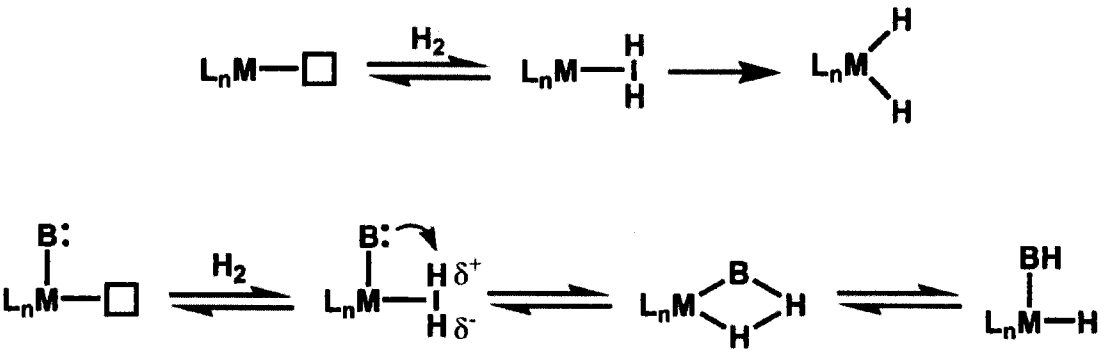
Chapter 1 Introduction

1.1 Overview of Dissertation

The work in this document is comprised of three major parts. The first part describes the effect of phosphine size on interactions between Lewis basic tertiary, secondary, and primary phosphines and the Lewis acid $B(C_6F_5)_3$. Depending on the size of the phosphine, reactions with $B(C_6F_5)_3$ can yield donor-acceptor adducts, zwitterionic phosphonium borates of the form $R_3P(C_6F_4)BF(C_6F_5)_2$, or 'frustrated' Lewis pairs (Chapter 2). The second part describes the conversion of phosphonium borates into anionic phosphines, cationic boranes, and phosphino-boranes and explores the individual reactivity of each derivative (Chapter 3). The third and final part describes the reactivity of 'frustrated' Lewis pairs with the small molecules THF and H_2 and details the reversible H_2 activation by a series of phosphino-boranes (Chapters 4 and 5).

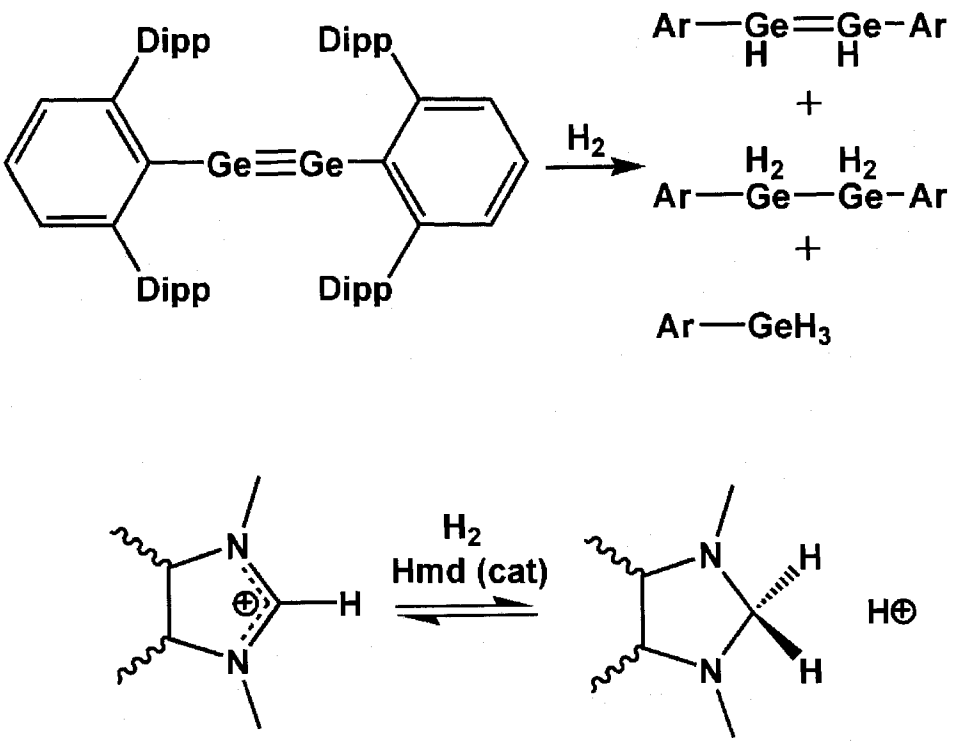
1.2 Activation and Liberation of Hydrogen

The generation and use of molecular hydrogen (H_2) are important processes to fundamental chemical transformations,[26-32] biological functions,[33] and the hydrogen fuel economy. Specifically, catalytic hydrogenations, the addition of H_2 to unsaturated molecules, are the largest volume reactions in the world being involved in the hydrocracking of crude oil and the synthesis of ammonia fertilizer via the Haber process.[34, 35]



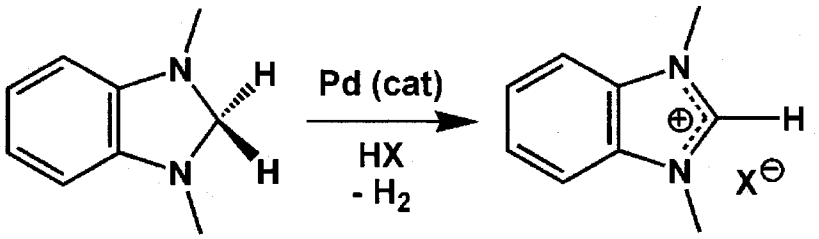
Scheme 1.1 Activation of H_2 with transition metals. (**Top**) Homolytic cleavage of H_2: Formation of metal-H_2 complex followed by oxidative addition. (**Bottom**) Heterolytic cleavage of H_2. Formation of metal-H_2 complex followed by proton abstraction by a pendant Lewis base.

The overwhelming majority of systems known to either liberate or react with H_2 involve reaction at a transition metal center. Hydrogenase enzymes, as well as a plethora of synthetic stoichiometric and catalytic reagents for hydrogenation reactions, are based on the processes of oxidative addition and reductive elimination of H_2 at a metal center (Scheme 1.1). Ligand-metal bifunctional catalysts, such as Noyori's[36, 37] or Shvo's[38] asymmetric hydrogenation catalysts, have been shown to activate H_2 via a heterolytic process where a metal-H_2 complex is deprotonated by a basic ligand (Scheme 1.1). Metal-free systems that either react with or liberate H_2 are rare. A unique metal-free hydrogenase from methanogenic archaea has been shown to catalyze reactions with H_2 (Scheme 1.2). Although recent work has shown that these enzymes do contain iron, these metal centers are not believed to be the site of H_2 activation.[39-41] Theoretical studies have also suggested the role of a folate-like cofactor in the reversible activation or liberation of H_2.[42, 43]



Scheme 1.2 (Top) Reaction of an unsaturated digermanium complex with H_2. **(Bottom)** Iron-sulphur hydrogenase catalysizes the activation of H_2 with a folate-like cofactor.

Additionally, sulphide ligands bridging two transition metal centers can heterolytically cleave H_2 to give SH ligands.[44] Several metal-free systems have been shown to activate H_2. For example, main group element–H_2 reactions in low-temperature matrices have been reported,[45-48] and computational studies have probed the occurrence of H_2 bonds in main-group compounds.[49, 50] Trialkyl- and triiodo-boranes have been used in the hydrogenation of alkenes and coal at high temperatures (> 220°C) and H_2 pressures (> 67 atm).[51-57] More recently, Power and co-workers[58] reported that the addition of H_2 to RGeGeR-alkyne analogs affords a mixture of RGeGeR-alkene and primary germane products (Scheme 1.2). Metal-free systems that liberate H_2 are of interest for their potential in H_2 storage applications.



RH_2PBH_3 or RH_2NBH_3 $\xrightarrow[-H_2]{\Delta}$ Cyclic and oligomeric PB or NB materials

R = H, alkyl or aryl

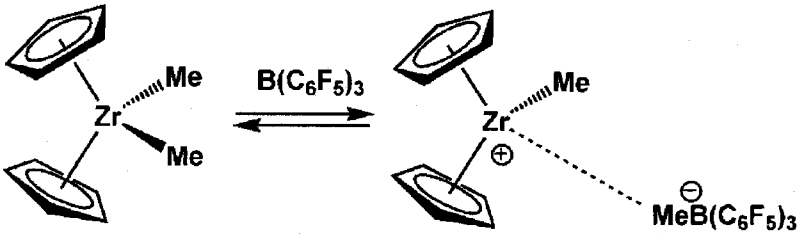
Scheme 1.3 (**Top**) Liberation of H_2 from an 'organic' hydride. (**Bottom**) Liberation of H_2 from phosphine- and amine-boranes.

While much effort has focused on hydride salts,[59-63] a recent report by Thorn and co-workers describes an organic "hydride" system that reacts with protic compounds to eliminate H_2, although the assistance of a metal-based catalyst is required (Scheme 1.3).[64] Much attention has been focused on H_3NBH_3 and H_3PBH_3 due to their high H_2 content by mass (Scheme 1.3); however reversibility has been a problem and often metal catalysts are employed to promote the loss of H_2.[65, 66] Despite these advances, no metal-free system has yet been reported to effect both the clean liberation and addition of H_2. Such metal-free systems are of great significance to both chemical hydrogen storage and catalytic hydrogenation. The use of main group elements offers the ability to develop light weight materials to store high percentages of H_2 while precious metals, such as platinum or rhodium, commonly used to reduce unsaturated molecules with H_2, are very costly due to their low natural abundance and are environmentally unfriendly. In order to develop non-metal systems that exhibit metal-like reactivity, a fundamental understanding of such chemistry is required. Our interest in non-metal chemistry lies with the interactions of

Lewis acids and bases, specifically the properties and reactivity of Lewis acidic boranes and Lewis basic phosphines.

1.3 Lewis Acids and Bases

Lewis acids and bases play dominant roles in much of chemistry. For example, Lewis basic phosphines are ubiquitous ligands in transition metal chemistry and many forms of catalysis.[67] On the other hand, Lewis acidic boranes are pervasive in studies of olefin polymerization[68, 69] and a variety of Lewis acid catalyzed reactions in organic chemistry.[70-76] In the case of polymerization catalysis, Lewis acid reagents such as the triorganoborane $B(C_6F_5)_3$ or its carbocation analog $[CPh_3]^+$ (trityl) have an important niche. They act as co-catalysts to generate catalytically active cationic early metal alkyl complexes as a result of the vacant 2p-orbitals on boron and carbon, respectively, which act as powerful alkyl abstractors (Scheme 1.4).[76-78] In 1923, Lewis first proposed his now universally accepted rationale for acid-base reactions to describe dative donor-acceptor adducts.[79]

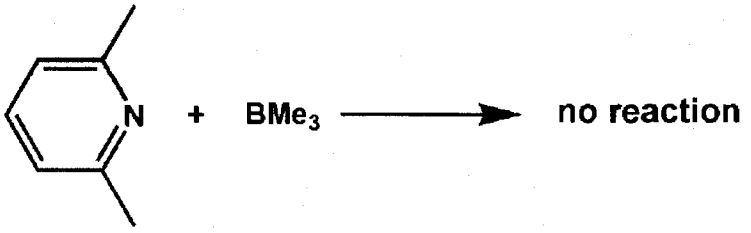


Scheme 1.4 Utility of $B(C_6F_5)_3$. Methyl abstraction from dimethylzirconocene forming an ion-pair active for olefin polymerization.

Lewis defined an acid as a substance capable of accepting a lone pair of electrons from another molecule and a base as a substance capable of donating a lone pair of electrons to another molecule. Lewis adducts, or donor-acceptor adducts, are the common product upon the reaction of Lewis acids and bases. The strong Lewis acid $B(C_6F_5)_3$ and related perfluorylaryl derivatives are known to form such Lewis adducts with a wide variety of Lewis bases. A recent review by Piers has described some 60 plus Lewis adducts of the form (donor)$B(C_6F_5)_3$, where donor molecules include phosphines, amines, pyridines, nitriles, imidazoles, ketones, aldehydes, among a long list of other P, N, and O atom containing bases.[80] However, we have observed several systems in which sterically demanding phosphine donors and Lewis acids generate what we now term 'frustrated' Lewis pairs (FLP's) in that this Lewis acid-base couple is sterically incapable of adduct formation, which opens alternate reaction pathways.

1.4 'Frustrated' Lewis pairs

In 1942, Cardon and co-workers reported that BMe_3 forms a stable adduct with pyridine in the presence of NMe_3. This surprised the authors as NMe_3 is a stronger base than pyridine, and they therefore concluded that steric strain between the Me groups of Me_3N-BMe_3 reduced the strength of the B-N dative bond. Further experiments showed that lutidine undergoes reversible adduct formation with BF_3 and shows no reaction towards BMe_3 (Scheme 1.5).



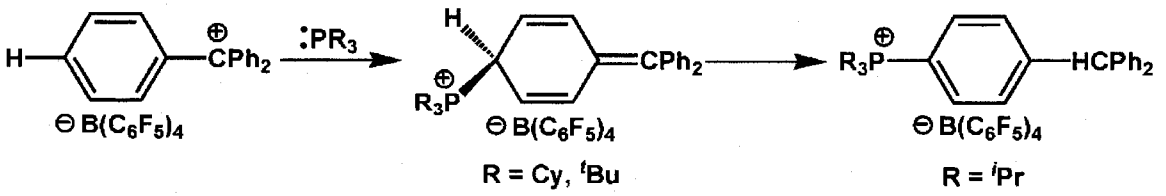
Scheme 1.5 First, literature example of steric bulk precluding traditional Lewis adduct formation.

The authors concluded that steric strain between the Lewis acid and base was responsible for the observed results.[81] This report marked the first literature example of what we now term 'frustrated' Lewis pairs. 'Frustrated' Lewis pairs or FLP's, are defined as combinations of a Lewis acid and a Lewis base that can co-exist without forming a traditional Lewis adduct due to steric interactions between the two compounds. The inability of the Lewis pair to form a stable adduct opens new reaction pathways, allowing the Lewis acidic and Lewis basic sites to react in a cooperative fashion towards other molecules in an unprecedented fashion. While many examples of FLP's likely exist in the literature, the full potential of cooperative reactivity between Lewis acids and bases was not realized until our our work on sterically demanding phosphines and boranes, described herein. This thesis describes the effect of steric bulk on the reaction between phosphines and boranes, and details the unprecedented reactivity of sterically 'frustrated' Lewis pairs.

Chapter 2 Synthesis and Characterization of Phosphonium Fluoroborates and 'Frustrated' Lewis Pairs

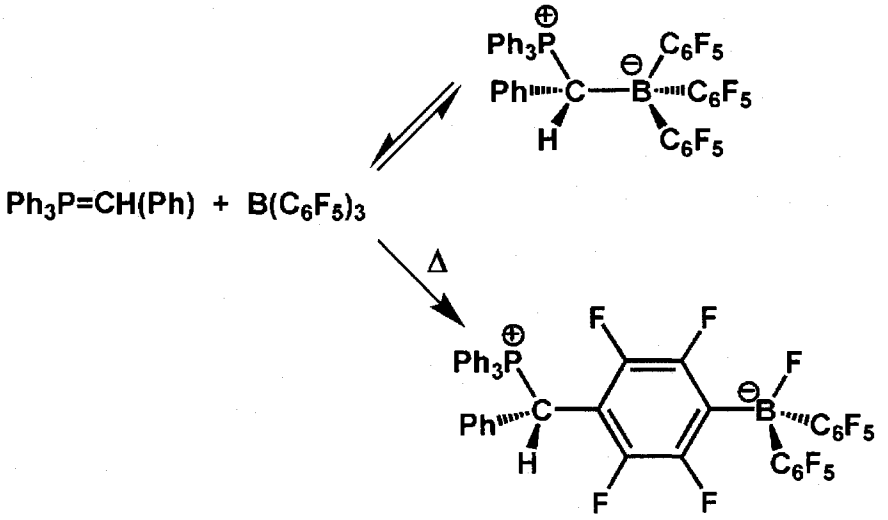
2.1 Introduction

As mentioned in the opening chapter, amines, pyridines and phosphines have been shown to form traditional Lewis acid–base adducts with $B(C_6F_5)_3$[70, 80, 82] and trityl cation.[83-91] In the case of trityl cation, recent work in our research group has shown that sterically demanding phosphines are too large to interact with the carbocation and instead effect nucleophilic aromatic substitution at a position *para* to the central trityl carbon.[12, 92] Such chemistry was both unexpected and unique; however, the resulting cyclohexadienyl and benzylhydryl-phenyl derivatives, generated by reaction of Cy_3P and $^{i}PrP_3$ with triyl cation respectively, proved to be extremely stable species and thus have limited reactivity. (Scheme 2A) In a similar fashion, it was discovered that the sterically demanding phosphines, Cy_3P and $^{i}Pr_3P$, do not form adducts with $B(C_6F_5)_3$ but rather generate zwitterionic phosphonium borates of the form $R_3P(C_6F_4)BF(C_6F_5)_2$, by a similar nucleophilic aromatic substitution pathway.[92]



Scheme 2A Reaction of trityl borate, $[Ph_3C][B(C_6F_5)_4]$, with bulky phosphines.

Such unusual reactivity has only been reported once in the literature by Erker and co-workers, where the ylide adduct $(Ph_3PC(H)Ph)B(C_6F_5)_3$ thermally rearranged to give the zwitterion *para*-$(Ph_3PC(H)Ph)(C_6F_4)BF(C_6F_5)_2$ (Scheme 2B).[93] Related zwitterions of the form *para*-$R_2EH(C_6F_4)B(C_6F_5)_3$[94] and *para*-$R_2EH(C_6H_4)B(C_6F_5)_3$[95] (E = N, P) have been claimed in the patent literature, but were synthesized via traditional routes involving the reaction of aryl lithium reagents with boron trihalides. The ability to generate phosphonium borate zwitterions rapidly in this convenient one step procedure is important because these compounds have the potential to act as bifunctional amphoteric complexes with applications in organic catalysis, olefin polymerization, and metal complexation. Herein is described the reactivity of $B(C_6F_5)_3$ with a range of phosphines providing a family of phosphonium borates of the form $R_3P(C_6F_4)BF(C_6F_5)_2$ (R = aryl, alkyl, and/or H) and novel 'frustrated' Lewis pairs.



Scheme 2B Reaction of a phosphorus-ylide with $B(C_6F_5)_3$.

2.2 Experimental

2.2.1 General Data

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents (pentane, hexanes, toluene, and methylene chloride) were purified employing a Grubbs' type column system manufactured by Innovative Technology and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 °C under vacuum for 24 hours prior to use. Uninhibited THF was purchased from EMD and distilled from sodium/benzophenone prior to use. Deuterated solvents were dried over sodium/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br) and vacuum distilled prior to use. All common organic reagents were purified by conventional methods unless otherwise noted. ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-300 spectrometer at 300 K unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR experiments were referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. DEPT and 2-D $^1H/^{13}C$ correlation experiments were completed for assignment of the carbon atoms. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. $B(C_6F_5)_3$ was generously donated by NOVA Chemicals Corporation. All phosphines were purchased from Aldrich or Strem and used as received unless otherwise noted.

$(Mes)_2PH$[96] and (^{t}Bu)(Mes)PH[97] were prepared as reported in the literature. Paratone-N oil was purchased from Hampton Research.

2.2.2 Synthesis of Phosphonium Borates

$(Cy)_3P(C_6F_4)BF(C_6F_5)_2$ (2-1): A clear yellow solution of $B(C_6F_5)_3$ (0.500 g, 0.98 mmol) and *tri*-cyclohexylphosphine (0.274 g, 0.98 mmol) in toluene (20 mL) was allowed to stir for 12 hours at room temperature during which time a white precipitate formed. Pentane (10 mL) was added and the mixture filtered and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.738 g (96 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 3.05 (m, 3H, P{C_6H_{11}}), 2.10-1.22 (br m, 30H, P{C_6H_{11}}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -0.70 (d, $^1J_{B\text{-}F}$ = 58 Hz). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 150.40 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 148.71 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 147.62 (dm, $^1J_{C\text{-}F}$ = 255 Hz, C_6F_4), 139.84 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 137.40 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 90.20 (dm, $^1J_{C\text{-}P}$ = 70 Hz, P-C_6F_4), 33.31 (d, $^1J_{C\text{-}P}$ = 39 Hz, P{C_6H_{11}}$_3$), 28.22 (d, $^2J_{C\text{-}P}$ = 3 Hz, P{C_6H_{11}}$_3$), 27.40 (d, $^3J_{C\text{-}P}$ = 12 Hz, P{C_6H_{11}}$_3$), 25.93 (s, P{C_6H_{11}}$_3$). **^{19}F NMR** (CD_2Cl_2): δ -128.76 (s, 2F, C_6F_4), -132.03 (s, 2F, C_6F_4), -135.81 (d, 4F, $^3J_{F\text{-}F}$ = 16 Hz, *ortho*-C_6F_5), -161.92 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -166.83 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5), -193.11 (d, 1F, $^1J_{F\text{-}B}$ = 72 Hz, $Ar^F{}_3BF$). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 41.6 (m). **Anal. Calcd.** for $C_{36}H_{33}BF_{15}P$: C, 54.57; H, 4.20. Found: C, 54.22; H, 3.98 %.

(^{i}Pr$_3$)P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ (2-2): A clear yellow solution of B(C$_6$F$_5$)$_3$ (0.500 g, 0.98 mmol) and *tri*-isopropylphosphine (0.156 g, 0.98 mmol) in toluene (20 mL) was allowed to stir for 12 hours at room temperature during which time a white precipitate formed. Pentane (10 mL) was added and the mixture filtered and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.620 g (94 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 3.23 (m, 3H, P{C*H*(CH_3)$_2$}), 1.47 (dd, 18H, $^{3}J_{H\text{-}P}$ = 18 Hz, $^{3}J_{H\text{-}H}$ = 6 Hz, P{CH(C*H*$_3$)$_2$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -0.89 (d, $^{1}J_{B\text{-}F}$ = 64 Hz). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.83 (dm, $^{1}J_{C\text{-}F}$ = 247 Hz, *C*F), 148.20 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *C*F), 147.12 (dm, $^{1}J_{C\text{-}F}$ = 255 Hz, *C*F), 139.34 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 136.95 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 89.30 (dm, $^{1}J_{C\text{-}P}$ = 70 Hz, *p*-*C*$_6$F$_4$), 23.85 (d, $^{1}J_{C\text{-}P}$ = 40 Hz, P{*C*H(CH_3)$_2$}), 17.20 (s, P{CH(*C*H$_3$)$_2$}). **^{19}F NMR** (CD_2Cl_2): δ -124.84 (s, 2F, C$_6$*F*$_4$), -127.71 (s, 2F, C$_6$*F*$_4$), -132.14 (d, 4F, $^{3}J_{F\text{-}F}$ = 16 Hz, *ortho*-C$_6$*F*$_5$), -158.11 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz, *para*-C$_6$*F*$_5$), -163.07 (t, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C$_6$*F*$_5$), -189.37 (d, 1F, $^{1}J_{F\text{-}B}$ = 68 Hz, Ar$^{F}_3$B*F*). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 53.20 (m). **Anal. Calcd.** for $C_{27}H_{21}BF_{15}P$: C, 48.24; H, 4.61. Found: C, 48.52; H, 4.76 %.

(*o*-C$_6$H$_4$OMe)$_3$P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ (2-3): To a clear solution of B(C$_6$F$_5$)$_3$ (0.310 g, 0.61 mmol) in toluene (10 mL) was added tris(*ortho*-methoxy)phenylphosphine (0.210 mg, 0.59 mmol) in toluene (5 mL). The reaction was allowed to stir under nitrogen for 24 hours. Note: Heating to 125 °C in glass bomb sealed with a Teflon cap resulted in a reduction of the reaction time from 24 hours to 6 hours. During such time the product precipitated out of solution as a yellow oil. The solvent was removed *in vacuo* to give an

off white solid. The solid was slurried in hexanes (10 mL) and stirred at room temperature for 12 hours. The mixture was filtered, washed with benzene (2 x 10 mL) and hexanes (5 x 10 mL) and dried *in vacuo* to give the product as a white solid. Yield 400 mg (76 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 7.77-7.72 (m, 3H, Ph), 7.50-7.45 (m, 3H, Ph), 7.19-7.09 (m, 3H, Ph), 7.06-7.01 (m, 3H, Ph), 3.52 (br s, 9H, OMe). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -0.52 (br s). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ 162.13 (s, quaternary *Ph*OMe), 149.37 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 148.52 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 148.85 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 139.46 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 137.75 (s, Ph), 135.82 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 135.12 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, Ph), 122.39 (d, $^{2}J_{C\text{-}P}$ = 16 Hz, Ph), 113.16 (d, $^{3}J_{C\text{-}P}$ = 5 Hz, Ph), 106.42 (d, $^{1}J_{C\text{-}P}$ = 106 Hz, quaternary Ph), 56.42 (s, O*Me*). **^{19}F NMR** (CD_2Cl_2): δ -127.94 (br, 1F, C_6F_4), -131.38 (br s, 2F, C_6F_4), -136.00 (m, 5F, C_6F_4, *ortho*-C_6F_5), -162.20 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -165.54 (m, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5), -192.78 (br m, 1F, $Ar^{F}{}_3BF$). **^{31}P {^{1}H} NMR** (CD_2Cl_2): δ 10.88 (s).

(^{t}Bu)$_2$PH(C_6F_4)BF(C_6F_5)$_2$ (2-4): To a clear yellow solution of $B(C_6F_5)_3$ (0.548 g, 1.07 mmol) in toluene (20 mL) was added di-*t*-butylphosphine (0.20 mL, 1.07 mmol) via syringe. The reaction was allowed to stir for 12 hours during which time a white precipitate formed. Pentane (10 mL) was added and the mixture filtered and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.552 g (78 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 6.32 (d, 1H, $^{1}J_{H\text{-}P}$ = 465 Hz, P*H*), 1.58 (d, 18H, $^{3}J_{H\text{-}P}$ = 19 Hz, P{C(CH_3)$_3$}. **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ 0.80 (d,

$^{1}J_{B\text{-}F}$ = 62 Hz). **^{13}C {^{1}H}NMR** (CD_2Cl_2) partial: δ 149.33 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *C*F), 146.65 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *C*F), 139.64 (dm, $^{1}J_{C\text{-}F}$ = 280 Hz, *C*F), 137.50 (dm, $^{1}J_{C\text{-}F}$ = 260 Hz, *C*F), 136.58 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *C*F), 36.92 (d, $^{1}J_{C\text{-}P}$ = 30 Hz, P{*C*(CH_3)$_3$}), 28.41 (s, C(*C*H_3)$_3$). **^{19}F NMR** (CD_2Cl_2): δ -126.23 (s, 1F, C_6F_4), -127.90 (s, 1F, C_6F_4), -128.40 (s, 1F, C_6F_4), -132.52 (s, 1F, C_6F_4), -135.81 (d, 4F, $^{3}J_{F\text{-}F}$ = 23 Hz, *ortho*-C_6F_5), -161.64 (t, 2F, $^{3}J_{F\text{-}F}$ = 23 Hz, *para*-C_6F_5), -166.69 (t, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5), -192.06 (bs, 1F, $Ar^{F}_{3}BF$). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 34.21 (m). **Anal. Calcd.** for $C_{26}H_{19}BF_{15}P$: C, 47.45; H, 2.91. Found: C, 47.06; H, 2.86 %.

$(Mes)_2PH(C_6F_4)BF(C_6F_5)_2$ (2-5): A clear yellow solution of $B(C_6F_5)_3$ (1.5 g, 2.93 mmol) and dimesityl phosphine (0.800 g, 2.96 mmol) in toluene (10 mL) was heated to 100 °C. The reaction was allowed to stir for 8 hours during which time the solution turned red and a white precipitate formed. Upon cooling, pentane (10 mL) was added and the mixture filtered and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 1.72 g (75 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane / pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 8.52 (d, 1H, $^{1}J_{H\text{-}P}$ = 503 Hz, P*H*), 7.14 (d, $^{4}J_{H\text{-}P}$ = 6 Hz, 4H, P(C_6H_2)$_2$), 2.39 (s, 6H, P(C_6H_2*Me-4*)$_2$), 2.28 (s, 12H, P(C_6H_2*Me-2,6*)$_2$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ 0.44 (d, $^{1}J_{B\text{-}F}$ = 62 Hz). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 148.36 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 148.33 (d, $^{4}J_{C\text{-}P}$ = 3 Hz, *para*-C_6H_2), 146.88 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 144.26 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, *ortho*-C_6H_2), 137.25 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 132.95 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, *C*F), 108.90 (d, $^{1}J_{C\text{-}P}$ = 88 Hz, P-C_6H_2), 21.99 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, C_6H_2*Me-2,6*), 21.81 (s, C_6H_2*Me-4*). **^{19}F NMR** (CD_2Cl_2): δ -129.02 (s, 2F, C_6F_4), -133.93 (s, 2F, C_6F_4), -135.81 (d, 4F, $^{3}J_{F\text{-}F}$ = 14 Hz, *ortho*-C_6F_5), -161.75 (t,

2F, $^{3}J_{F\text{-}F}$ = 17 Hz , *para*-C_6F_5), - 166.76 (t, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5), -192.74 (bs, 1F, $Ar^{F}{}_3BF$). **$^{31}P\{^{1}H\}$ NMR** (CD_2Cl_2): δ -37.65 (m, $^{3}J_{P\text{-}F}$ = 8 Hz). **Anal. Calcd.** for $C_{36}H_{23}BF_{15}P$: C, 55.27; H, 2.96. Found: C, 54.75; H, 3.09 %.

(^{t}Bu)(Mes)PH(C_6F_4)BF(C_6F_5)$_2$ (2-6): To a clear yellow solution of $B(C_6F_5)_3$ (0.500 g, 0.98 mmol) in toluene (20 mL) was added *tert*-butyl-2,4,6-trimethylphenylphosphine (0.203 mg, 0.98 mmol) in toluene (5 mL) via syringe. The reaction was heated to 125 °C a sealed glass bomb with a teflon cap for 24 hours. During such time the reaction turned orange in color and a white precipitate formed. Pentane (10 mL) was added and the mixture filtered and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.450 g (64 %). Crystals suitable for X-ray diffraction were grown via slow diffusion of pentane into a CH_2Cl_2/toluene solution of the product at 25 °C (open to air in wet solvents) **^{1}H NMR** (THF-d_8): δ 8.21 (d, 1H, $^{1}J_{H\text{-}P}$ = 505 Hz, P*H*), 7.17 (d, $^{4}J_{H\text{-}P}$ = 7 Hz, 2H, P(C_6H_2)), 2.47 (br s, 6H, P(C_6H_2*Me-2,6*), 2.32 (s, 3H, P(C_6H_2*Me-4*), 1.61 (d, 9H, $^{3}J_{H\text{-}P}$ = 21 Hz, P{$C(CH_3)_3$}). **^{11}B NMR** (THF-d_8): δ 0.38 (d, $^{1}J_{B\text{-}F}$ = 59 Hz). **$^{13}C\{^{1}H\}$ NMR** (THF-d_8) partial: δ 149.88 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *C*F), 148.96 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 148.12 (s, *para*-C_6H_2), 146.57 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 145.08 (d, $^{2}J_{C\text{-}P}$ = 11 Hz, *ortho*-C_6H_2), 139.76 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 137.33 (dm, $^{1}J_{C\text{-}F}$ = 275 Hz, *C*F), 132.62 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, *meta*-C_6H_2), 110.64 (d, $^{1}J_{C\text{-}P}$ = 77 Hz, P-C_6H_2), 37.76 (d, $^{1}J_{C\text{-}P}$ = 40 Hz, P{*C*$(CH_3)_3$}), 26.40 (s, C(*C*$H_3)_3$), 22.67 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, C_6H_2*Me-2,6*), 20.99 (s, C_6H_2*Me-4*). **^{19}F NMR** (THF-d_8): δ -129.99 (br s, 4F, C_6F_4), -135.23 (m, 4F, *ortho*-C_6F_5), -163.37 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5), -167.83 (t, 4F, $^{3}J_{F\text{-}F}$ = 23 Hz, *meta*-C_6F_5), -193.24 (br

s, 1F, $Ar^F{}_3BF$). **$^{31}P\{^1H\}$ NMR** (THF-d_8): δ -2.89 (m). **Anal. Calcd.** for $C_{31}H_{21}BF_{15}P$: C, 51.69; H, 2.94. Found: C, 52.26; H, 3.20 %.

$(Cp)_2PH(C_6F_4)BF(C_6F_5)_2$ (2-17): To a clear yellow solution of $B(C_6F_5)_3$ (0.556 g, 1.09 mmol) in toluene (20 mL) was added *bis*-cyclopentylphosphine (0.199 g, 1.18 mmol) in toluene (5 mL) via syringe. The reaction was heated to 130 °C in a sealed glass bomb with a teflon cap for 24 hours. During such time the reaction turned yellow in color and a white precipitate formed. Pentane (40 mL) was added and the mixture was filtered, washed with pentane (3 x 10mL), and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.560 g (76 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane / benzene / pentane solution at 25 °C. **^1H NMR** (THF-d_8): δ 7.24 (d, 1H, $^1J_{H\text{-}P}$ = 508 Hz, P*H*), 3.11 (m, 2H, P{C_5H_9}), 2.25 (m, 2H, P{C_5H_9}), 2.07 (m, 2H, P{C_5H_9}), 1.86-1.68 (br m, 12H, P{C_5H_9}). **^{11}B {^1H} NMR** (THF-d_8): δ -0.07 (d, $^1J_{B\text{-}F}$ = 54 Hz). **$^{13}C\{^1H\}$ NMR** (THF-d_8) partial: δ 148.79 (dm, $^1J_{C\text{-}F}$ = 255 Hz, *C*F), 148.07 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 146.30 (dm, $^1J_{C\text{-}F}$ = 255 Hz, *C*F), 138.89 (dm, $^1J_{C\text{-}F}$ = 252 Hz, *C*F), 136.61 (dm, $^1J_{C\text{-}F}$ = 252 Hz, *C*F), 123.32 (br m, quaternary), 92.14 (m, $^1J_{C\text{-}P}$ = 70 Hz, quaternary), 30.64 (d, $^1J_{C\text{-}P}$ = 45 Hz, P{C_5H_9}$_2$), 29.94 (s, P{C_5H_9}$_2$), 29.68 (s, P{C_5H_9}$_2$), 27.17 (d, $^3J_{C\text{-}P}$ = 12 Hz, P{C_5H_9}$_2$), 26.40 (d, $^3J_{C\text{-}P}$ = 12 Hz, P{C_5H_9}$_2$). **^{19}F NMR** (THF-d_8): δ -129.84 (s, 2F, C_6F_4), -133.48 (s, 2F, C_6F_4), -135.32 (m, 4F, *ortho*-C_6F_5), -163.41 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -167.88 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5), -193.28 (br m, 1F, $Ar^F{}_3BF$). **$^{31}P\{^1H\}$ NMR** (THF-d_8): δ 12.68 (m). **Anal. Calcd.** for $C_{28}H_{19}BF_{15}P$: C, 49.30; H, 2.81. Found: C, 48.76; H, 2.93 %.

$(Cy)_2PH(C_6F_4)BF(C_6F_5)_2$ (2-18): To a clear yellow solution of $B(C_6F_5)_3$ (0.500 g, 0.98 mmol) in toluene (20 mL) was added *bis*-cyclohexylphosphine (0.200 g, 1.00 mmol) in toluene (5 mL) via syringe. The reaction was heated to 130 °C in a sealed glass bomb with a teflon cap for 24 hours. During such time the reaction turned light yellow in color and a white precipitate formed. Pentane (40 mL) was added and the mixture filtered, washed with pentane (3 x 10mL), and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.510 g (73 %). **^{1}H NMR** (CD_2Cl_2): δ 6.50 (d, 1H, $^1J_{H\text{-}P}$ = 480 Hz, P*H*), 3.80 (m, 2H, P{C_6H_{11}}$_2$), 2.09-1.27 (br m, 20H, P{C_6H_{11}}$_2$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -0.21 (br). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.34 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 148.37 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 146.31 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 139.37 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 137.23 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 129.12, 122.74, 87.10 (quaternary), 33.31 (d, $^1J_{C\text{-}P}$ = 41 Hz, P{*C*$_6$H$_{11}$}$_2$), 28.25 (s, P{*C*$_6$H$_{11}$}$_2$), 27.18 (s, P{*C*$_6$H$_{11}$}$_2$), 26.42 (s, P{*C*$_6$H$_{11}$}$_2$), 26.19 (d, $^3J_{C\text{-}P}$ = 15 Hz, P{*C*$_6$H$_{11}$}$_2$), 25.17 (s, P{*C*$_6$H$_{11}$}$_2$). **^{19}F NMR** (CD_2Cl_2): δ -129.22 (s, 2F, C_6F_4), -131.87 (s, 2F, C_6F_4), -135.80 (d, 4F, $^3J_{F\text{-}F}$ = 19 Hz, *ortho*-C_6F_5), -161.63 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5), -166.62 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5), -191.47 (br, 1F, $Ar^F{}_3BF$). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 11.5 (m). **Anal. Calcd.** for $C_{30}H_{23}BF_{15}P$: C, 50.73; H, 3.26. Found: C, 50.65; H, 3.22 %.

$(Ph)_2PH(C_6F_4)BF(C_6F_5)_2$ (2-19): In a resealable J-Young NMR tube the adduct Ph_2PH-$B(C_6F_5)_3$ (0.050 mg, 0.072 mmol) was dissolved in C_6D_5Br (0.75 mL) and heated to 140 °C for 24 hours. Near quantitative product formation was observed by NMR spectroscopy. NMR resonances for the major product are reported. Minor products were observed (< 15 %) and were not identified. It is critical to ensure that the adduct Ph_2PH-

$B(C_6F_5)_3$ is H_2O and H_2O-$B(C_6F_5)_3$ free before heating. **^{1}H NMR** (CD_2Cl_2): δ 7.9-7.4 (m, 10H, Ph), 7.5 (br d, 1H, P*H*). **^{11}B {^{1}H} NMR** (CD_2Cl_2): δ -1.0 (br s). **^{19}F NMR** (CD_2Cl_2): δ -129.3 (m, 2F, C_6F_4), -132.5 (m, 2F, C_6F_4), -135.8 (m, 4F, *ortho*-C_6F_5), -160.7 (m, 2F, *para*-C_6F_5), -166.1 (m, 4F, *meta*-C_6F_5), -194.8 (br s, 1F, $Ar^F{}_3BF$). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 6.5 (m).

$(Bu)_3P(C_6F_4)BF(C_6F_5)_2$ (2-20): To a clear solution of $B(C_6F_5)_3$ (0.200 g, 0.40 mmol) in bromobenzene (10 mL) was added tri-*n*-butylphosphine (0.080 mg, 0.40 mmol). The reaction was allowed to stir for 1 hour at room temperature to ensure adduct formation. The reaction was then heated at 125 °C for 2 days. Pentane (30 mL) was added, the precipitate filtered, washed with pentane (3 x 10mL) and dried *in vacuo* to give the product as a white solid. Yield 205 mg (74 %). Crystals suitable for X-ray diffraction were grown via slow diffusion of pentane into a CH_2Cl_2/toluene solution of the product at 25 °C (open to air in wet solvents) **^{1}H NMR** (C_6D_5Br): δ 2.22 (m, 2H, C*H*$_2$), 1.25 (m, 4H, C*H*$_2$C*H*$_2$), 0.74 (m, 3H, C*H*$_3$). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -0.76 (bs). **^{13}C{^{1}H} NMR** (C_6D_5Br, 75 MHz, 300K): δ 149.24 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 148.17 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 146.45 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 139.23 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 136.98 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 92.35 (dt, $^1J_{C\text{-}P}$ = 78 Hz, $^2J_{C\text{-}F}$ = 20 Hz, quaternary), 23.57 (br m, *C*H$_2$*C*H$_2$), 20.00 (d, $^1J_{C\text{-}P}$ = 50 Hz, *C*H$_2$), 12.98 (s, *C*H$_3$). **^{19}F NMR** (C_6D_5Br): δ -129.17 (s, 2F, C_6F_4), -133.48 (m, 2F, C_6F_4), -135.13 (m, 4F, *ortho*-C_6F_5), -160.46 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -166.04 (m, 4F, *meta*-C_6F_5), -190.28 (br s, 1F, $Ar^F{}_3BF$). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 33.14 (bs). **Anal. Calcd.** for $C_{30}H_{27}BF_{15}P$: C, 50.44; H, 3.81. Found: C, 50.24; H, 3.63 %.

$(Ph)_3P(C_6F_4)BF(C_6F_5)_2$ (2-21): To a clear solution of $B(C_6F_5)_3$ (0.100 g, 0.20 mmol) in bromobenzene (10 mL) was added triphenylphosphine (0.052 mg, 0.20 mmol). The reaction was allowed to stir for 1 hour at room temperature to ensure complete adduct formation. The reaction was then heated at 125 °C for 2 days. Pentane (30 mL) was added, the precipitate filtered, washed with pentane (3 x 10mL) and dried *in vacuo* to give the product as a white solid. Yield 110 mg (73 %). Crystals suitable for X-ray diffraction were grown via slow evaporation of a concentrated bromobenzene solution at 25 °C. **^{1}H NMR** (C_6D_5Br): δ 7.44-7.14 (m, 3H, Ph), 7.28-7.23 (m, 12H, Ph). **$^{11}B\{^1H\}$ NMR** (C_6D_5Br): δ -0.26 (br s). **$^{13}C\{^1H\}$ NMR** (C_6D_5Br): δ 149.53 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 148.47 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 146.38 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 139.34 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 136.47 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 135.45 (d, $^4J_{C\text{-}P}$ = 3 Hz, Ph), 133.54 (d, $^3J_{C\text{-}P}$ = 11 Hz, Ph), 130.24 (d, $^2J_{C\text{-}P}$ = 14 Hz, Ph), 116.96 (d, $^1J_{C\text{-}P}$ = 92 Hz, quaternary Ph). **^{19}F NMR** (C_6D_5Br): δ -127.88 (m, 2F, C_6F_4), -127.99 (m, 2F, C_6F_4), -133.60 (m, 4F, *ortho*-C_6F_5), -160.74 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -165.54 (m, 4F, *meta*-C_6F_5), -193.01 (br s, 1F, $Ar^F{}_3BF$). **$^{31}P\{^1H\}$ NMR** (C_6D_5Br): δ 15.10 (s). **Anal. Calcd.** for $C_{36}H_{15}BF_{15}P$: C, 55.84; H, 1.95. Found: 55.65; H, 1.87%.

$(Et)_3P(C_6F_4)BF(C_6F_5)_2$ (2-22): In a resealable J-Young NMR tube $(Et_3P)B(C_6F_5)_3$ (0.050 mg, 0.056 mmol) was dissolved in C_6D_5Br (0.75 mL) and heated to 120 °C for 24 hours. Quantitative product formation was observed by NMR spectroscopy. **^{1}H NMR** (C_6D_5Br): δ 2.04-1.93 (m, 6H, $^2J_{H\text{-}P}$ = 20 Hz, $^3J_{H\text{-}H}$ = 7 Hz, CH_2), 0.85-0.76 (dt, 9H, $^3J_{H\text{-}P}$ = 21 Hz, $^3J_{H\text{-}H}$ = 7 Hz, CH_3). **$^{11}B\{^1H\}$ NMR** (C_6D_5Br): δ 0.47 (br s). **$^{13}C\{^1H\}$ NMR** (C_6D_5Br): δ 149.70 (dm, $^1J_{C\text{-}F}$ = 248 Hz, *C*F), 148.21 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 146.30 (dm, $^1J_{C\text{-}F}$ =

255 Hz, *C*F), 139.34 (dm, $^{1}J_{C\text{-}F}$ = 248 Hz, *C*F), 137.01 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 91.04 (dt, $^{1}J_{C\text{-}P}$ = 80 Hz, $^{2}J_{C\text{-}F}$ = 18 Hz, quaternary), 13.67 (d, $^{1}J_{C\text{-}P}$ = 48 Hz, *C*H$_2$), 5.29 (d, $^{2}J_{C\text{-}P}$ = 5 Hz, *C*H$_3$). **^{19}F NMR** (C_6D_5Br): δ -129.77 (m, 2F, C_6F_4), -134.04 (m, 2F, C_6F_4), -135.78 (m, 6F, $^{3}J_{F\text{-}F}$ = 20 Hz, *ortho*-C_6F_5), -161.10 (m, 3F, $^{3}J_{F\text{-}F}$ = 21 Hz, *para*-C_6F_5), -166.21 (m, 6F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5), -192.22 (br s, 1F, Ar$^{F}_{3}$B*F*). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 39.06 (s).

(*p*-FC$_6$H$_4$)$_3$P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ (2-23): To a clear solution of B(C_6F_5)$_3$ (0.100 g, 0.20 mmol) in bromobenzene (10 mL) was added 4-fluoro-triphenylphosphine (0.062 mg, 0.20 mmol). The reaction was then heated at 125 °C for 12 hours. Pentane (30 mL) was added, the precipitate filtered, washed with pentane (3 x 10mL) and dried *in vacuo* to give the product as a white solid. Yield 122 mg (75 %). Crystals suitable for X-ray diffraction were grown via slow evaporation of a concentrated bromobenzene solution at 25 °C. **^{1}H NMR** (C_6D_5Br): δ 7.25-7.15 (ddd, 6H, $^{3}J_{H\text{-}F}$ = 13 Hz, $^{3}J_{H\text{-}H}$ = 8 Hz, $^{4}J_{H\text{-}P}$ = 5 Hz, Ph), 6.85-6.78 (ddd, 6H, $^{3}J_{H\text{-}P}$ = 8 Hz, $^{3}J_{H\text{-}H}$ = 8 Hz, $^{4}J_{H\text{-}F}$ = 3 Hz, Ph). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -0.17 (br s). **^{13}C{^{1}H} NMR** (C_6D_5Br): δ 167.25 (d, $^{1}J_{C\text{-}F}$ = 260 Hz, *C*F), 149.94 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 148.65 (dm, $^{1}J_{C\text{-}F}$ = 235 Hz, *C*F), 139.94 (dm, $^{1}J_{C\text{-}F}$ = 246 Hz, *C*F), 137.10 (dm, $^{1}J_{C\text{-}F}$ = 247 Hz, *C*F), 136.95 (dd, $^{2}J_{C\text{-}P}$ = 13 Hz, $^{3}J_{C\text{-}F}$ = 11 Hz, Ph), 118.61 (dd, $^{2}J_{C\text{-}F}$ = 16 Hz, $^{3}J_{C\text{-}P}$ = 13 Hz, Ph), 113.04 (d, $^{1}J_{C\text{-}P}$ = 97 Hz, quaternary Ph). **^{19}F NMR** (C_6D_5Br): δ -97.77 (s, 3F, *F*-C_6H_4), -128.10 (m, 4F, C_6F_4), -134.91 (m, 4F, *ortho*-C_6F_5), -160.40 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -165.44 (m, 4F, *meta*-C_6F_5), -192.25 (br s, 1F, Ar$^{F}_{3}$B*F*). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 14.1 (s). **Anal. Calcd.** for $C_{36}H_{12}BF_{18}P$: C, 52.21; H, 1.46. Found: C, 53.05; H, 2.10 %.

(^{t}Bu)(Ph)PH(C_6F_4)BF(C_6F_5)$_2$ (2-24): To a clear yellow solution of $B(C_6F_5)_3$ (0.500 g, 0.98 mmol) in toluene (20 mL) was added *tert*-butyl-phenylphosphine (0.162 mg, 0.98 mmol) in toluene (5 mL) via syringe. The reaction was heated to 125 °C in a sealed glass bomb with a teflon cap for 24 hours. During such time the reaction turned yellow in color and a white precipitate formed. Pentane (10 mL) was added and the mixture filtered and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.510 g (77 %). **^{1}H NMR** (CD_2Cl_2): δ 7.98-7.89 (m, 3H, P(C_6H_5)), 7.76-7.69 (m, 2H, P(C_6H_5)), 7.39 (d, 1H, $^1J_{H\text{-}P}$ = 487 Hz, P*H*), 1.54 (d, 9H, $^3J_{H\text{-}P}$ = 21 Hz, P{C(CH_3)$_3$}). **^{11}B NMR** (CD_2Cl_2): δ 0.39 (d, $^1J_{B\text{-}F}$ = 63 Hz). **^{13}C {^{1}H} NMR** (CD_2Cl_2) partial: δ 149.85 (dm, $^1J_{C\text{-}F}$ = 246 Hz, C_6F_4), 147.87 (dm, $^1J_{C\text{-}F}$ = 240 Hz, C_6F_5), 145.52 (dm, $^1J_{C\text{-}F}$ = 250 Hz, C_6F_5), 140.05 (dm, $^1J_{C\text{-}F}$ = 240 Hz, C_6F_4), 136.95 (dm, $^1J_{C\text{-}F}$ = 246 Hz, C_6F_5), 136.89 (s, C_6H_5), 134.44 (d, $^3J_{C\text{-}P}$ = 11 Hz, C_6H_5), 131.31 (d, $^2J_{C\text{-}P}$ = 12 Hz, C_6H_5), 112.41 (d, $^1J_{C\text{-}P}$ = 82 Hz, P-C_6H_5), 34.96 (d, $^1J_{C\text{-}P}$ = 40 Hz, P{*C*(CH_3)$_3$}), 26.03 (s, C(*C*H_3)$_3$). **^{19}F NMR** (CD_2Cl_2): δ -128.66 (s, 2F, C_6F_4), -130.32 (m, 2F, C_6F_4), -135.80 (m, 4F, *ortho*-C_6F_5), -161.51 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5), - 166.64 (t, 4F, $^3J_{F\text{-}F}$ = 22 Hz, *meta*-C_6F_5), -191.39 (br s, 1F, $Ar^F{}_3BF$). **^{31}P {^{1}H} NMR** (CD_2Cl_2): δ 14.70 (m). **Anal. Calcd.** for $C_{28}H_{15}BF_{15}P$: C, 49.59; H, 2.23. Found: C, 49.50; H, 2.33 %.

(Cy)$_3$P(C_6F_4)BF(C_6F_5)(Ph) (2-26): A clear yellow solution of $PhB(C_6F_5)_2$ (0.100 g, 0.237 mmol) and *tri*-cyclohexylphosphine (0.067 g, 0.240 mmol) in toluene (20 mL) was allowed to stir for 12 hours at room temperature during which time a white precipitate formed. Pentane (10 mL) was added and the mixture filtered and dried *in vacuo* for 1 hour. The product was collected as a white solid. Yield 0.110 g (80 %). Crystals suitable

for X-ray diffraction were grown from a layered dichloromethane / pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 7.40 (d, 2H, $^3J_{H-H}$ = 7 Hz, Ph), 7.16 (d, 2H, $^3J_{H-H}$ = 7 Hz, Ph), 7.10 (m, 2H, $^3J_{H-H}$ = 7 Hz, Ph), 2.92 (m, 3H, $^3J_{H-H}$ = 12 Hz, P{C_6H_{11}}), 1.95-1.27 (br m, 30H, P{C_6H_{11}}). **^{11}B {^{1}H} NMR** (CD_2Cl_2): δ 2.15 (br). **^{13}C {^{1}H} NMR** (CD_2Cl_2) partial: δ 149.99 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 148.52 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 147.58 (dm, $^1J_{C-F}$ = 255 Hz, *C*F), 139.17 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 137.59 (dm, $^1J_{C-F}$ = 245 Hz, *C*F), 131.98 (s, Ph), 127.17 (s, Ph), 125.41 (s, Ph), 88.73 (dm, $^1J_{C-P}$ = 70 Hz, P-C_6F_4), 33.24 (d, $^1J_{C-P}$ = 40 Hz, P{C_6H_{11}}$_3$), 28.03 (s, P{C_6H_{11}}$_3$), 27.48 (d, $^3J_{C-P}$ = 14 Hz, P{C_6H_{11}}$_3$), 25.90 (s, P{C_6H_{11}}$_3$). **^{19}F NMR** (CD_2Cl_2): δ -126.85 (m, 2F, C_6F_4), -132.14 (m, 2F, C_6F_4), -133.59 (d, 2F, $^3J_{F-F}$ = 16 Hz, *ortho*-C_6F_5), -162.93 (t, 1F, $^3J_{F-F}$ = 20 Hz , *para*-C_6F_5), -166.82 (t, 2F, $^3J_{F-F}$ = 20 Hz, *meta*-C_6F_5), -193.38 (br s, $Ar^F{}_3BF$). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 41.2 (s).

2.2.3 Synthesis of Phosphine-B(C_6F_5)$_3$ Adducts and Novel Triaryl Boranes

(Mes_2PH)B(C_6F_5)$_3$ (2-7): Method A) A clear yellow solution of B(C_6F_5)$_3$ (1.50 g, 2.93 mmol) and Mes_2PH (0.800 g, 2.96 mmol) in toluene (10 mL) was heated to 100 °C. The reaction was allowed to stir for 8 hours during which time the solution turned red and a white precipitate formed. Pentane (10 mL) was added and the mixture filtered. The resulting red filtrate was dried *in vacuo* to give the product as a pink solid. Yield 0.475 g. (20 %). **Method B**) A NMR tube was charged with B(C_6F_5)$_3$ (0.030 g, 0.059 mmol), Mes_2PH (0.016 g, 0.059 mmol), and CD_2Cl_2 (0.75 mL). Adduct formation was observed by NMR spectroscopy. **^{1}H NMR** (CD_2Cl_2): δ 6.88 (s, 4H, P(C_6H_2)$_2$), 6.64 (bs, 1H, P*H*),

2.26 (s, 6H, P(C_6H_2*Me-4*)$_2$), 2.15 (s, 12H, P(C_6H_2*Me-2,6*)$_2$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ 23.61 (bs). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ 148.92 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 142.97 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 142.93 (d, $^2J_{C\text{-}P}$ = 9 Hz, *ortho*-C_6H_2), 140.91 (s, *para*-C_6H_2), 138.12 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 130.33 (d, $^3J_{C\text{-}P}$ = 5 Hz, *meta*-C_6H_2), 120.73 (d, $^1J_{C\text{-}P}$ = 80 Hz, P-C_6H_2), 23.06 (d, $^3J_{C\text{-}P}$ = 17 Hz, C_6H_2*Me-2,6*), 21.24 (s, C_6H_2*Me-4*). **^{19}F NMR** (CD_2Cl_2): δ -127.95 (s, 6F, *ortho*-C_6F_5), -151.53 (s, 3F, *para*-C_6F_5), -163.04 (s, 6F, *meta*-C_6F_5). **^{19}F NMR** (CD_2Cl_2, 203 K): **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ -67.7 (bs).). **^{31}P NMR** (CD_2Cl_2, 203 K): δ -43.2 (d, $^1J_{P\text{-}H}$ = 434 Hz). **Anal. Calcd.** for $C_{36}H_{23}BF_{15}P$: C, 55.27; H, 2.96. Found: C, 55.34; H, 3.24 %.

(Cp_2PH)$B(C_6F_5)_3$ (2-8): To a clear solution of $B(C_6F_5)_3$ (0.100 g, 0.20 mmol) in toluene (5 mL) was added *bis*-cyclopentylphosphine (0.034 g, 0.20 mmol). The reaction was allowed to stir for 1 hour at room temperature. The solvent was removed *in vacuo* to give the product as a white solid. Yield 0.127 g (95 %). Crystals suitable for X-ray diffraction were grown via slow diffusion of pentane into a CH_2Cl_2/toluene solution of the product at 25 °C **^{1}H NMR** (CD_2Cl_2): δ 5.60 (d, 1H, $^1J_{H\text{-}P}$ = 408 Hz, P*H*), 2.16 (m, 2H, P{C_5H_9}), 1.95 (m, 2H, P{C_5H_9}), 1.69-1.35 (br m, 14H, P{C_5H_9}).**^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -15.90 (d, $^1J_{B\text{-}P}$ = 80 Hz). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 148.67 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 140.50 (dm, $^1J_{C\text{-}F}$ = 254 Hz, *C*F), 137.96 (dm, $^1J_{C\text{-}F}$ = 254 Hz, *C*F), 117.42 (br s, quaternary), 32.47 (s, P{C_5H_9}$_2$), 30.34 (br m, P{C_5H_9}$_2$), 29.83 (s, P{C_5H_9}$_2$), 26.23 (d, $^2J_{C\text{-}P}$ = 8 Hz, P{C_5H_9}$_2$), 25.72 (d, $^2J_{C\text{-}P}$ = 8 Hz, P{C_5H_9}$_2$). **^{19}F NMR** (CD_2Cl_2): δ -129.68 (s, 6F, *ortho*-C_6F_5), -157.91 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -164.11 (m, 6F, $^3J_{F\text{-}F}$

= 20 Hz *meta*-C_6F_5). **^{31}P NMR** (CD_2Cl_2): δ 11.2 (dq, $^1J_{P\text{-}H}$ = 402 Hz, $^1J_{P\text{-}B}$ = 80 Hz). **Anal. Calcd.** for $C_{28}H_{19}BF_{15}P$: C, 49.30; H, 2.81. Found: C, 49.20; H, 2.75 %.

(Bu_3P)$B(C_6F_5)_3$ (2-11): To a clear solution of $B(C_6F_5)_3$ (0.100 g, 0.20 mmol) in toluene (5 mL) was added tri-*n*-butylphosphine (0.040 mg, 0.20 mmol). The reaction was allowed to stir for 1 hour at room temperature. The solvent was removed *in vacuo* to give the product as a white sticky solid. Yield 135 mg (97 %). **^{1}H NMR** (C_6D_5Br): δ 1.77 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 0.75 (t, 3H, $^3J_{H\text{-}H}$ = 7 Hz, CH_3). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -13.46 (bs). **^{13}C{^{1}H} NMR** (C_6D_5Br): δ 148.25 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 139.52 (dm, $^1J_{C\text{-}F}$ = 252 Hz, *C*F), 136.91 (dm, $^1J_{C\text{-}F}$ = 254 Hz, *C*F), 115.93 (br s, quaternary), 25.30 (d, $^3J_{C\text{-}P}$ = 5 Hz, *C*H_2), 23.87 (d, $^2J_{C\text{-}P}$ = 11 Hz, *C*H_2), 20.13 (d, $^1J_{C\text{-}P}$ = 30 Hz, *C*H_2), 12.80 (s, *C*H_3). **^{19}F NMR** (C_6D_5Br): δ -129.25 (d, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *ortho*-C_6F_5), -155.98 (t, 3F, $^3J_{F\text{-}F}$ = 23 Hz, *para*-C_6F_5), -162.99 (m, 6F, $^3J_{F\text{-}F}$ = 24 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ -0.6 (br). **Anal. Calcd.** for $C_{30}H_{27}BF_{15}P$: C, 50.44; H, 3.81. Found: C, 50.24; H, 3.75 %.

(Et_3P)$B(C_6F_5)_3$ (2-13): To a clear solution of $B(C_6F_5)_3$ (0.560 g, 1.09 mmol) in pentane (10 mL) was added triethylphosphine (0.130 mg, 0.1.10 mmol). The reaction was allowed to stir for 1 hour at room temperature under a nitrogen atmosphere. The reaction mixture was filtered and the white solid washed with pentane (3 x 20 mL) and dried *in vacuo* overnight. Yield 595 mg (86 %). Crystals suitable for X-ray diffraction were grown via slow evaporation of a concentrated THF solution at 25 °C **^{1}H NMR** (THF-d_8): δ 1.94-1.88 (br m, 6H, CH_2), 1.24-1.14 (m, 9H, CH_3). **^{11}B {^{1}H} NMR** (THF-d_8): δ -13.35 (d, $^1J_{B\text{-}}$

$_P$ = 75 Hz). **^{13}C {^{1}H} NMR** (THF-d$_8$): δ 149.18 (dm, $^1J_{C\text{-}F}$ = 239 Hz, *C*F), 140.92 (dm, $^1J_{C\text{-}F}$ = 249 Hz, *C*F), 138.43 (dm, $^1J_{C\text{-}F}$ = 254 Hz, *C*F), 117.60 (br s, quaternary), 14.64 (d, $^1J_{C\text{-}P}$ = 35 Hz, *C*H$_2$), 8.61 (d, $^2J_{C\text{-}P}$ = 8 Hz, *C*H$_3$). **^{19}F NMR** (THF-d$_8$): δ -130.23 (d, 6F, $^3J_{F\text{-}F}$ = 22 Hz, *ortho*-C$_6F_5$), -158.65 (m, 3F, $^3J_{F\text{-}F}$ = 22 Hz, *para*-C$_6F_5$), -165.28 (m, 6F, $^3J_{F\text{-}F}$ = 22 Hz, *meta*-C$_6F_5$). **^{31}P {^{1}H} NMR** (THF-d$_8$): δ 5.55 (dm, $^1J_{P\text{-}B}$ = 80 Hz). **Anal. Calcd.** for $C_{24}H_{15}BF_{15}P$: C, 45.75; H, 2.40. Found: C, 46.20; H, 2.55 %.

(Et$_2$PH)B(C$_6$F$_5$)$_3$ (2-15): To a clear solution of B(C$_6$F$_5$)$_3$ (0.100 g, 0.20 mmol) in toluene (5 mL) was added diethylphosphine (0.018 g, 0.20 mmol). The reaction was allowed to stir for 1 hour at room temperature. The solvent was removed *in vacuo* to give the product as a white solid. Yield 0.110 g (94 %). Crystals suitable for X-ray diffraction were grown via slow evaporation of a concentrated bromobenzene solution at 25 °C **^{1}H NMR** (C$_6$D$_5$Br): δ 4.42 (dm, 1H, $^1J_{H\text{-}P}$ = 410 Hz, P*H*), 0.90 (dm, 4H, $^2J_{H\text{-}P}$ = 132 Hz, C*H*$_2$), 0.45 (dt, 6H, $^3J_{H\text{-}P}$ = 16 Hz, $^3J_{H\text{-}H}$ = 18 Hz C*H*$_3$). **^{11}B{^{1}H} NMR** (C$_6$D$_5$Br): δ -16.16 (d, $^1J_{B\text{-}P}$ = 95 Hz). **^{13}C{^{1}H} NMR** (C$_6$D$_5$Br) partial: δ 148.25 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 140.11 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 137.13 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 115.79 (br s, quaternary), 11.91 (d, $^1J_{C\text{-}P}$ = 36 Hz, *C*H$_2$), 10.90 (d, $^2J_{C\text{-}P}$ = 8 Hz, *C*H$_3$). **^{19}F NMR** (C$_6$D$_5$Br): δ -130.44 (s, 6F, *ortho*-C$_6F_5$), -155.61 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C$_6F_5$), -162.93 (m, 6F, $^3J_{F\text{-}F}$ = 20 Hz *meta*-C$_6F_5$). **^{31}P NMR** (C$_6$D$_5$Br): δ 5.74 (dq, $^1J_{P\text{-}H}$ = 412 Hz, $^1J_{P\text{-}B}$ = 95 Hz). **Anal. Calcd.** for $C_{22}H_{11}BF_{15}P$: C, 43.98; H, 1.84. Found: C, 44.20; H, 2.05 %.

(CyPH$_2$)B(C$_6$F$_5$)$_3$ (2-16): To a clear solution of B(C$_6$F$_5$)$_3$ (0.200 g, 0.39 mmol) in toluene (5 mL) was added cyclohexylphosphine (0.08 mL, 0.60 mmol). The reaction was allowed

to stir for 1 hour at room temperature. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 0.230 g (93 %). **^{1}H NMR** (C_6D_5Br): δ 4.65 (d, 1H, $^{1}J_{H\text{-}P}$ = 393 Hz, P*H*), 1.68 (br s, 1H, P{C_6H_{11}}), 1.43-1.36 (br m, 5H, P{C_6H_{11}}), 0.95-0.84 (br m, 5H, P{C_6H_{11}}). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -17.46 (br). **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 147.90 (dm, $^{1}J_{C\text{-}F}$ = 242 Hz, *C*F), 140.34 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 137.08 (dm, $^{1}J_{C\text{-}F}$ = 246 Hz, *C*F), 114.80 (quaternary), 31.42 (d, $^{3}J_{C\text{-}P}$ = 6 Hz, P{C_6H_{11}}), 27.66 (d, $^{1}J_{C\text{-}P}$ = 33 Hz P{C_6H_{11}}), 26.13 (d, $^{2}J_{C\text{-}P}$ = 12 Hz P{C_6H_{11}}), 24.81 (s, P{C_6H_{11}}). **^{19}F NMR** (C_6D_5Br): δ -130.49 (s, 6F, *ortho*-C_6F_5), -155.25 (t, 3F, $^{3}J_{F\text{-}F}$ = 21 Hz, *para*-C_6F_5), -162.27 (m, 6F, $^{3}J_{F\text{-}F}$ = 20 Hz *meta*-C_6F_5). **^{31}P NMR** (C_6D_5Br): δ -30.0 (br t, $^{1}J_{P\text{-}H}$ = 392 Hz).

(*p*-$C_6F_4CF_3$)$_3$B (2-27): To a 500 mL round bottom flask charged with Mg turnings (0.164 g, 6.7 mmol) and Et_2O (50 mL) was added *p*-$CF_3C_6F_4Br$ (2.0 g, 1.04 mL, 6.7 mmol) via syringe. The reaction mixture was gently warmed to reflux for 10 minutes and then stirred at room temperature until all the Mg turnings had reacted (~ 90 minutes). CuCl (1.33 g, 13.5 mmol) was added to the black solution resulting in the precipitation of a brown solid. The mixture was diluted with Et_2O (15 mL) to ensure good mixing and stirred for 30 minutes. Dry 1,4-dioxane (10 mL) was added, which resulted in further precipitation. The mixture was filtered and the solid washed with a 4:1 Et_2O:dioxane solution (3 x 30 mL). The filtrate was collected and reduced *in vacuo* to give a tan solid (*p*-$C_6F_4CF_3$)Cu(1,4-dioxane)$_2$. The solid was slowly heated to 100 °C under vacuum over the course of 60 minutes and left at 100 °C under vacuum for a further 60 minutes to ensure removal of 1,4-dioxane. *Caution! Erratic heating will result in rapid decomposition of the copper*

compound. The product was isolated as an off-white solid. Yield 563 mg (30 %). **^{19}F NMR** (CD_2Cl_2): δ - 57.68 (m, 3F, CF_3), -104.70 (s, 2F, *o*-C_6F_4), -138.83 (s, 2F, *m*-C_6F_4). The solid (*p*-$C_6F_4CF_3$)Cu (0.25 g, 0.891 mmol) was dissolved in CH_2Cl_2 (15 mL) and cooled to -90 °C in an EtOH / N_2 (l) bath. BCl_3 (0.28 mL, 1M in hexanes) was diluted with hexanes (2 mL) and added dropwise to the above solution. The reaction was warmed to room temperature over 6 hours and stirred at room temperature overnight during which time a white precipitate formed. The mixture was filtered, the filtrate collected, and all volatiles were removed *in vacuo* to give an off-white solid (hint of purple). Yield 200 mg (34 %). **^{11}B{^{1}H} NMR** (CD_2Cl_2): 40 (br). **^{19}F NMR** (CD_2Cl_2): δ - 57.68 (m, 3F, CF_3), -130.04 (s, 2F, *o*-C_6F_4), -141.34 (s, 2F, *m*-C_6F_4).

Table 2.1 Selected NMR data for compounds resulting from the reaction of tertiary phosphines with $B(C_6F_5)_3$.

Compound	δ ^{31}P	δ ^{11}B	^{19}F Δ_{p-m}*	δ ^{19}F (o-F, p-F, m-F, B-F)
Starting Materials				
$B(C_6F_5)_3$[98]		59	18.2	-128.5, -143.1, -161.3
Cy_3P[a]	11.1			
$^{i}Pr_3P$[99]	19.3			
Bu_3P[a]	-31.6			
Ph_3P[a]	-4.6			
Et_3P[a]	-19.1			
Me_3P[99]	-63.3			
$(p\text{-}C_6H_4F)_3P$[a]	-9.0			
$(o\text{-}C_6H_4OMe)_3P$[a]	-29.3			
Phosphine Borane Adducts $(R_3P)B(C_6F_5)_3$				
2-12 R = Bu[b]	-0.6	-13.5	7.0	-129.3, -156.0, -163.0
2-13 R = Ph[a,100]	-5.2	-2.5	7.1	-134.8, -157.3, -164.4
2-13 R = Et[c]	5.6	-13.4	6.6	-130.3, -158.7, -165.3
2-14 R = Me[b,101]	-6.1	-14.7	6.9	-129.8, -156.5, -163.4
Phosphonium Borates $R_3P(C_6F_4)BF(C_6F_5)_2$				
2-1 R = Cy[b]	41.6	-0.7	4.9	-135.8, -161.9, -166.8,- 193.1
2-2 R = ^{i}Pr[b]	53.2	-0.9	5.0	-132.1, -158.1, -163.1, -189.4
2-3 R =o-C_6H_4OMe[b]	10.9	-0.5	3.3	-136.0, -162.2, -165.5, -192.8
2-20 R = Bu[d]	33.1	-0.8	5.5	-135.1, -160.5, -166.0, -190.3
2-21 R = Ph[d]	15.1	-0.3	4.8	-133.6, -160.7, -165.5, -193.0
2-22 R= Et[d]	39.1	0.5	5.1	-135.8, -161.1, -166.2, -192.2
2-23 R = p-C_6H_4F[d]	14.1	-0.2	5.0	-134.9, -160.4, -165.4, -192.3

[a]C_6D_6, [b]CD_2Cl_2, [c]THF, [d]C_6D_5Br, *Chemical shift difference between *para* and *meta* resonances in ^{19}F NMR spectrum

Table 2.2 Selected NMR data for compounds resulting from the reaction of secondary and primary phosphines with $B(C_6F_5)_3$.

Compound	δ ^{31}P ($^1J_{P-H}$)	δ ^{11}B	^{19}F Δ_{p-m}*	δ ^{19}F (o-F, p-F, m-F, B-F)
Starting Materials				
$B(C_6F_5)_3$[98]		59	18.2	-128.5, -143.1, -161.3
^{t}Bu$_2$PH[a]	20.1(199)			
Mes$_2$PH[a]	-92.7(229)			
Cp$_2$PH[b]	-35.2(191)			
Cy$_2$PH[a,102]	-27.5(192)			
Et$_2$PH[a,99]	-55.5(190)			
^{t}BuMesPH[c]	-49.1(214)			
^{t}BuPhPH[b]	-5.3(208)			
Ph$_2$PH	-40.1(215)			
CyPH$_2$[d]	-110.1(184)			
Phosphine Borane Adducts $(R_2PH)B(C_6F_5)_3$ and $(R'PH_2)B(C_6F_5)_3$				
2-7 R = Mes[b]	-67.7	23.6	11.5	-128.0, -151.5, -163.0
2-8 R = Cp[b]	11.2(408)	-15.9	6.2	-129.7, -157.9, -164.1
2-9 R = Cy[a,103]	9.3(406)	-13.5	6.4	-128.5, -156.7, -163.1
2-10 R = Ph[a,103]	0.9(411)	-9.4	7.2	-128.5, -156.1, -163.3
2-15 R = Et[d]	5.7(412)	-16.2	7.3	-130.4, -155.6, -162.9
2-16 R' = Cy[d]	-30.0(392)	-17.5	7.0	-130.5, -155.3, -162.3
Phosphonium Borates $R_2PH(C_6F_4)BF(C_6F_5)_2$				
2-4 R = ^{t}Bu[b]	34.2(465)	0.8	5.1	-135.8, -161.6, -166.7,- 192.1
2-5 R = Mes[b]	-37.7(503)	0.4	5.0	-135.8, -161.8, -166.8, -192.7
2-6 R = ^{t}BuMes[c]	-2.9(505)	0.4	4.4	-135.2, -163.4, -167.8, -193.2
2-17 R = Cp[c]	12.7(508)	-0.1	4.5	-135.3, -163.4, -167.9, -193.3
2-18 R = Cy[b]	11.5(480)	-0.2	5.0	-135.8, -161.6, -166.6, -191.5
2-19 R = Ph[b]	6.5 (500)	-1.0	5.4	-135.8, -160.7, -166.1, -194.8
2-24 R = ^{t}BuPh[b]	14.7(487)	0.4	4.9	-135.8, -161.5, -166.6, -191.4

[a]C_6D_6, [b]CD_2Cl_2, [c]THF, [d]C_6D_5Br *Chemical shift difference between *para* and *meta* resonances in ^{19}F NMR spectrum

2.2.4 X-ray Data Collection, Reduction, Solution and Refinement

Single crystals were mounted in thin-walled capillaries either under an atmosphere of dry N_2 in a glove box and flame sealed or coated in Paratone-N oil. The data were collected using the SMART software package[104] on a Siemens SMART System CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71069 Å) at 25 °C. A hemisphere of data was collected in 1448 frames with 10 second exposure times unless otherwise noted. Data reductions were performed using the SAINT software package[105] and absorption corrections were applied using SADABS.[106] The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[107] All non-H atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Phosphorus-bound hydrogen atoms were located in the electron difference map and their positions refined isotropically. For compounds **2-1**, **2-6**, **2-23** disordered CH_2Cl_2 solvent molecules were removed using the 'squeeze' command in PLATON.[108, 109] For **2-3** preliminary X-ray data confirmed connectivity but due to the disordered solvent a fully satisfactory structure solution was not obtained and thus only the cell parameters are listed in Table 2.3.

Table 2.3 Selected crystallographic data for compounds **2-1**, **2-2**, **2-3**.

Crystal	**2-1**	**2-2**	**2-3**
Formula	$C_{37}H_{35}BCl_2F_{15}P$	$C_{27}H_{21}BF_{15}P$	$C_{39}H_{21}BF_{15}O_3P$
Formula weight	877.33	672.22	
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a(Å)	14.235(3)	9.544(6)	12.041
b(Å)	25.588(5)	18.426(11)	12.245
c(Å)	21.701(3)	17.134(10)	14.757
$\alpha(^o)$	90	90	99.370
$\beta(^o)$	101.113(5)	105.156(12)	111.626
$\gamma(^o)$	90	90	90.521
V ($Å^3$)	7756(2)	2908(3)	
Z	8	4	
d(calc) g cm^{-1}	1.357	1.535	
Abs coeff, μ, cm^{-1}	0.167	0.208	
Data collected	17798	12247	
Data $F_o^2>3\sigma(F_o^2)$	9898	4120	
Variables	955	398	
R^a	0.0702	0.0385	
$R_w{}^b$	0.1645	0.1065	
Goodness of Fit	0.870	0.945	

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).

$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 2.4 Selected crystallographic data for compounds **2-4**, **2-6**, **2-8**.

Crystal	**2-4**	**2-6**	**2-8**
Formula	$C_{26}H_{19}BF_{15}P$	$C_{31}H_{21}BF_{15}P$	$C_{28}H_{19}BF_{15}P$
Formula weight	658.19	720.26	682.21
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	P-1	$P2_1/n$
a(Å)	8.955(5)	11.819(5)	9.8263(11)
b(Å)	15.767(9)	12.003(6)	12.5957(14)
c(Å)	19.743(11)	14.964(7)	22.117(2)
$\alpha(^o)$	90	66.442(5)	90
$\beta(^o)$	90.482(12)	69.594(5)	96.3620(10)
$\gamma(^o)$	90	74.705(6)	90
V ($Å^3$)	2788(3)	1772.1(14)	2720.5(5)
Z	4	2	4
d(calc) g cm^{-1}	1.568	1.350	1.666
Abs coeff, μ, cm^{-1}	0.215	0.176	0.224
Data collected	11750	16895	25274
Data $F_o^2>3\sigma(F_o^2)$	3951	6214	4474
Variables	392	437	410
R^a	0.0436	0.0486	0.0431
$R_w{}^b$	0.1008	0.1078	0.1019
Goodness of Fit	0.862	0.907	1.038

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 2.5 Selected crystallographic data for compounds **2-10**, **2-13**, **2-15**.

Crystal	**2-10**	**2-13**	**2-15**
Formula	$C_{30}H_{11}BF_{15}P$	$C_{24}H_{15}BF_{15}P$	$C_{22}H_{11}BF_{15}P$
Formula weight	698.17	630.14	602.09
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1$
a(Å)	16.064(2)	13.197(2)	8.2030(16)
b(Å)	8.3163(11)	10.5908(18)	16.295(3)
c(Å)	21.102(3)	18.211(3)	8.4244(17)
$\alpha(^{\circ})$	90	90	90
$\beta(^{\circ})$	102.364(2)	93.850(2)	97.57(3)
$\gamma(^{\circ})$	90	90	90
V ($Å^3$)	2753.8(6)	2539.6(7)	1116.3(4)
Z	4	4	2
d(calc) g cm^{-1}	1.684	1.648	1.791
Abs coeff, μ, cm^{-1}	0.224	0.232	0.260
Data collected	25561	23727	6659
Data $F_o^2>3\sigma(F_o^2)$	4837	4463	3553
Variables	428	386	356
R^a	0.0378	0.0479	0.0400
$R_w{}^b$	0.0892	0.0968	0.1007
Goodness of Fit	1.045	1.014	1.030

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 2.6 Selected crystallographic data for compounds **2-17**, **2-20**, **2-21**.

Crystal	**2-17**	**2-20**	**2-21**·C_6H_5Br
Formula	$C_{28}H_{19}BF_{15}P$	$C_{30}H_{26}BF_{15}P$	$C_{42}H_{20}BF_{15}P$
Formula weight	682.21	630.14	931.27
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	P-1
a(Å)	11.321(4)	9.2247(16)	12.9407(16)
b(Å)	8.895(3)	16.029(3)	13.0760(16)
c(Å)	28.018(10)	21.638(4)	13.2779(16)
$\alpha(^o)$	90	90	68.326(2)
$\beta(^o)$	100.216(6)	100.781(2)	65.310(2)
$\gamma(^o)$	90	90	72.050(2)
V (Å^3)	2776.6(17)	3143.0(9)	1865.3(4)
Z	4	4	2
d(calc) g cm^{-1}	1.632	1.507	1.658
Abs coeff, μ, cm^{-1}	0.219	0.197	1.253
Data collected	13952	29420	18019
Data $F_o^2>3\sigma(F_o^2)$	2575	5502	6552
Variables	410	424	541
R^a	0.0812	0.0563	0.0448
$R_w{}^b$	0.1237	0.1509	0.1184
Goodness of Fit	0.985	1.033	0.957

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 2.7 Selected crystallographic data for compounds **2-23**, **2-24**, **2-25**.

Crystal	**2-23**	**2-24**	**2-25**
Formula	$C_{36}H_{12}BF_{18}P$	$C_{28}H_{15}BF_{15}P$	$C_{18}H_5BF_{10}$
Formula weight	828.24	678.18	422.03
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	P-1	C2/c	Pbca
a(Å)	12.9545(15)	23.155(5)	10.6539(13)
b(Å)	13.2370(16)	10.399(2)	16.736(2)
c(Å)	13.5614(16)	23.014(5)	19.095(2)
$\alpha(^o)$	66.727(2)	90	90
$\beta(^o)$	63.9130(10)	93.67(3)	90
$\gamma(^o)$	72.990(2)	90	90
V ($Å^3$)	1898.7(4)	5530.4(19)	3404.7(7)
Z	2	8	8
d(calc) g cm^{-1}	1.449	1.629	1.647
Abs coeff, μ, cm^{-1}	0.186	0.220	0.172
Data collected	18290	25443	36577
Data $F_o^2>3\sigma(F_o^2)$	6669	4840	4098
Variables	505	410	262
R^a	0.0445	0.0685	0.0484
$R_w{}^b$	0.1216	0.1717	0.1022
Goodness of Fit	1.020	1.027	1.002

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 2.8 Selected crystallographic data for compound **2-26·CH_2Cl_2**.

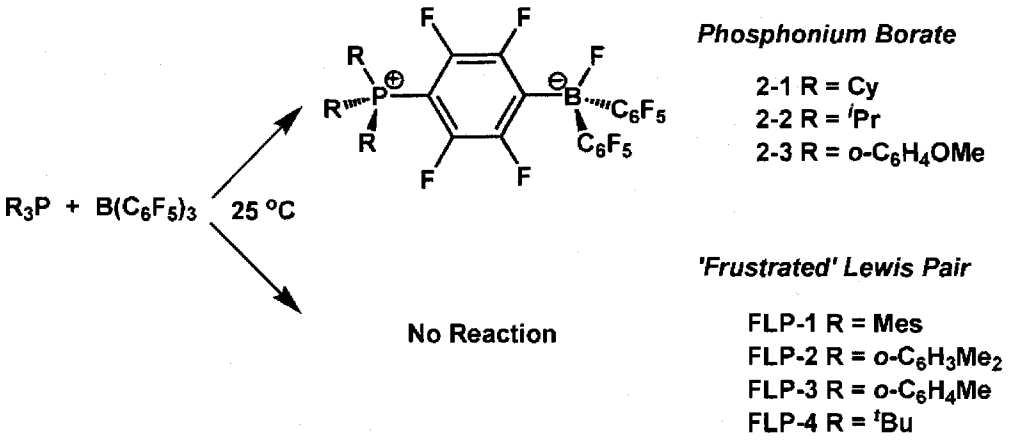
Crystal	**2-26·CH_2Cl_2**
Formula	$C_{37}H_{40}BF_{10}PCl_2$
Formula weight	787.37
Crystal system	Triclinic
Space group	P-1
a(Å)	11.635(3)
b(Å)	12.659(3)
c(Å)	13.371(3)
α(°)	73.387(3)
β(°)	77.620(3)
γ(°)	82.653(3)
V (Å^3)	1838.7(7)
Z	2
d(calc) g cm^{-1}	1.422
Abs coeff, μ, cm^{-1}	0.298
Data collected	17839
Data $F_o^2>3\sigma(F_o^2)$	6441
Variables	460
R^a	0.0769
$R_w{}^b$	0.0979
Goodness of Fit	1.047

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

2.3 Results and Discussion

2.3.1 Reaction of Sterically Demanding Tertiary Phosphines with $B(C_6F_5)_3$

The reaction of $B(C_6F_5)_3$ with sterically hindered tertiary phosphines R_3P (R = Cy, ^{i}Pr, *o*-C_6H_4OMe) in toluene proceeds over a 12 h period at 25 °C. Subsequent work-up afforded the white, air and moisture stable solids $[R_3P(C_6F_4)BF(C_6F_5)_2]$ (R = Cy **2-1**, ^{i}Pr **2-2**, *o*-C_6H_4OMe **2-3**) in isolated yields ranging from 75-87% (Scheme 2.1). The products **2-1**, **2-2**, and **2-3** give rise to ^{31}P NMR signals at 41.6, 53.2, and 10.9 ppm, respectively, that are shifted downfield from the corresponing phosphines, consistent with quaternization at phosphorus.[99, 110] The room temperature ^{19}F NMR spectra of **2-1** and **2-2** exhibited two peaks for the fluorine atoms of the C_6F_4 fragment as well as a set of *ortho*, *meta*, and *para* signals due to two C_6F_5 rings on anionic borate centers (Figure 2.1).



Scheme 2.1 Reaction of sterically demanding tertiary phosphines with $B(C_6F_5)_3$.

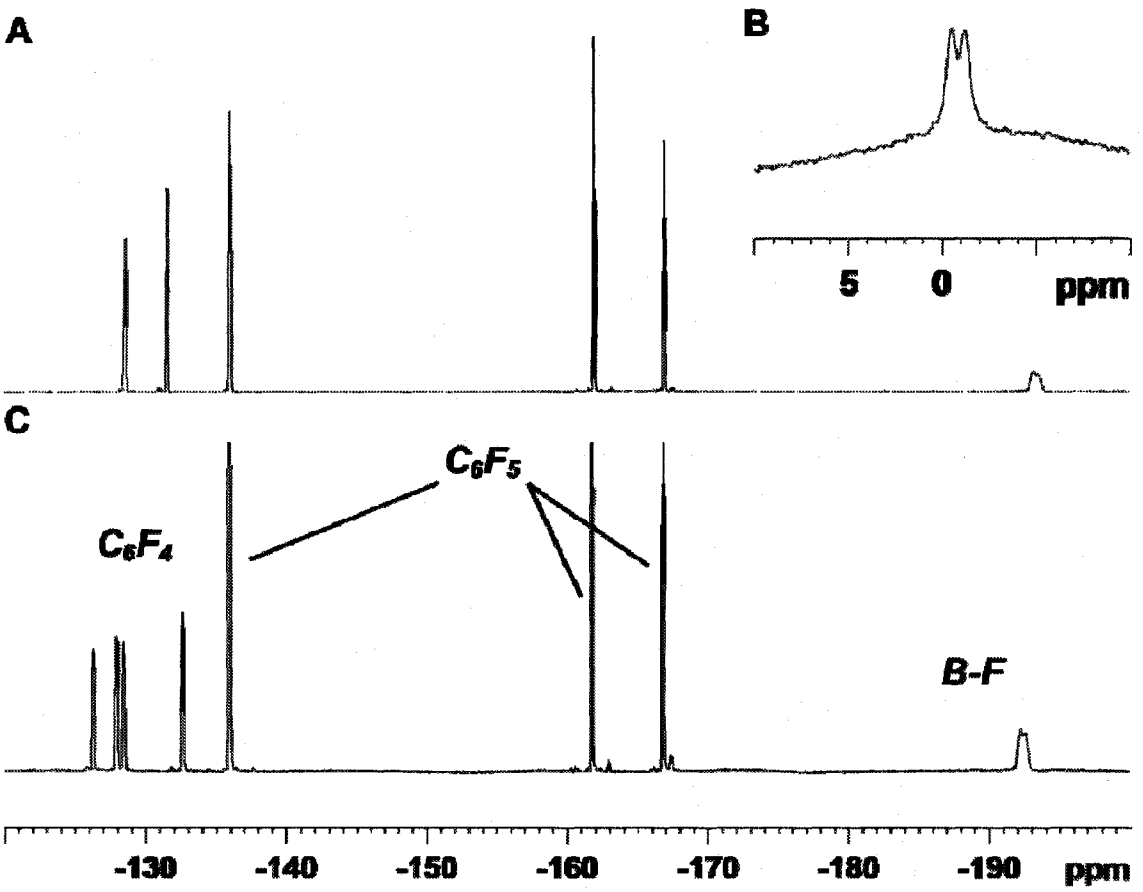


Figure 2.1 Representative NMR spectra for phosphonium borates **A)** ^{19}F NMR spectrum of **2-2** showing equivalent bridging C_6F_4 resonances. (**B**) ^{11}B NMR spectrum of **2-2** showing the distinct B-F coupling. (**C**) ^{19}F NMR spectrum of **2-4** (*vide infra*) showing four inequivalent bridging C_6F_4 resonances. Selected NMR data are summarized in Tables 2.1 and 2.2.

In the case of compound **2-3**, the ^{19}F NMR spectrum exhibits four distinct resonances for the bridging C_6F_4 ring due to restricted rotation about the P-C_{ArF} bond which can be attributed to the large size of the *ortho*-methoxyphenyl groups on phosphorus and weak intramolecular CH...F interactions. The resonances for the methoxy groups in the ^1H NMR spectrum were broadened, which is also characteristic of slowed rotation about the P-C_{ArF} bond. In addition, the ^{19}F NMR spectra of **2-1** to **2-3** show broad resonances in the range -189 to -193 ppm, which were attributed to a B-F linkage.

The corresponding ^{11}B NMR doublets, due to B-F coupling ($^{1}J_{B\text{-}F}$ = 62 Hz) were observed between -0.8 and 0.8 ppm (Figure 2.1). The atom connectivites in compounds **2-1** to **2-3** were unambiguously confirmed by X-ray crystallography (Table 2.3) and are consistent with the proposed zwitterionic formulations. POV-ray depictions of **2-1** and **2-2** are shown in Figure 2.2. In both species the phosphorus and boron centers are pseudo-tetrahedral. The average C-P-C bond angles are 109.9° and 109.5° for **2-1** and **2-2**, respectively, while the average C-B-C bond angles are 109.5° and 111.7° for **2-1** and **2-2**, respectively.

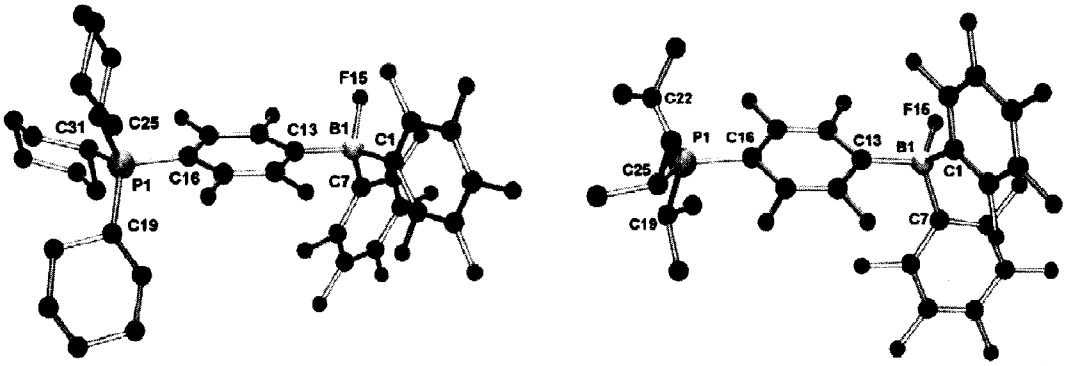


Figure 2.2 POV-ray depictions of (left) **2-1**, (right) **2-2**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green. Hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **2-1**: P(1)-C(31) 1.809(5), P(1)-C(19) 1.811(6), P(1)-C(25) 1.820(5), P(1)-C(16) 1.826(4), B(1)-C(13) 1.674(7), B(1)-C(1) 1.652(8), B(1)-C(7) 1.632(8), B(1)-F(15) 1.396(6), C(31)-P(1)-C(16) 109.2(2), C(13)-B(1)-C(7) 109.6(4), C(13)-B(1)-F(15) 106.3(4). **2-2**: P(1)-C(19) 1.814(5), P(1)-C(22) 1.820(5), P(1)-C(25) 1.825(4), P(1)-C(16) 1.822(4), B(1)-C(13) 1.649(6), B(1)-C(1) 1.635(7), B(1)-C(7) 1.652(7), B(1)-F(15) 1.405(10), C(25)-P(1)-C(16) 108.95(18), C(13)-B(1)-C(1) 107.0(3), C(13)-B(1)-F(15) 113.3(4).

The B-F bond lengths of 1.396(6) and 1.405(10) Å for **2-1** and **2-2** compare well with the those found in the zwitterions 1,4-$Ph_3PC(H)Ph(C_6F_4)BF(C_6F_5)_2$ (1.392(12) Å),[93] 1,4-$Ph_2MeP(C_6H_4)BF(Mes)_2$ (1.467(4) Å)[111] and the anions $(C_6F_5)_3BF$ (1.428(4) Å)[112], and {*ortho*-$(C_6F_5)C_6F_4\}_3BF$ (1.472 (11) Å),[113] while they are longer than those found in the diarylboranes Mes_2BF (1.339(2) Å) and {*ortho,para*-$C_6H_3(CF_3)_2\}_2BF$ (1.313(3) Å).[114] The remaining metrical parameters are unexceptional. Monitoring the reaction of $B(C_6F_5)_3$ and Cy_3P by ^{31}P and ^{11}B NMR spectroscopy at 25 °C showed immediate formation of **2-1** within 10 minutes and no evidence of the phosphine-borane adduct. This stands in stark contrast to the simple Lewis acid-base adducts formed by sterically less demanding donors.[80] The sterically congested environment of the bulky phosphines preclude coordination to boron thus generating a FLP ('frustrated' Lewis pair) which prompts nucleophilic aromatic substitution (NAS) at the electrophilic *para*-carbon of an arene ring. Increasing the steric bulk of the tertiary phosphine resulted in no reaction with $B(C_6F_5)_3$. Toluene-d_8 and CD_2Cl_2 solutions of stoichiometric mixtures of triaryl phosphines PR_3 (R = Mes, *o*-$C_6H_3Me_2$, *o*-C_6H_4Me) and $B(C_6F_5)_3$ were monitored by ^1H, ^{31}P, ^{11}B, and ^{19}F NMR spectroscopy. These experiments showed no evidence of the formation of Lewis acid-base adducts at 25 °C or on cooling to -70 °C. Even upon standing at 25 °C for several days no reaction was observed. The absence of Lewis adduct formation is consistent with the sterically demanding nature of the phosphines, which precludes coordination to the Lewis acidic B center or nucleophilic aromatic substitution at a *para*-carbon of $B(C_6F_5)_3$ seen for **2-1** to **2-3**. These mixtures of phosphines and boranes constitute stable FLP's and have been designated **FLP-1**, **FLP-2**, and **FLP-3** (Scheme 2.1).

Table 2.9 Selected tertiary phosphines and their respective cone angles and pKa values.

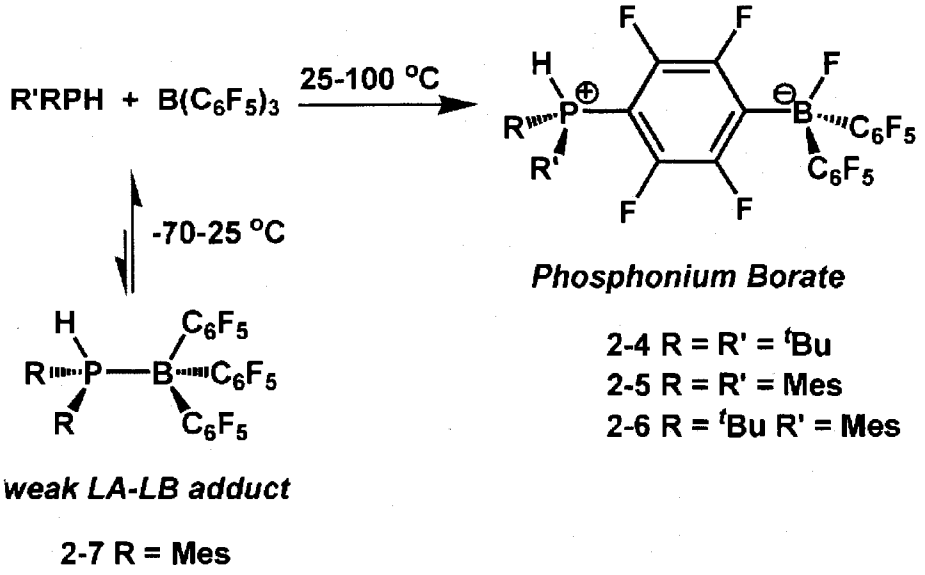
Phosphine	Cone angle[115]	pKa[116]	Product upon mixing with $B(C_6F_5)_3$ at 25°C
Me_3P	118°	8.6	Adduct Me_3P-$B(C_6F_5)_3$
Bu_3P	132°	8.7	Adduct Bu_3P-$B(C_6F_5)_3$
Ph_3P	145°	2.7	Adduct Ph_3P-$B(C_6F_5)_3$
$^{i}Pr_3P$	160°	9.3	Zwitterion $^{i}Pr_3P$-C_6F_4-$BF(C_6F_5)_2$
Cy_3P	170°	9.7	Zwitterion Cy_3P-C_6F_4-$BF(C_6F_5)_2$
$^{t}Bu_3P$	182°	11.4	no reaction
o-$tolyl_3P$	194°	3.1	no reaction
Mes_3P	212°	N/A	no reaction

It is noteworthy that solutions of $(Mes)_3P$ and $B(C_6F_5)_3$ are violet in color (λmax = 519 nm), while solutions of $B(C_6F_5)_3$ and (*o*-$C_6H_3Me_2)_3P$, (*o*-$C_6H_4Me)_3P$, or $^{t}Bu_3P$ (*vide infra*) are intense yellow, faint yellow, and colorless, respectively. These observations are thought to arise from π-stacking of electron-rich and electron-poor arene rings of the borane and phosphine, with the interaction becoming weaker as electron density is removed from the phosphorus aryl rings.[117, 118] This postulate is supported by recent calculations that show Mes_3P and $B(C_6F_5)_3$ form an encounter complex which is held together by C-H···F-C interactions and a parallel orientation of close-lying $C_6H_2Me_3$ and C_6F_5 arene rings is noted,[17] although HOMO-LUMO charge-transfer cannot be ruled out. Additionally, solutions of **FLP-1** are EPR inactive ruling out a electron transfer process. The extremly bulky trialkyl phosphine $^{t}Bu_3P$, shows no tendency to form a phosphine-borane adduct or effect nucleophilic aromatic substitution in the precence of an equal molar amount of $B(C_6F_5)_3$ in solution. This was confirmed by multinuclear NMR spectroscopy over a temperature range from -70 °C to 25 °C in toluene-d_8 or CD_2Cl_2. The

combination of $^{t}Bu_3P$ and $B(C_6F_5)_3$ in solution has been desginated **FLP-4** (Scheme 2.1). However, upon standing for several hours at 25 °C, **FLP-4** shows minor decompostion to unidentifiable products.[92] Additionally, prolonged heating of FLP's **1**, **2** and **3** above 100 °C results in minor degradation of the compunds. It should be noted as well that in the presence of an electrophilic metal center, phosphine/borane combinations will activate chloroalkane solvents yielding alkyl phosphonium chloroborates.[92, 119] Overall, the products of the reaction of tertiary phosphines with $B(C_6F_5)_3$ are heavily dependent on the steric bulk at phosphorus and therefore there exists a relationship between size and reactivity. Table 2.9 lists a series of tertiary phosphines and their corresponding cone angles,[115] which are known to give a good approximation of the relative size of phosphines. Phosphines with cone angles greater than 180° show no reactivity towards $B(C_6F_5)_3$ while those with cone angles below 160° form adducts with $B(C_6F_5)_3$ at 25 °C. Phosphines with intermediate cone angles undergo NAS with $B(C_6F_5)_3$ giving phosphonium borates. The pKa of the phosphines seems to have little impact on reactivity.

2.3.2 Reaction of Sterically Demanding Secondary Phosphines with $B(C_6F_5)_3$

The unique reactivity of tertiary phosphines towards $B(C_6F_5)_3$ prompted the investigation of the reaction between $B(C_6F_5)_3$ and secondary phosphines. In a similar fashion to that observed for tertiary phosphines, the reaction of the sterically demanding secondary phosphines R'RPH (R' = R = ^{t}Bu or Mes, R' = ^{t}Bu, R = Mes) with $B(C_6F_5)_3$ gave phosphonium borates of the form $R'RPH(C_6F_4)BF(C_6F_5)_2$ (R' = R = ^{t}Bu **2-4**, R' = R = Mes **2-5**, R' = ^{t}Bu, R = Mes **2-6**) over the course of 12 hours at 25 °C (Scheme 2.2).



Scheme 2.2 Reaction of sterically demanding secondary phosphines with $B(C_6F_5)_3$.

In the case of **2-5**, heating to 100 °C was required to obtain near quantitative yields. Compounds **2-4** to **2-6** are white solids that are tolerant to air and moisture for extended periods of time. All three compounds were characterized by multinuclear NMR spectroscopy (Table 2.2). The ^{31}P NMR spectra gave rise to characteristic doublets at 34.2 ($^1J_{P\text{-}H}$ = 465 Hz), -37.7 ($^1J_{P\text{-}H}$ = 500 Hz), and -2.9 ($^1J_{P\text{-}H}$ = 505 Hz) ppm for **2-4**, **2-5** and **2-6**, respectively, which are shifted downfield from the parent phosphines. Corresponding doublets were also observed in the ^1H NMR spectra of each. The large P-H coupling constants relative to the parent phosphines are typical for 4-coordinate cationic P-H moieties.[99] The ^{11}B NMR spectra showed the expected doublets between 0.4 and 0.8 ppm, due to B-F coupling ($^1J_{B\text{-}F}$ = 62 Hz). The ^{19}F NMR spectra of each compound gave rise to *ortho*, *meta*, and *para* resonances for two C_6F_5 rings bound to a 4-coordinate anionic borate center as well as resonances for a B-F fragment. Four fluorine resonances were

observed from -126.23 to -132.52 attributable to the C_6F_4 bridging unit for **2-4**, whereas two sharp fluorine resonances were observed for the same fragment in **2-5**. The ^{19}F NMR of **2-6** reveals two significantly broadened resonances for the four fluorine atoms of the C_6F_4 unit. In the case of **2-4**, restricted rotation about the P-C_{ArF} bond renders all bridging fluorine atoms inequivalent as seen for **2-3**. This observation was initially surprising as based on cone angle approximations,[115] the Mes substituent is larger than the ^{t}Bu substituent and therefore in **2-5** the Mes groups should prevent rotation about the P-C_{ArF}. Although, it has been reported that pairs of Mes groups can mesh together and rotate creating a 'cog-wheel' effect which reduces their combined steric bulk.[97] As expected, the steric bulk of the phosphonium moiety of **2-6** with both Mes and ^{t}Bu substituents fall between that of **2-4** and **2-5**. The solid-state structures of **2-4** and **2-6** were determined by X-ray crystallography and confirm the proposed connectivity (Figure 2.3, Table 2.4). The metrical parameters are similar to those described above for **2-1** and **2-2** and remain unexceptional, although it is noteworthy that for compounds **2-4** and **2-6**, the molecules pack in a dimeric head-to-tail fashion in the solid state accommodating intermolecular P-H...F-B interactions of 2.55(3) Å and 2.20(2) Å, respectively (Table 2.10). These interactions are less than or equal to the sum of van der Waals radii (2.55 Å) for a fluorine and a hydrogen atom and therefore can be considered hydrogen bonded.[120] This orientation also provides parallel yet offset π-stacking of the phosphorus and boron substituted (P-C_6F_4-B) arene-rings (Figure 2.3). Additionally the PH moiety is orientated parallel to an *ortho*-fluorine of the bridging C_6F_4 unit, which results in intramolecular P-H...F-C contacts of 2.50(3) Å and 2.47(2) Å for **2-4** and **2-6** respectively (Table 2.10).

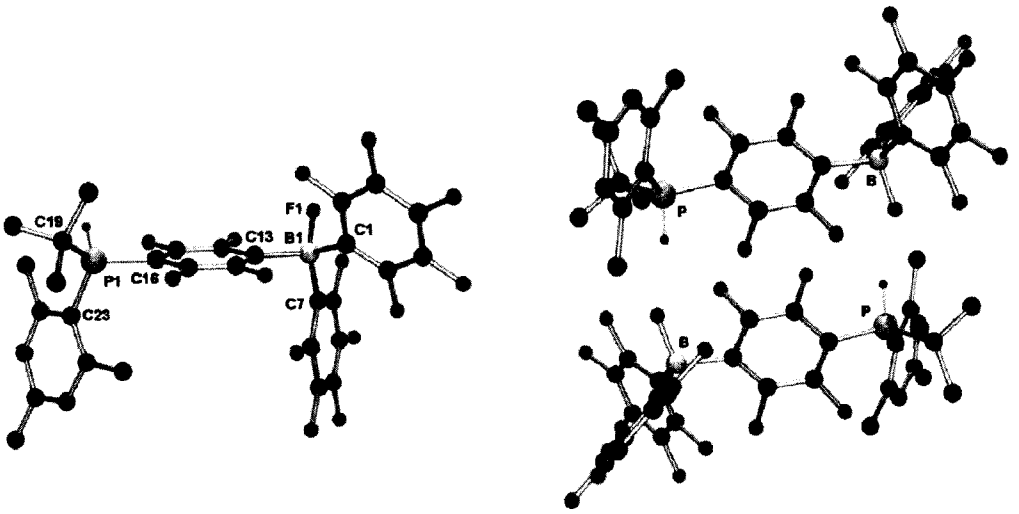


Figure 2.3 POV-ray depictions of (left) **2-6**, (right) **2-6** crystal packing. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green. Hydrogen atoms on carbon omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **2-6**: P(1)-H 1.26(2), P(1)-C(23) 1.798(3), P(1)-C(19) 1.850(3), P(1)-C(16) 1.807(3), B(1)-C(13) 1.664(4), B(1)-C(1) 1.646(4), B(1)-C(7) 1.638(4), B(1)-F(1) 1.436(4), C(23)-P(1)-C(16) 112.02(12), C(13)-B(1)-C(7) 106.8(4), C(13)-B(1)-F(1) 106.4(2).

Unlike the reactions of sterically demanding tertiary phosphines with $B(C_6F_5)_3$ mentioned previously, it has been observed that bulky secondary phosphines can form weak Lewis acid-base adducts with $B(C_6F_5)_3$. The adduct $(Mes_2PH)B(C_6F_5)_3$ (**2-7**) was isolated as a minor by-product during the synthesis of **2-5**. The multinuclear NMR spectra of **2-7** at 25 °C are uncharacteristic when compared to known phosphine-borane adducts (Table 2.2). The ^{31}P and ^{11}B NMR spectra show very broad signals at -67 and 23 ppm, respectively. The latter is shifted considerably downfield for 4-coordinate boron centers. The broad ^{31}P NMR signal indicates equilibrium exists between free and bound phosphine. The ^{19}F NMR spectrum exhibits three broad resonances for the *ortho*, *meta*, and *para* fluorines of the C_6F_5 arene rings. The difference in chemical shift between the *meta* and *para* signals of 12 ppm is comparable to that observed for weak $(H_2O)B(C_6F_5)_3$

adducts.[121] Upon cooling to -70 °C, the 3 broad fluorine resonances split into 13 sharp peaks with 2 of double intensity, representing 15 inequivalent fluorine atoms. Additionally at -70°C the ^{31}P NMR resonance resolves as a doublet at -43.2 ppm ($^{1}J_{PH}$ = 434 Hz). These NMR data support the notion that Mes_2PH forms a weak adduct with $B(C_6F_5)_3$ at 25 °C. Here, cooling favours the more stable P-B adduct and slows the rate of exchange between free and bound phosphine, which allows for observation of the adduct on the NMR timescale. Upon standing at 25 °C or with added heat, compound **2-7** dissociates into a FLP prompting NAS at a C_6F_5 ring yielding the zwitterion **2-5**. Weak P-B interactions between $^{t}Bu_2PH$ and ^{t}BuMesPH with $B(C_6F_5)_3$ were observed transiently by NMR spectroscopy, but adducts were never isolated or fully characterized.

Table 2.10 Intermolecular PH...FB and intramolecular PH...$FC_{(C_6F_4)}$ distances for $R'RPH(C_6F_4)BF(C_6F_5)_2$.

Compound	PH...FB (Å)*	PH...FC (Å)*
2-4 R = ^{t}Bu	2.55(3)	2.50(3)
2-6 R = ^{t}Bu, R' = Mes	2.20(2)	2.47(2)
2-17 R = Cp	2.10(6)	2.44(5)
2-24 R = ^{t}Bu, R' = Ph	2.29(3)	2.55(3)

*P-H bond distances reported were experimentally determined. X-ray data are known to underestimate these distances and thus the H...F distances are over estimated[122]

2.3.3 Thermal Rearrangement of Phosphine-$B(C_6F_5)_3$ Adducts

The ability of Mes_2PH to form a classical Lewis adduct with $B(C_6F_5)_3$ and undergo NAS lead to the investigation of the thermal stability of a range of phosphine-$B(C_6F_5)_3$ adducts. Following a standard procedure, the phosphine Cp_2PH was combined in toluene with $B(C_6F_5)_3$ and stirred for 1 hour at 25 °C. Concentration of the solvent afforded the near quantitative yield of the adduct $(Cp_2PH)B(C_6F_5)_3$ **2-8**. In a similar fashion, the adducts $(Cy_2PH)B(C_6F_5)_3$ **2-9**,[103] $(Ph_2PH)B(C_6F_5)_3$ **2-10**,[103] $(Bu_3P)B(C_6F_5)_3$ **2-11**, $(Ph_3P)B(C_6F_5)_3$ **2-12**,[100, 125] $(Et_3P)B(C_6F_5)_3$ **2-13**, $(Me_3P)B(C_6F_5)_3$ **2-14**,[101, 126, 127] $(Et_2PH)B(C_6F_5)_3$ **2-15**, and $(CyPH_2)B(C_6F_5)_3$ **2-16** were also prepared (Scheme 2.3). These phosphines were employed to give a range of adducts with varying steric and electronic properties at P. All compounds are easily characterized by ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, ^{19}F, ^{31}P NMR spectroscopy (Tables 2.1 and 2.2). These NMR data are typical for such adducts with each displaying a gap of the ^{19}F NMR resonances attributable to the *meta* and *para* fluorine atoms and a $^{11}B\{^1H\}$ NMR chemical shift characteristic of a four-coordinate boron center.[128-133] In addition, the solid-state structures of **2-8**, **2-10**, **2-13**, and **2-15** were determined by X-ray crystallography (Figure 2.4, Tables 2.4 and 2.5), while

Table 2.11 Selected phosphorus-boron bond distances.

R_3P-$B(C_6F_5)_3$	P-B (Å)	R_2PH-$B(C_6F_5)_3$	P-B (Å)	RPH_2-$B(C_6F_5)_3$	P-B (Å)
R = H[123]	2.046(8)	2-15 R = Et	2.036(4)	R = ^{t}Bu[120]	2.015(3)
2-14 R = Me[101]	2.061(4)	2-8 R = Cp	2.0243(3)	R = Ph[124]	2.039(3)
2-13 R = Et	2.081(4)	2-9 R = Cy[103]	2.0270(14)		
2-12 R = Ph[93]	2.180(6)	2-10 R = Ph	2.098(3)		

those of **2-9**,[103] **2-12**,[100] and **2-14**[101] have been previously determined. As expected, the geometries at boron and phosphorus are both pseudo-tetrahedral in each case. Phosphorus-boron bond distances range from 2.024(3)-2.180(6) Å and are listed in Table 2.11 along with related phosphorus-$B(C_6F_5)_3$ adducts known in the literature. The phosphorus-boron bond lengths are dependent on both the relative steric bulk and basicity of the phosphine. For example, increasing the size of the substituents on phosphorus from HPh_2 to Ph_3 results in a lengthening of the phosphorus-boron bond length while changing the substituents from Ph groups to more electron releasing Cy groups results in a shortening of the phosphorus-boron bond length.

Heating of **2-8** in a Teflon-capped, sealed reaction bomb to 125 °C for 24 hours in toluene solution resulted in the formation of a white precipitate. Addition of pentane and filtration allowed isolation of the white solid **2-17** in 73% yield (Scheme 2.3). The $^{11}B\{^1H\}$ NMR signal shifted from -13.5 ppm in the adduct to -0.2 ppm in **2-17** while the ^{31}P NMR resonance shifted downfield slightly to 11.5 ppm. Notably this latter signal exhibits a $^1J_{P\text{-}H}$ coupling constant of 480 Hz, which is typical of phosphonium salts.[99, 110] A new ^{19}F NMR signal was observed at -191.5 ppm typical of a B-F unit while resonances at -129.2 and -131.9 ppm confirmed the presence of a 1,4-di-substituted C_6F_4 aryl ring. Collectively, these data are consistent with the formulation of **2-17** as $Cp_2PH(C_6F_4)BF(C_6F_5)_2$ (Table 2.2). An X-ray crystallographic study of **2-17** (Figure 2.4, Table 2.6) confirmed the zwitterionic nature, in which a fluoroborate center is linked to a phosphonium center by a C_6F_4 unit. The metric parameters are similar to those previous reported for **2-1** to **2-4** derived from sterically 'frustrated' Lewis pairs. The molecules of **2-17** pack in the solid state such that the closest intermolecular approach between the PH and the BF fragments is 2.10(6) Å (Table 2.10). These head-to-tail interactions form an

extended hydrogen-fluorine bonded structure. The relatively shorter P-H···F-B interactions seen for **2-17** compared to the ^{t}Bu (**2-4**) and ^{t}BuMes (**2-6**) derivatives can be attributed to the smaller size of the Cp substituents which allows for a closer intermolecular approach. This close approach is reflected in the compound's lack of solubility in solvents other than the highly coordinating and polar solvent THF, whereas all previously described phosphonium borates have some degree of solubility in chloroalkane and bromoarene solvents.

In a similar fashion, heating of the adducts **2-9** to **2-13** to 125 °C for 24 hours in toluene results in rearrangement to give the *para*-substituted zwitterions $R_2PH(C_6F_4)BF(C_6F_5)_2$ (R = Cy **2-18**, R = Ph **2-19**) and $R_3P(C_6F_4)BF(C_6F_5)_2$ (R = Bu **2-20**, Ph **2-21**, Et **2-22**) (Scheme 2.3). Heating to 140 °C in C_6H_5Br was required for **2-19**. Multinuclear NMR spectroscopy confirmed the nature of these products (Tables 2.1 and 2.2). Interestingly, the ^{31}P NMR chemical shifts for the secondary phosphine derivatives **2-17** to **2-19** were similar to those seen for their corresponding adducts **2-8** to **2-10** ($\Delta\delta$ = 1-5 ppm). In contrast, the ^{31}P NMR chemical shifts for the tertiary phosphine derivatives **2-20** to **2-22** are approximately 30, 20, and 34 ppm, respectively, downfield of the precursor adducts. These observations reflect the greater steric congestion for the tertiary phosphine adducts. The solid state structures of **2-20** and **2-21** were determined by X-ray crystallography (Table 2.6) All metrical parameters are consistent with the previously described analogues and are not discussed. In a similar procedure for the synthesis of **2-17**, the compounds R''R'RP-C_6F_4-$BF(C_6F_5)_2$ (R = R' = R'' = *p*-C_6F_4F **2-23**, R'' = Ph, R' = ^{t}Bu, R = H **2-24**) were prepared and characterized by NMR spectroscopy (Tables 2.1 and 2.2) and X-ray crystallography (Table 2.7).

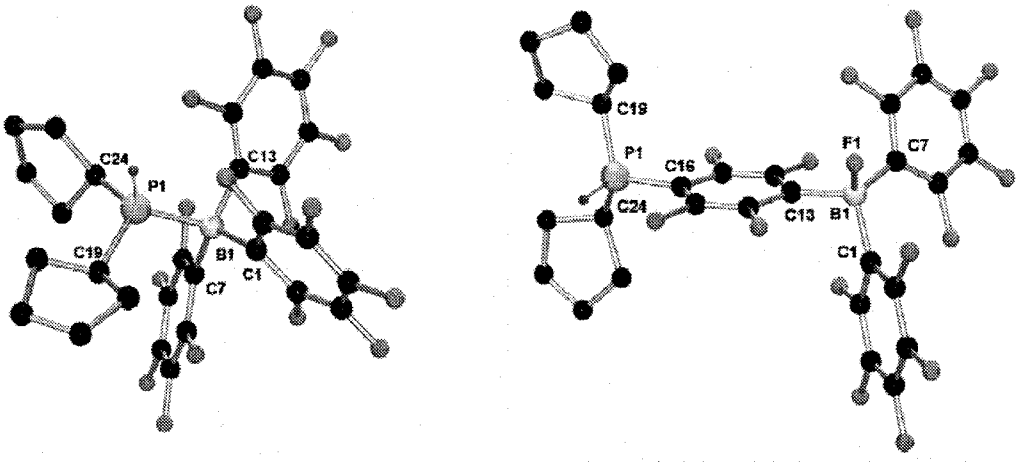


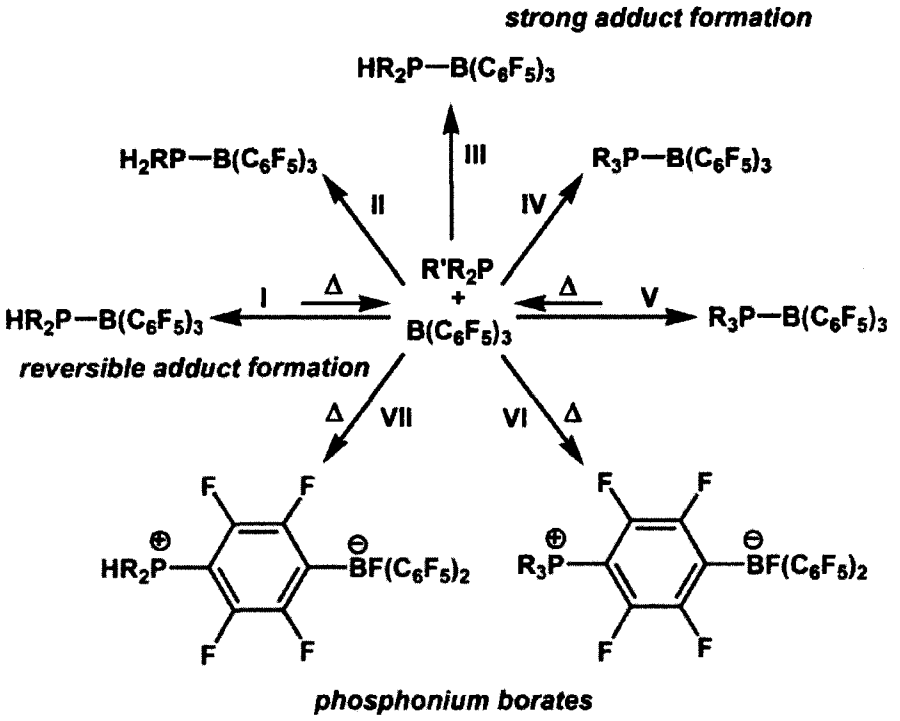
Figure 2.4 POV-ray depictions of (left) **2-8**, (right) **2-17**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green. Hydrogen atoms on carbon omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **2-8**: P(1)-H 1.27(2), P(1)-C(24) 1.883(2), P(1)-C(19) 1.819(2), P(1)-B(1) 2.024(3), B(1)-C(1) 1.648(3), B(1)-C(7) 1.650(3), B(1)-C(13) 1.646(3), C(24)-P(1)-C(19) 111.60(12), C(24)-P(1)-B(1) 109.94(11). **2-17**: P(1)-H 1.44(9), P(1)-C(24) 1.747(13), P(1)-C(19) 1.784(13), P(1)-C(16) 1.777(18), B(1)-C(13) 1.66(3), B(1)-C(1) 1.64(3), B(1)-C(7) 1.59(3), B(1)-F(1) 1.437(18), C(24)-P(1)-C(19) 118.5(8), C(24)-P(1)-C(16) 111.4(9), C(13)-B(1)-F(1) 106.7(18).

It should be noted that recently, Royo and co-workers have reported the formation of the related zwitterion $Ph_3P(C_6F_4)BMe(C_6F_5)_2$ as a by-product of a mixture of Ph_3P and the ion pair $[Zr\{C_5H_3[SiMe_2(\eta^1\text{-}N^tBu)]_2\}][RB(C_6F_5)_3]$ left at 80 °C for one week.[134]

Heating of the solutions of adducts **2-14** to **2-16** under similar conditions described above resulted in no reaction. Even after prolonged heating in bromobenzene to 140 °C for several days, no evidence of reaction was observed. The inability of the adducts **2-14** to **2-16** to undergo thermal rearrangement suggests that small, highly basic phosphines form strong phosphorus-boron bonds with $B(C_6F_5)_3$ that are thermally stable. This is reflected in the shorter phosphorus-boron bond lengths of **2-14** and **2-15** compared to those determined for **2-10** to **2-13** (Table 2.11) which undergo thermal rearrangement.

Although the adducts **2-8** and **2-9** have relatively short phosphorus-boron bond lengths, secondary H…F contacts analogous to those seen for amine adducts[103, 135] may strengthen the Lewis acid-base interaction for **2-14** to **2-16**. Short inter- and intramolecular CH…F contacts exist in the adduct $(Me_3P)B(C_6F_5)_3$ (**2-14**)[101] and have been thought to contribute to the compound's lack of solubility in organic solvents. Short intramolecular CH…F and PH…F and intermolecular CH…F contacts less than the sum of the van der Waal radii (< 2.55 Å) are found in the solid state structure of $(Et_2PH)B(C_6F_5)_3$ (**2-15**). Bradley and coworkers[120] have attributed the relative strengths of the adducts $(^tBuPH_2)B(C_6F_5)_3$ and $(H_3P)B(C_6F_5)_3$ to both short inter- and intramolecular H…F interactions only present in the former. Presumably, such interactions exist in the adduct $(CyPH_2)B(C_6F_5)_3$ (**2-16**). In each case the CH…F and/or PH…F interactions are not retained in solution as determined using ^{19}F NMR spectroscopy, indicating such interactions are significantly weaker than similar NH…F contacts which can be observed in solution.[103] Interestingly, the solid state structure of the adduct $(Ph_2PH)B(C_6F_5)_3$ (**2-10**) exhibits a short intramolecular PH…F contact of 2.27(2) yet it still thermally rearranges to give the zwitterions **2-21**, albeit at a higher temperature. Hence, the basicity of the phosphine does play a role in the strength of the phosphorus-boron bond.

The series of phosphonium borate zwitterions (Scheme 2.3) are air and moisture stable although their preparations in toluene require anaerobic conditions as a result of the high reactivity of the borane with moisture.[120] Interestingly, we have found that employing dry, coordinating solvents allows the preparation of these zwitterions without strict anaerobic precautions.



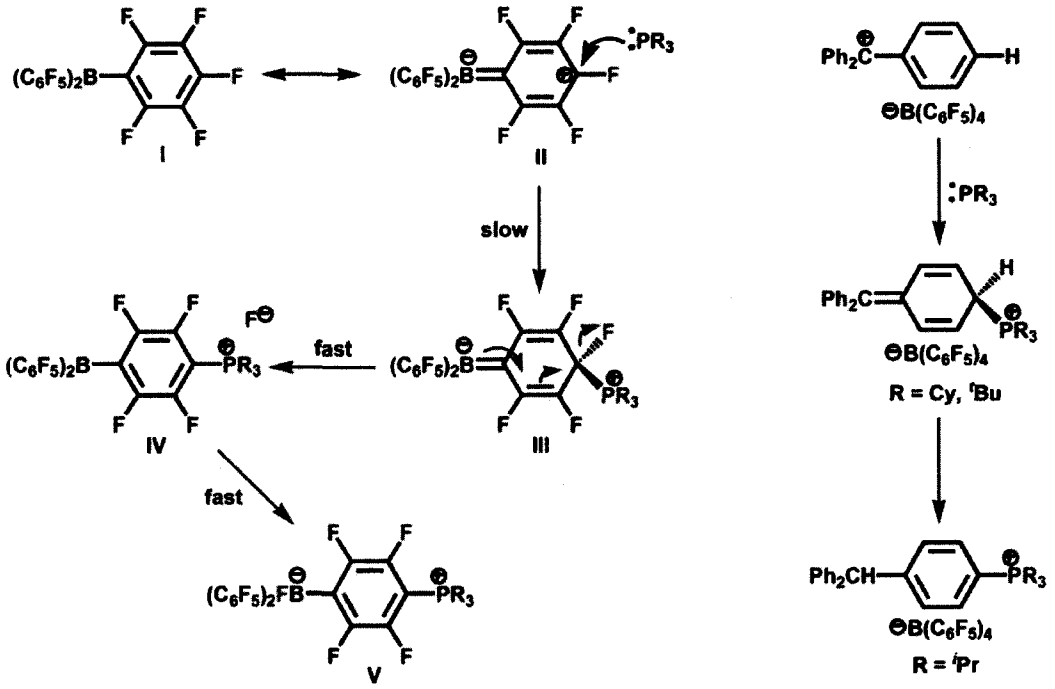
Scheme 2.3 Reaction of tertiary, secondary, and primary phosphines with $B(C_6F_5)_3$. (Blue) II *R* = *Et*, III *R* = *Cy*, IV *R* = *Me*. (Red) I *R* = *Cp, Cy, Ph*, V *R* = *Bu, Ph, Et*. (Purple) VI *R* = *Bu, Ph, Et*, VII *R* = *Cp, Cy, Ph*.

For example, heating pyridine or acetonitrile solutions of (Base)$B(C_6F_5)_3$ (Base = NC_5H_5[136] or CH_3CN[100]) with Cy_3P to 100 °C for 12 h gave $Cy_3P(C_6F_4)BF(C_6F_5)_2$ **2-1** in good yield, while no reaction was observed at room temperature after 24 hours. However, this procedure is limited to phosphines which can tolerate limited exposure to air and moisture. Of note, heating of the pyridine or acetonitrile adducts of $B(C_6F_5)_3$, which are known to be labile,[82] to 150 °C in bromobenzene resulted in no reaction as per the ^1H and ^{19}F NMR spectra, which indicates that such N-containing bases are not strong enough nucleophiles to effect NAS or that higher temperatures are required, as the reaction may be thermodynamically unfavorable. The results demonstrate that synthesis of the precursor compounds $R_3P(C_6F_4)BF(C_6F_5)_2$ or $R_2PH(C_6F_4)BF(C_6F_5)_2$ described in sections

2.3.1 and 2.3.2 are not limited to sterically frustrated phosphine/borane combinations. Indeed, it has been shown that certain classical Lewis phosphine-borane adducts rearrange readily upon heating providing access to a range of phosphonium borate zwitterions.

2.3.4 Mechanistic Insights

The proposed mechanism for zwitterion formation is shown in Scheme 2.4. The ability of phosphines to attack the *para*-carbon of a C_6F_5 ring on $B(C_6F_5)_3$ to give zwitterions of the form $R'R_2P(C_6F_4)BF(C_6F_5)_2$ (R' = R or H) is consistent with a zwitterionic resonance structure of $B(C_6F_5)_3$ (**II**), wherein electron density is removed from the *para*-carbon. Mechanistically it is thought that the first step in the reaction involves nucleophilic attack by phosphine at a *para*-carbon forming a zwitterionic intermediate (**III**). This step is followed by fluoride loss (**IV**) and subsequent rapid boron-fluorine bond formation (**V**). The strength of the newly formed phosphorus-carbon and boron-fluorine bonds renders the reaction irreversible. In the case of phosphine-$B(C_6F_5)_3$ adducts, the rearrangement reaction requires phosphine dissociation from boron,[110] which is accomplished by heating the adducts. A similar mechanism was described by Erker and co-workers[93] for the generation of $(Ph_3PC(H)Ph)C_6F_4BF(C_6F_5)_2$, while the reaction of tertiary phosphines with trityl cation proceeds in a similar fashion giving the (4-benzhydrylidene-cyclohexa-2,5-dienyl)-phosphonium cations $R_3P(C_6H_5)=CPh_2$ and subsequent [*p*-benzhydryl-phenyl]-phosphonium cations $R_3P(C_6H_4)CHPh_2$ (Scheme 2.4).[12]



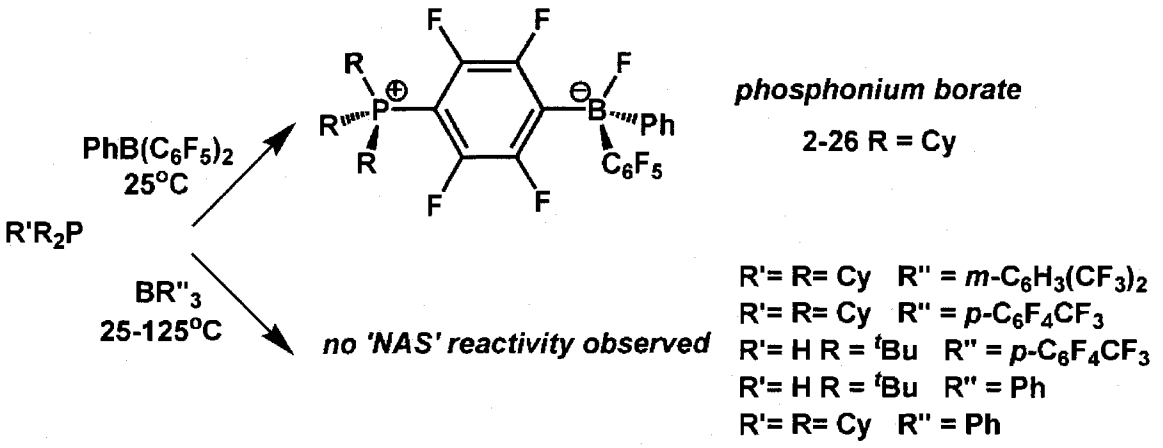
Scheme 2.4 (**Left**) Proposed mechanism for the formation of phosphonium borate zwitterions. (**Right**) Reaction between tertiary phosphines and $[Ph_3C][B(C_6F_5)_4]$.

In an effort to observe the intermediate (**III**) in Scheme 2.4, the reaction of $^tBu_2PH$ and $B(C_6F_5)_3$ in CD_2Cl_2 and toluene-d_8 solutions at 25 °C was monitored by ^{19}F and ^{31}P NMR spectroscopy over a 12 hour period. The phosphine, $^tBu_2PH$, was employed as it reacts slowly with $B(C_6F_5)_3$ over 12 hours to give the zwitterion **2-4**. The NMR spectra showed no evidence of formation of the intermediate (**III**). Presumably this type of anionic borylene is unstable and is likely only to exist transiently. None-the–less the rapid rearrangement of **III** to **V** throught **IV** is proposed. However, it cannot be ruled out that the reaction proceeds through a S_N2 concerted mechanism where the phosphine attacks a *para*-carbon with concurrent loss of fluoride, which is rapidly scavenged by boron. The formation of the zwitterions $R'R_2P(C_6F_4)BF(C_6F_5)_2$ (R' = R or H) is greatly dependent on the size of the parent phosphine. Smaller phosphines (Et_3P, Cp_2PH, etc.) that form typical adducts with $B(C_6F_5)_3$ require heat to thermally generate free phosphine

and borane which can then react to give the desired zwitterions. Weak $(R_2PH)B(C_6F_5)_3$ adducts (R = Mes, ^{t}Bu, etc.) slowly dissociate at 25 °C prompting nucleophilic aromatic substitution. Larger phosphines (Cy_3P, $^i Pr_3P$, etc.) do not form adducts with $B(C_6F_5)_3$ and thus readily attack the *para* carbon of a fluoroaryl ring. Extremely bulky phosphines (Mes_3P, $^t Bu_3P$) show no reactivity towards $B(C_6F_5)_3$, as they are too sterically hindered to form an adduct or approach the *para* carbon to effect NAS.

2.3.5 Reactivity of Phosphines with Triarylboranes other than $B(C_6F_5)_3$

It has been shown that a range of phosphines react with the Lewis acid $B(C_6F_5)_3$ to give a series of phosphonium borates of the form $R_3P(C_6F_4)BF(C_6F_5)$ and $R_2PH(C_6F_4)BF(C_6F_5)$ where R can be a alkyl or aryl substituent. To expand the scope of the NAS reactivity, the reaction of phosphines with triarylboranes other than $B(C_6F_5)_3$ was investigated. The partially fluorinated Lewis acid $PhB(C_6F_5)_2$[137] (**2-25**) has similar steric bulk when compared to $B(C_6F_5)_3$ while the Lewis acidity at boron is diminished.[138, 139] Although the synthesis of $PhB(C_6F_5)_2$ has been reported previously, the solid state structure has never been determined. Crystals of $PhB(C_6F_5)_2$ were grown from a concentrated hexanes solution at -35 °C and the solid-state structure determined by X-ray diffraction (Table 2.7). A POV-ray depiction is shown in Figure 2.5. The structure is planar at boron ($\Sigma_{C\text{-}B\text{-}C} = 360°$) and exhibits a propeller configuration with the two C_6F_5 rings turned 43° and 50° out of the BC_3 plane and the C_6H_5 ring rotated 24° out of the BC_3 plane which is typical for related triarylboranes.[114, 140-146] Upon addition of Cy_3P to a toluene solution of $PhB(C_6F_5)_2$ at 25 °C, a white solid precipitated and was identified as the phosphonium borate $Cy_3P(C_6F_4)BF(Ph)(C_6F_5)$ (**2-26**).



Scheme 2.5 Reaction of sterically demanding phosphines with aryl- and fluoroaryl-boranes, BR_3.

The ^{31}P NMR spectrum is similar to that of **2-1**, while the ^{1}H NMR spectrum gives rise to 3 additional downfield resonances from 7.1-7.4 ppm attributed to the five aromatic protons of the phenyl ring. The ^{11}B NMR resonance is shifted downfield 3 ppm from **2-1**, while the gap between the *meta* and *para* resonances (Δ_{p-m} = 4 ppm) is slightly smaller than in **2-1** (Δ_{p-m} = 5 ppm). For the latter, the *para*-fluorine is shifted slightly upfield in **2-26** compared to **2-1** due to an increase in shielding caused by greater electron density at boron. The solid-state structure of **2-26** was determined by X-ray diffraction (Table 2.8) and is shown in Figure 2.5. The metrical parameters are as expected and remain unexceptional. The preferential attack of the phosphine at the electron deficient C_6F_5 ring over the C_6H_5 ring implies that this type of reactivity is not only dependent on the sterics of the borane but also the electronics. Therefore the non-fluorinated borane Ph_3B was employed in an attempt to test the limits of reactivity. Mixtures of Ph_3B and Cy_3P or $^{t}Bu_2PH$ showed no reactivity at 25 °C, while at 125 °C only minor decomposition of the borane was observed. There was no evidence of phosphonium or borate formation by ^{11}B or ^{31}P NMR spectroscopy.

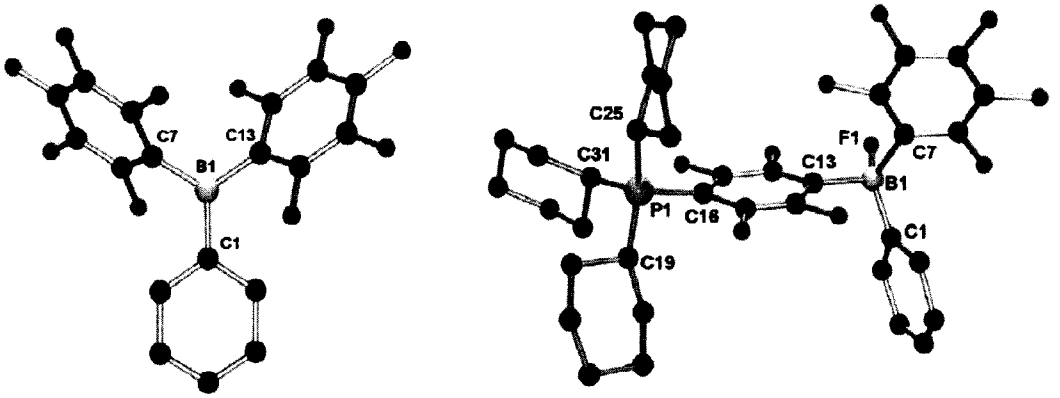
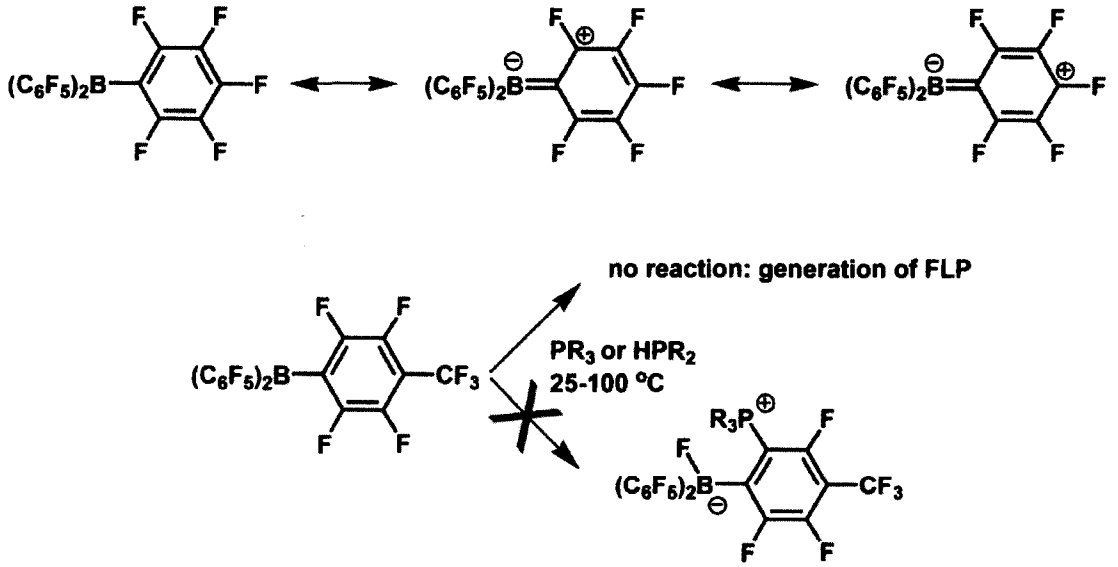


Figure 2.5 POV-ray depictions of (left) **2-25**, (right) **2-26**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green. Hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **2-25**: B(1)-C(1) 1.542(3), B(1)-C(7) 1.567(3), B(1)-C(13) 1.573(3), C(1)-B(1)-C(7) 122.03(19), C(1)-B(1)-C(13) 119.8(2), C(7)-B(1)-C(13) 118.1(2), **2-26**: P(1)-C(31) 1.826(4), P(1)-C(19) 1.823(4), P(1)-C(25) 1.831(4), P(1)-C(16) 1.818(4), B(1)-C(13) 1.656(6), B(1)-C(1) 1.619(7), B(1)-C(7) 1.670(6), B(1)-F(1) 1.433(5), C(31)-P(1)-C(16) 110.97(17), C(13)-B(1)-C(7) 116.5(3), C(13)-B(1)-F(15) 111.1(3).

The decomposition products were not identified but are presumably hydrolysis products caused by trace amounts of water in the starting materials and/or solvents. The inability of the phosphine to effect NAS of a C_6H_5 ring of BPh_3, indicates that the borane must be sufficiently Lewis acidic to render the *para*-carbon electrophilic. Ph_3B is significantly less Lewis acidic than $B(C_6F_5)_3$ or $PhB(C_6F_5)_3$ and therefore is not susceptible to NAS. Additionally, fluoride is an excellent leaving group for the nucleophilic substitution of aryl halides due to its large electronegativiy as it renders the directly bonded carbon electrophilic;[147] therefore, it could be assumed that only arylboranes with F substituents are susceptible to NAS. This thought is supported by the observation that no reactivity was observed between Cy_3P and the Lewis acidic borane $B(m\text{-}C_6H_3(CF_3)_2)_3$ from 25-125 °C, although the increased bulk about the *para*-position

casued by the adjacned CF_3 groups, likey prevents a close approach of P towards the *para*-carbon. In each case mentioned above, the reactivity may be thermodynamically controlled and thus a higher temperature regime may be required to observe reactivity.

$B(C_6F_5)_3$ has two resonance forms where positive charge can be placed on the *ortho-* or *para-* carbons of one fluoroaryl ring (Scheme 2.6). Sterically demanding phosphines prefer to react at the *para-* carbon, therefore by replacing the *para*-fluorine with a CF_3 group, we envisioned forcing reactivity at the *ortho* position in an effort to yield 1,2-disubstituted fluorophenyl phosphonium borates. The novel borane (p-$C_6F_4CF_3)_3B$ (**2-27**) was synthesized following a procedure using copper reagents developed by Jäkle and co-workers.[137] Mixing the borane with Cy_3P or $^tBu_2PH$ at 25 °C and 100 °C resulted in no reaction. Presumably the phosphines are too large to effect NAS at the *ortho* position. Therefore replacing the *para*-fluorines of $B(C_6F_5)_3$ with CF_3 substituents prevents NAS, allowing for the generation of 'frustrated' Lewis pairs.



Scheme 2.6 (Top) Resonance forms of $B(C_6F_5)_3$. **(Bottom)** Replacing the *para*-fluorine with a CF_3 prevents NAS type reactivity and generates a stable FLP.

2.4 Summary and Conclusion

In summary, it has been demonstrated that the reactivity between Lewis basic phosphines and the Lewis acid $B(C_6F_5)_3$ is not limited to simple adduct formation. Instead, novel phosphonium borate zwitterions and what we now term 'frustrated' Lewis pairs can be readily synthesized by altering the steric bulk of the parent phosphine. Whereas small phosphine-$B(C_6F_5)_3$ adducts are stable, large phosphine-$B(C_6F_5)_3$ adducts thermally rearrange to give phosphonium borate zwitterions. Sterically demanding tertiary phosphines do not interact with $B(C_6F_5)_3$ via P to B electron donation, but rather effect the nucleophilic aromatic substitution of a C_6F_5 giving phosphonium borate zwitterions in a facile, one step process. Extremely bulky tertiary phosphines with large cone angles do not react with $B(C_6F_5)_3$ yielding 'frustrated' Lewis pairs where a Lewis acidic and a Lewis basic site coexist without quenching each other. The reactivity and modification of these compounds is described in subsequent chapters.

Chapter 3 Synthesis, Characterization, and Reactivity of Phosphonium Borates, Anionic Phosphines, Cationic Boranes, and Phosphino-Boranes

3.1 Introduction

Catalysis is a very important process in organometallic chemistry. From the polymerization of olefins to the coupling of two organic molecules, catalysts have the ability to initiate and speed up chemical reactions. The development of new catalysts to make reactions more efficient and allow for rigorous product control is an ongoing process. Phosphines often play an integral part in organic or inorganic chemistry. A large range of phosphines are either commercially available or readily prepared. Phosphines of the form PR_3 have proved to be good ligands for transition metal catalysts due to their strong ability to donate electrons. Phosphine ligands can be easily functionalized, thus allowing for fine tuning of the steric and electronic properties of the catalyst. [67, 148, 149] Anionic, electron releasing phosphines that have the ability to coordinate to metal centers are promising reagents for organometallic catalysis.[150-152] Unlike neutral mono- and bidentate phosphine ligands which have been extensively used in all facets of chemistry, anionic phosphine ligand systems have remained in relative obscurity. Stradiotto and co-workers have made headway in this area by developing a range of zwitterionic rhodium(I) compounds based on anionic P,N-substituted indenide ligands.[153] Their complexes have proved to be highly effective catalysts for E-H (E = main group element) bond activation. More recently, Peters and co-workers have synthesized a series of monodentate (phosphino)tetraphenylborate ligands, which upon coordination with various palladium reagents, yield extremely effective catalysts for Suzuki crossing-coupling reactions.[154-158]

As shown in Figure 3A, each ligand is based on a trivalent phosphorus center with a pendant anionic borate moiety.

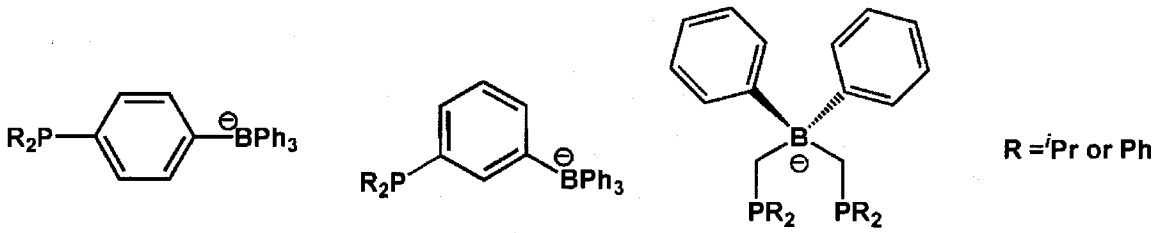
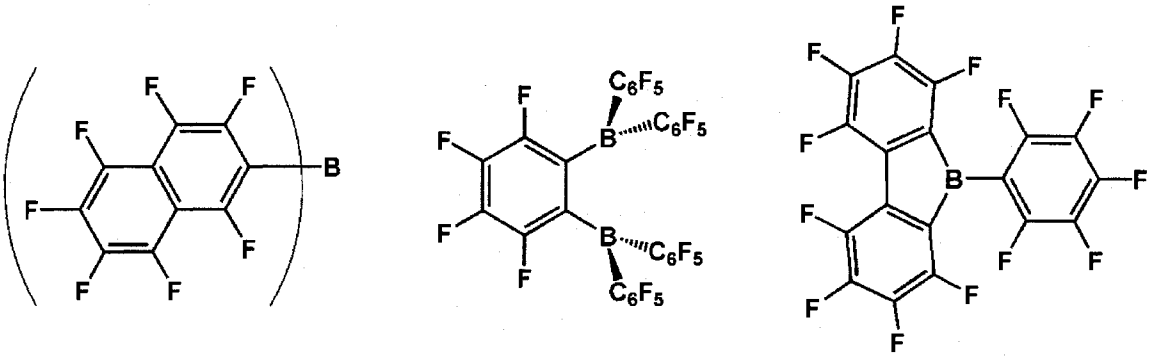


Figure 3A Examples of anionic phosphines. Variation of the sterics and electronics of a ligand can be used to tune catalyst activity by altering electron density at metal centers.

On the other hand, while the borane $B(C_6F_5)_3$ is very commonly used in organic and inorganic chemsitry,[70, 76] studies targeting structural modifications of this borane class have only begun to appear in the last few years. In particular, the groups of Marks[142, 159-168] and Piers[128, 169-178] have developed elegant syntheses to either elaborate the substituents on B or to access *bis*-borane compounds (Figure 3B).[179] Others have developed seemingly more straightforward routes to fluoroarylborane derivatives[72, 141, 180, 181] but in all cases these syntheses are not trivial. Nonetheless, such modifications of Lewis acids have been shown to dramatically impact the catalyst activity, stability and polymer properties derived from olefin polymerization processes.[182-191] In addition, Lewis acid perturbations serve to modify reactivity in a number of catalytic organic transformations.[138, 192]



Figures 3B Derivatives of $B(C_6F_5)_3$. Increasing the number of aryl fluorine atoms or incorporating a 5-membered boryl ring alters the Lewis acidity at boron, but at significant synthetic cost.

This chapter describes the simple modification of the phosphonium borates $R_2PH(C_6F_4)BF(C_6F_5)_2$ and $R_3P(C_6F_4)BF(C_6F_5)_2$ (R = alkyl or aryl) to give anionic phosphine-borates, cationic phosphonium boranes, as well as the bifunctional phosphino-boranes, thus providing a simple and conveint method to uniquely modified families of Lewis acids and Lewis bases. Each derivative has the potential to be applied to a wide range of applications.

3.2 Experimental

3.2.1 General Data

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents (pentane, hexanes, toluene, and methylene chloride) were purified employing a Grubbs' type column system manufactured by Innovative

Technology and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 °C under vacuum for 24 hours prior to use. Uninhibited THF was purchased from EMD and distilled from sodium/benzophenone prior to use. Deuterated solvents were dried over sodium/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br) and vacuum distilled prior to use. All common organic reagents were purified by conventional methods unless otherwise noted. ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer at 300 K unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR experiments were referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute vaules. DEPT and 2-D $^1H/^{13}C$ correlation experiments were completed for assignment of the carbon atoms. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ were generously donated by NOVA Chemicals Corporation. 1,8-(*N,N*-dimethylamino)napthalene (Proton sponge), silanes, Et_3PO, and $(COD)PtMe_2$ were purchased from Aldrich and used as received. Paratone-N oil was purchased from Hampton Research.

3.2.2 Synthesis of Anionic Phosphines

$[^tBu_2P(C_6F_4)BF(C_6F_5)_2][C_{10}H_6N_2(Me)_4H]$ (3-1): To a slurry of $^tBu_2PH(C_6F_4)BF(C_6F_5)_2$ (0.050 g, 0.076 mmol) in benzene (2 mL) was added a solution of proton sponge (0.016 g, 0.075 mmol) in benzene (1 mL). The reaction was stirred for 30 minutes, at which time

all volatiles were removed *in vacuo* to give a white solid. Yield 0.060 g (91 %). Crystals suitable for X-ray diffraction were grown via slow evaporation of a concentrated benzene solution at 25 °C. **^{1}H NMR** (C_6D_6): δ 18.16 (s, 1H, N*H*), 7.39 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, $C_{10}H_6$), 7.08 (t, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, $C_{10}H_6$), 6.84 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, $C_{10}H_6$), 2.31 (s, 12H, $\{N(CH_3)_2\}_2$), 1.25 (d, 18H, $^{1}J_{H\text{-}P}$ = 14 Hz, $P\{C(CH_3)_3\}$. **^{11}B{^{1}H} NMR** (C_6D_6): δ -0.8 (br). **^{13}C{^{1}H} NMR** (C_6D_6) partial: δ 149.20 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *C*F), 148.76 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 147.37 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 143.74 (s, quaternary, $C_{10}H_6N_2(CH_3)_4H$), 139.48 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 137.10 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 135.68 (s, quaternary, $C_{10}H_6N_2(CH_3)_4H$), 129.43 (s, *ortho*-$C_{10}H_6N_2(CH_3)_4H$), 126.97 (s, *meta*-$C_{10}H_6N_2(CH_3)_4H$), 120.81 (s, *para*-$C_{10}H_6N_2(CH_3)_4H$), 118.68 (s, quaternary, $C_{10}H_6N_2(CH_3)_4H$), 45.29 (s, $N(CH_3)_2$), 32.71 (d, $^{1}J_{C\text{-}P}$ = 28 Hz, $P\{C(CH_3)_3\}$), 30.55 (d, $^{2}J_{C\text{-}P}$ = 20 Hz, $C(CH_3)_3$). **^{19}F NMR** (C_6D_6): δ -123.92 (ddd, 1F, $^{3}J_{F\text{-}F(D)}$ = 38 Hz, $^{3}J_{F\text{-}P}$ = 21 Hz, $^{4}J_{F\text{-}F(B)}$ = 14 Hz, C_6F_4 A), -130.99 (ddd, 1F, $^{3}J_{F\text{-}P}$ = 110 Hz, $^{3}J_{F\text{-}F(C)}$ = 24 Hz, $^{4}J_{F\text{-}F(A)}$ = 14 Hz C_6F_4 B), -134.56 (ddd, 1F, $^{3}J_{F\text{-}F(B)}$ = 24 Hz, $^{4}J_{F\text{-}P}$ = 14 Hz, $^{4}J_{F\text{-}P}$ = 7 Hz, C_6F_4 C), -134.91 (m, 1F, C_6F_4 D), -134.91 (dm, 4F, $^{3}J_{F\text{-}F}$ = 15 Hz, *ortho*-C_6F_5), -161.51 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), - 166.17 (ddd, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, $^{3}J_{F\text{-}F}$ = 15 Hz, $^{6}J_{F\text{-}F}$ = 9 Hz *meta*-C_6F_5), -190.63 (bs, 1F, $Ar^F{}_3BF$). **^{31}P{^{1}H} NMR** (C_6D_6): δ 21.67 (dddd, $^{3}J_{P\text{-}F(B)}$ = 110 Hz, $^{3}J_{P\text{-}F(A)}$ = 21 Hz, $^{5}J_{P\text{-}F(C)}$ = 7 Hz, $^{5}J_{P\text{-}F(D)}$ = 5 Hz). **Anal. Calcd.** for $C_{40}H_{37}BF_{15}N_2P$: C, 55.06; H, 4.27; N, 3.21. Found: C, 55.11; H, 4.37; N, 3.07 %.

$[Mes_2P(C_6F_4)BF(C_6F_5)_2][C_{10}H_6N_2(Me)_4H]$ (3-2): To a slurry of $Mes_2PH(C_6F_4)BF(C_6F_5)_2$ (0.050 g, 0.064 mmol) in benzene (2 mL) was added a solution of proton sponge (0.014 g, 0.65 mmol) in benzene (1 mL). The reaction was stirred for 30

minutes, at which time all volatiles were removed *in vacuo* giving **3-2** as a white solid. Yield 0.057 g (90 %). **^{1}H NMR** (C_6D_6): δ 18.06 (s, 1H, N*H*), 7.34 (d, 2H, $^3J_{H\text{-}H}$ = 8 Hz, $C_{10}H_6$), 7.02 (t, 2H, $^3J_{H\text{-}H}$ = 8 Hz, $C_{10}H_6$), 6.79 (d, 2H, $^3J_{H\text{-}H}$ = 8 Hz, $C_{10}H_6$), 6.67 (d, $^4J_{H\text{-}P}$ = 3 Hz, 4H, P(C_6H_2)$_2$), 2.35 (s, 12H, {N(CH_3)$_2$}$_2$), 2.32 (d, 12H, $^4J_{H\text{-}P}$ = 3 Hz, P(C_6H_2*Me-2,6*)$_2$), 2.28 (s, 6H, P(C_6H_2*Me-4*)$_2$). **^{11}B{^{1}H} NMR** (C_6D_6): δ -0.70 (bs). **^{13}C{^{1}H} NMR** (C_6D_6) partial: δ 149.40 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 149.18 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 148.26 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 144.35 (s, P*C*$_6H_2$), 143.50 (d, $^2J_{C\text{-}P}$ = 18 Hz, P*C*$_6H_2$), 139.93 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *C*F), 138.23 (s, quaternary, *C*$_{10}H_6N_2(CH_3)_4H$), 137.63 (dm, $^1J_{C\text{-}F}$ = 251 Hz, *C*F), 135.78 (s, quaternary, *C*$_{10}H_6N_2(CH_3)_4H$), 130.84 (d, $^3J_{C\text{-}P}$ = 4 Hz, *meta-C*$_6H_2$), 129.22 (s, *ortho-C*$_{10}H_6N_2(CH_3)_4H$), 127.25 (s, *meta-C*$_{10}H_6N_2(CH_3)_4H$), 121.14 (s, *para-C*$_{10}H_6N_2(CH_3)_4H$), 119.13 (s, quaternary, *C*$_{10}H_6N_2(CH_3)_4H$), 90.1 (d, $^1J_{C\text{-}P}$ = 70 Hz, P*C*$_6H_2$), 45.70 (s, N(CH_3)$_2$), 23.20 (d, $^3J_{C\text{-}P}$ = 16.6 Hz, C_6H_2*Me-2,6*), 21.21 (s, C_6H_2*Me-4*). **^{19}F NMR** (C_6D_6): δ -134.46 (m, 2F, C_6F_4), -134.82 (m, 4F, *ortho*-C_6F_5), -135.04 (m, 2F, C_6F_4), -161.32 (m, 2F, *para*-C_6F_5), -166.13 (m, 4F, *meta*-C_6F_5), -190.43 (bs, 1F, $Ar^F{}_3BF$). **^{31}P {^{1}H} NMR** (C_6D_6): δ -48.33 (t, $^3J_{P\text{-}F}$ = 37 Hz). **Anal. Calcd.** for $C_{50}H_{41}BF_{15}N_2P$: C, 60.26; H, 4.15; N, 2.81 Found: C, 60.51; H, 4.42; N, 2.67 %.

3.3.3 Synthesis of Chloro, Bromo, and Hydrido Borates

$Mes_2PH(C_6F_4)BCl(C_6F_5)_2$ (3-3) : To a solution of $Mes_2PH(C_6F_4)BF(C_6F_5)_2$ (0.400 g, 0.511 mmol) dissolved in dichloromethane (10 mL) was added $(CH_3)_3SiCl$ (0.65 mL, 5.11 mmol) via syringe. The reaction was allowed to stir 12 hours, during which time a precipitate formed. All volatiles were removed *in vacuo* to give the product as a white

solid. Yield 380 mg (93 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 8.54 (d, 1H, $^{1}J_{H\text{-}P}$ = 504 Hz, P*H*), 7.15 (d, $^{4}J_{H\text{-}P}$ = 7 Hz, 4H, P(C_6H_2)$_2$), 2.40 (s, 6H, P(C_6H_2*Me-4*)$_2$), 2.29 (s, 12H, P(C_6H_2*Me-2,6*)$_2$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -7.62 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.5 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 148.23 (d, $^{4}J_{C\text{-}P}$ = 3 Hz, *para*-C_6H_2), 147.02 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 144.50 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, *ortho*-C_6H_2), 137.90 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 133.15 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, *meta*-C_6H_2), 110.40 (d, $^{1}J_{C\text{-}P}$ = 88 Hz, P-C_6H_2), 22.32 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, C_6H_2*Me-2,6*), 22.41 (s, C_6H_2*Me-4*). **^{19}F NMR** (CD_2Cl_2): δ -126.12 (s, 2F, C_6F_4), -132.87 (d, 4F, $^{3}J_{F\text{-}F}$ = 18 Hz, *ortho*-C_6F_5), -134.02 (s, 2F, C_6F_4), -161.50 (t, 2F, $^{3}J_{F\text{-}F}$ = 18 Hz , *para*-C_6F_5), -166.86 (t, 4F, $^{3}J_{F\text{-}F}$ = 18 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ -34.34 (m, $^{3}J_{P\text{-}F}$ = 8 Hz). **Anal. Calcd.** for $C_{36}H_{23}BF_{14}ClP$: C, 54.13; H, 2.90. Found: C, 53.71; H, 3.23 %.

$Mes_2PH(C_6F_4)BBr(C_6F_5)_2$ (3-4) : To a solution of $Mes_2PH(C_6F_4)BF(C_6F_5)_2$ (0.300 g, 0.384 mmol) dissolved in dichloromethane (10 mL) was added $(CH_3)_3SiBr$ (0.51 mL, 3.84 mmol) via syringe. The reaction was allowed to stir 12 hours, during which time a yellow/brown solution formed. All volatiles were removed *in vacuo* to give the product as a peach solid. Yield 315 mg (97 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 8.53 (d, 1H, $^{1}J_{H\text{-}P}$ = 504 Hz, P*H*), 7.15 (d, $^{4}J_{H\text{-}P}$ = 6 Hz, 4H, P(C_6H_2)$_2$), 2.43 (s, 6H, P(C_6H_2*Me-4*)$_2$), 2.30 (s, 12H, P(C_6H_2*Me-2,6*)$_2$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -11.45 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.57 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 148.56 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 148.42 (d, $^{4}J_{C\text{-}P}$ = 3 Hz, *para*-C_6H_2) 144.28 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, *ortho*-C_6H_2), 139.88

(dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 137.25 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 133.01 (d, $^3J_{C\text{-}P}$ = 13 Hz, *meta*-C_6H_2), 108.81 (d, $^1J_{C\text{-}P}$ = 83 Hz, P-C_6H_2), 22.07 (d, $^3J_{C\text{-}P}$ = 10 Hz, C_6H_2*Me-2,6*), 21.85 (s, C_6H_2*Me-4*). **^{19}F NMR** (CD_2Cl_2): δ -124.98 (s, 2F, C_6F_4), -131.44 (t, 4F, $^3J_{F\text{-}F}$ = 14 Hz, *ortho*-C_6F_5), -134.14 (s, 2F, C_6F_4), -161.21 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5), -166.90 (t, 4F, $^3J_{F\text{-}F}$ = 23, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ -37.86 (m, $^3J_{P\text{-}F}$ = 8 Hz). **Anal. Calcd.** for $C_{36}H_{23}BBrF_{14}P$: C, 51.28; H, 2.75. Found: C, 51.56; H, 3.01 %.

^{t}Bu$_2$PH(C$_6$F$_4$)BH(C$_6$F$_5$)$_2$ (3-5): To a solution of ^{t}Bu$_2$PH(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ (0.200 g, 0.304 mmol) dissolved in dichloromethane (10 mL) was added $(CH_3)_2SiHCl$ (0.34 mL, 3.04 mmol) via syringe. The reaction was allowed to stir 12 hours, during which time a precipitate formed. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 160 mg (83 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 6.23 (d, 1H, $^1J_{H\text{-}P}$ = 462 Hz, P*H*), 3.46 (q, 1H, $^1J_{H\text{-}B}$ = 82 Hz, B*H*), 1.56 (d, 18H, $^1J_{H\text{-}P}$ = 19 Hz, P{C(CH_3)$_3$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -25.19 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 150.01 (dm, $^1J_{C\text{-}F}$ = 244 Hz, *C*F), 148.70 (dm, $^1J_{C\text{-}F}$ = 237 Hz, *C*F), 146.26 (dm, $^1J_{C\text{-}F}$ = 253 Hz, *C*F), 145.35 (dm, $^1J_{C\text{-}F}$ = 253 Hz, *C*F), 138.85 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 137.16 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *meta*-C_6F_5), 36.77 (d, $^1J_{C\text{-}P}$ = 31 Hz, P{*C*(CH_3)$_3$}), 28.37 (s, C(*C*H_3)$_3$). **^{19}F NMR** (CD_2Cl_2): δ -126.93 (s, 1F, C_6F_4), -127.38 (s, 2F, C_6F_4), -133.90 (m, 1F, C_6F_4), -134.13 (d, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *ortho*-C_6F_5), -163.98 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -167.56 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 33.97 (m). **Anal. Calcd.** for $C_{26}H_{19}BF_{15}P$: C, 48.78; H, 3.15. Found: C, 48.14; H, 3.26 %.

$Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (3-6): To a solution of $Mes_2PH(C_6F_4)BF(C_6F_5)_2$ (0.400 g, 0.511 mmol) dissolved in dichloromethane (10 mL) was added $(CH_3)_2SiHCl$ (0.57 mL, 5.11 mmol) via syringe. The reaction was allowed to stir 12 hours, during which time a precipitate formed. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 375 mg (96 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 8.49 (d, 1H, $^1J_{H\text{-}P}$ = 502 Hz, P*H*), 7.12 (d, $^4J_{H\text{-}P}$ = 6 Hz, 4H, P(C_6H_2)$_2$), 3.65 (q, $^1J_{H\text{-}B}$ = 85 Hz, B*H*), 2.37 (s, 6H, P(C_6H_2*Me-4*)$_2$), 2.26 (s, 12H, P(C_6H_2*Me-2,6*)$_2$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -25.16 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.92 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 148.85 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 148.28 (s, *para*-C_6H_2), 144.33 (d, $^2J_{C\text{-}P}$ = 11 Hz, *ortho*-C_6H_2), 137.19 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 133.14 (d, $^3J_{C\text{-}P}$ = 10 Hz, *meta*-C_6H_2), 109.46 (d, $^1J_{C\text{-}P}$ = 90 Hz, P-C_6H_2), 22.04 (d, $^3J_{C\text{-}P}$ = 9 Hz, C_6H_2*Me-2,6*), 21.86 (s, C_6H_2*Me-4*). **^{19}F NMR** (CD_2Cl_2): δ -127.52 (s, 2F, C_6F_4), -134.09 (d, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *ortho*-C_6F_5), -134.95 (s, 2F, C_6F_4), -163.87 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5), -167.43 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl): δ -37.86 (m, $^3J_{P\text{-}F}$ = 8 Hz). **Anal. Calcd.** for $C_{36}H_{24}BF_{14}P$: C, 56.57; H, 3.16. Found: C, 55.62; H, 3.33 %.

^{i}Pr$_3$P(C_6F_4)BH(C_6F_5)$_2$ (3-7): To a solution of ^{i}Pr$_3$P(C_6F_4)BF(C_6F_5)$_2$ (0.400 g, 0.600 mmol) dissolved in dichloromethane (10 mL) was added $(CH_3)_2SiHCl$ (0.66 mL, 0.600 mmol) via syringe. The reaction was allowed to stir 12 hours, during which time a precipitate formed. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 356 mg (92 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 3.68 (q, 1H,

$^{1}J_{H\text{-}B}$ = 90 Hz, B*H*), 3.25 (m, 3H, P{C*H*(CH_3)$_2$}), 1.46 (d, 18H, $^{3}J_{H\text{-}P}$ = 20 Hz, P{CH(C*H*$_3$)$_2$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -25.28 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 150.43 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 148.25 (dm, $^{1}J_{C\text{-}F}$ = 235 Hz, *C*F), 146.98 (dm, $^{1}J_{C\text{-}F}$ = 255 Hz, *C*F), 139.74 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 136.89 (dm, $^{1}J_{C\text{-}F}$ = 252 Hz, *C*F), 93.67 (dm, $^{1}J_{C\text{-}P}$ = 68 Hz, *p*-*C*$_6$F$_4$), 24.02 (d, $^{1}J_{C\text{-}P}$ = 44 Hz, P{*C*H(CH_3)$_2$}), 17.22 (s, P{CH(*C*H$_3$)$_2$}). **^{19}F NMR** (CD_2Cl_2): δ -127.60 (m, 2F, C$_6$*F*$_4$), -132.60 (m, 2F, C$_6$*F*$_4$), -134.18 (d, 4F, $^{3}J_{F\text{-}F}$ = 18 Hz, *ortho*-C$_6$*F*$_5$), -164.09 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz , *para*-C$_6$*F*$_5$), -167.66 (t, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C$_6$*F*$_5$). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 52.57 (m). **Anal. Calcd.** for $C_{27}H_{22}BF_{14}P$: C, 49.57; H, 3.39. Found: C, 49.92; H, 3.44 %.

$Cy_3P(C_6F_4)BH(C_6F_5)_2$ (3-8): To a solution of $Cy_3P(C_6F_4)BF(C_6F_5)_2$ (0.500 g, 0.631 mmol) dissolved in dichloromethane (10 mL) was added $(CH_3)_2SiHCl$ (0.71 mL, 0.639 mmol) via syringe. The reaction was allowed to stir 12 hours, during which time a precipitate formed. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 469 mg (95 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 3.67 (q, 1H, $^{1}J_{H\text{-}B}$ = 94 Hz, B*H*), 2.93 (m, 3H, P{C$_6$*H*$_{11}$}), 2.05-1.25 (br m, 30H, P{C$_6$*H*$_{11}$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -25.30 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 150.40 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 148.71 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 147.62 (dm, $^{1}J_{C\text{-}F}$ = 255 Hz, *C*F), 139.84 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 137.40 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 90.20 (dm, $^{1}J_{C\text{-}P}$ = 70 Hz, *p*-*C*$_6$F$_4$), 33.31 (d, $^{1}J_{C\text{-}P}$ = 39 Hz, P{*C*$_6$H$_{11}$}$_3$), 28.22 (d, $^{2}J_{C\text{-}P}$ = 3 Hz, P{*C*$_6$H$_{11}$}$_3$), 27.40 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, P{*C*$_6$H$_{11}$}$_3$), 25.93 (s, P{*C*$_6$H$_{11}$}$_3$). **^{19}F NMR** (CD_2Cl_2): δ -127.74 (s, 2F, C$_6$*F*$_4$), -133.16 (s, 2F, C$_6$*F*$_4$), -133.98 (d, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, *ortho*-C$_6$*F*$_5$), -164.02 (t, 2F, $^{3}J_{F\text{-}F}$ = 20

Hz, *para*-C_6F_5), -167.50 (t, 4F, $^3J_{F\text{-}F}$ = 24 Hz, *meta*-C_6F_5). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ 40.99 (m). **Anal. Calcd.** for $C_{36}H_{34}BF_{14}P$: C, 55.83; H, 4.43. Found: C, 56.12; H, 4.53 %.

3.3.4 Synthesis of Cationic Boranes

[^{t}Bu$_2$PH(C$_6$F$_4$)B(C$_6$F$_5$)$_2$][B(C$_6$F$_5$)$_4$] (3-9): An orange solution of [Ph_3C][$B(C_6F_5)_3$] (0.078 g, 0.085 mmol) in CH_2Cl_2 (2 mL) was added to a slurry of ^{t}Bu$_2$PH(C_6F_4)B(C_6F_5)$_2$ (0.054 g, 0.084 mmol) in CH_2Cl_2 (5 mL) to give a yellow solution. The reaction was allowed to stir for 30 minutes at which time all volatiles were removed *in vacuo*. Pentane (5 mL) was added and the mixture filtered and washed with toluene (2 mL) and pentane (3 × 2 mL) to give an off-white solid. Yield 0.110 g (97 %). **^1H NMR** (CD_2Cl_2): δ 6.38 (d, 1H, $^1J_{H\text{-}P}$ = 460 Hz, P*H*), 1.63 (d, 18H, $^1J_{H\text{-}P}$ = 20 Hz, P{C(CH_3)$_3$}. **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2) partial: δ -16.83 (s, $B(C_6F_5)_3$). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2) partial: δ 147.33 (dm, $^1J_{C\text{-}F}$ = 235 Hz, *C*F), 138.62 (dm, $^1J_{C\text{-}F}$ = 260 Hz, *C*F), 136.82 (dm, $^1J_{C\text{-}F}$ = 260 Hz, *C*F), 37.68 (d, $^1J_{C\text{-}P}$ = 28 Hz, P{*C*(CH_3)$_3$}), 28.40 (s, C(*C*H$_3$)$_3$). **^{19}F NMR** (CD_2Cl_2): δ -121.45 (s, 1F, C_6F_4), -123.58 (s, 1F, C_6F_4), -124.39 (s, 1F, C_6F_4), -126.41 (s, 1F, C_6F_4), -126.41 (s, 4F, *ortho*-C_6F_5 borane), -133.42 (s, 8F, *ortho*-C_6F_5 borate), -139.89 (s, 2F, *para*-C_6F_5 borane), -160.14 (s, 4F, *meta*-C_6F_5 borane), -164.03 (t, 8F, $^3J_{F\text{-}F}$ = 23 Hz , *para*-C_6F_5 borate), -167.93 (t, 8F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ 35.42 (m). **Anal. Calcd.** for $C_{50}H_{19}B_2F_{34}P$: C, 45.56; H, 1.45. Found: C, 45.94; H, 1.68 %.

[$Mes_2PH(C_6F_4)B(C_6F_5)_2$][$B(C_6F_5)_4$] (3-10): An orange solution of [Ph_3C][$B(C_6F_5)_3$] (0.121 g, 0.131 mmol) in CH_2Cl_2 (2 mL) was added to a slurry of $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (0.100 g, 0.131 mmol) in CH_2Cl_2 (5 mL) to give a faint yellow solution. The reaction was allowed to stir for 30 minutes at which time all volatiles were removed *in vacuo*. Pentane (5 mL) was added and the mixture filtered and washed with toluene (2 mL) and pentane (3 × 2 mL) to give an off-white solid. Yield 0.168 g (89 %). **^1H {^1H} NMR** (CD_2Cl_2): δ 8.66 (d, 1H, $^1J_{H\text{-}P}$ = 508 Hz, P*H*), 7.14 (d, $^4J_{H\text{-}P}$ = 7 Hz, 4H, $P(C_6H_2)_2$), 2.42 (s, 6H, $P(C_6H_2Me\text{-}4)_2$), 2.32 (s, 12H, $P(C_6H_2Me\text{-}2,6)_2$). **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2) partial: δ -16.95 (s, $B(C_6F_5)_4$). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2) partial: δ 149.64 (dm, $^1J_{C\text{-}F}$ = 251 Hz, *C*F), 149.60 (s, *para*-C_6H_2), 148.65 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 147.10 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 144.37 (d, $^2J_{C\text{-}P}$ = 12 Hz, *ortho*-C_6H_2), 138.63 (dm, $^1J_{C\text{-}F}$ = 230 Hz, *C*F), 136.78 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *C*F), 135.15 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 133.34 (d, $^3J_{C\text{-}P}$ = 12 Hz, *meta*-C_6H_2), 107.08 (d, $^1J_{C\text{-}P}$ = 87 Hz, P-C_6H_2), 22.09 (d, $^3J_{C\text{-}P}$ = 10 Hz, $C_6H_2Me\text{-}2,6$), 21.82 (s, $C_6H_2Me\text{-}4$). **^{19}F NMR** (CD_2Cl_2): δ -125.18 (s, 2F, C_6F_4), -126.85 (s, 4F, *ortho*-C_6F_5 borane), -128.79 (s, 2F, C_6F_4), -133.49 (s, 8F, *ortho*-C_6F_5 borate), -140.67 (s, 2F, *para*-C_6F_5 borane), -160.36 (s, 4F, *meta*-C_6F_5 borane), -164.29 (t, 8F, $^3J_{F\text{-}F}$ = 23 Hz, *para*-C_6F_5 borate), -168.13 (t, 8F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2): δ -37.21 (m). **Anal. Calcd.** for $C_{60}H_{23}B_2F_{34}P$: C, 49.96; H, 1.61. Found: C, 50.55; H, 2.21 %.

[^{i}$Pr_3P(C_6F_4)B(C_6F_5)_2$][$B(C_6F_5)_4$] (3-11): An orange solution of [Ph_3C][$B(C_6F_5)_3$] (0.420 g, 0.456 mmol) in CH_2Cl_2 (2 mL) was added to a slurry of ^{i}$Pr_3P(C_6F_4)BH(C_6F_5)_2$ (0.300 g, 0.457 mmol) in CH_2Cl_2 (5 mL) to give a faint yellow solution. The reaction was

allowed to stir for 30 minutes at which time all volatiles were removed *in vacuo*. Pentane (5 mL) was added and the mixture filtered and washed with toluene (2 mL) and pentane (3 × 2 mL) to give an off-white solid. Yield 0.450 g (74 %). **^{1}H NMR** (CD_2Cl_2): δ 3.27 (m, 3H, P{C*H*(CH_3)$_2$}), 1.49 (dd, 18H, $^{3}J_{H\text{-}P}$ = 18 Hz, $^{3}J_{H\text{-}H}$ = 7 Hz, P{CH(C*H*$_3$)$_2$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2) partial: δ -16.55 (s, $B(C_6F_5)_4$). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 150.20 (dm, $^{1}J_{C\text{-}F}$ = 255 Hz, *C*F), 148.60 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 147.95 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 147.10 (dm, $^{1}J_{C\text{-}F}$ = 260 Hz, *C*F), 138.52 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 135.32 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 134.40 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 93.20 (dm, $^{1}J_{C\text{-}P}$ = 60 Hz, *p*-C_6F_4), 24.05 (d, $^{1}J_{C\text{-}P}$ = 40 Hz, P{*C*H(CH_3)$_2$}), 17.10 (s, P{CH(*C*H$_3$)$_2$}). **^{19}F NMR** (CD_2Cl_2): δ -125.35 (s, 2F, C_6F_4), -128.40 (s, 2F, C_6F_4), -129.0 (br s, 4F, *ortho*-C_6F_5 borane), -133.55 (s, 8F, *ortho*-C_6F_5 borate), -142.10 (br s, 2F, *para*-C_6F_5 borane), -162.18 (br s, 4F, *meta*-C_6F_5 borane), -164.20 (t, 8F, $^{3}J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5 borate), -168.08 (t, 8F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5 borate). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 56.10 (m, $^{3}J_{P\text{-}F}$ = 16 Hz). **Anal. Calcd.** for $C_{51}H_{21}B_2F_{34}P$: C, 45.98; H, 1.59. Found: C, 46.58; H, 1.79 %.

[$Cy_3P(C_6F_4)B(C_6F_5)_2$][$B(C_6F_5)_4$] (3-12): An orange solution of [Ph_3C][$B(C_6F_5)_3$] (0.238 g, 0.258 mmol) in CH_2Cl_2 (2 mL) was added to a slurry of $Cy_3P(C_6F_4)BH(C_6F_5)_2$ (0.200 g, 0.258 mmol) in CH_2Cl_2 (5 mL) to give a faint yellow solution. The reaction was allowed to stir for 30 minutes at which time all volatiles were removed *in vacuo*. Pentane (5 mL) was added and the mixture filtered and washed with toluene (2 mL) and pentane (3 × 2 mL) to give an off-white solid. Yield 0.332 g (87 %). **^{1}H NMR** (CD_2Cl_2): δ 2.98 (m, 3H, P{C_6H_{11}}), 2.01-1.29 (br m, 30H, P{C_6H_{11}}). **^{11}B{^{1}H} NMR** (CD_2Cl_2) partial: δ -16.97 (s, $B(C_6F_5)_4$). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.27 (dm, $^{1}J_{C\text{-}F}$ = 257 Hz, *C*F),

148.66 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 148.15 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 147.00 (dm, $^1J_{C\text{-}F}$ = 260 Hz, *C*F), 138.52 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 136.81 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 136.16 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 95.50 (dm, $^1J_{C\text{-}P}$ = 65 Hz, *p*-C_6F_4), 33.72 (d, $^1J_{C\text{-}P}$ = 36 Hz, P{C_6H_{11}}$_3$), 28.23 (d, $^2J_{C\text{-}P}$ = 4 Hz, P{C_6H_{11}}$_3$), 27.3 (d, $^3J_{C\text{-}P}$ = 12 Hz, P{C_6H_{11}}$_3$), 25.72 (s, P{C_6H_{11}}$_3$).**^{19}F NMR** (CD_2Cl_2): δ -124.33 (s, 2F, C_6F_4), -126.56 (br s, 4F, *ortho*-C_6F_5 borane), -126.92 (s, 2F, C_6F_4), -133.54 (s, 8F, *ortho*-C_6F_5 borate), -140.28 (br s, 2F, *para*-C_6F_5 borane), -160.25 (br s, 4F, *meta*-C_6F_5 borane), -164.28 (t, 8F, $^3J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5 borate), -168.12 (t, 8F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5 borate). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 45.42 (m, $^3J_{P\text{-}F}$ = 16 Hz). **Anal. Calcd.** for $C_{60}H_{33}B_2F_{34}P$: C, 49.62; H, 2.29. Found: C, 50.24; H, 2.62 %.

3.3.5 Synthesis of Phosphino-Boranes

^{t}Bu$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (3-13): A 20 mL vial was charged with ^{t}Bu$_2$PH(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$ (0.099 g, 0.150 mmol), toluene (10 mL) and diethyl ether (1 mL), forming a white slurry. The mixture was cooled to -35 °C and 3.0 M MeMgBr in diethyl ether (0.060 mL, 0.180 mmol) was added via syringe. Immediate formation of a clear yellow solution was observed. The reaction was allowed to warm to room temperature and stirred for 12 hours. All volatiles were removed *in vacuo* and the product extracted with hexanes (3 x 5 mL) and filtered through Celite. The solvent was removed *in vacuo* to give a yellow solid. Yield 54 mg (56 %). **^{1}H NMR** (C_6D_6): δ 1.15 (d, 18H, $^1J_{H\text{-}P}$ = 13 Hz, P{C(CH$_3$)$_3$}. **^{11}B{^{1}H} NMR** (C_6D_6): δ 50 (br). **^{13}C{^{1}H} NMR** (C_6D_6) partial: δ 149.85 (dm, $^1J_{C\text{-}F}$ = 234 Hz, *C*F), 148.72 (dm, $^1J_{C\text{-}F}$ = 252 Hz, *C*F), 147.63 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *C*F), 144.68 (dm,

$^{1}J_{C\text{-}F}$ = 220 Hz, *C*F), 137.86 (dm, $^{1}J_{C\text{-}F}$ = 255 Hz, *C*F), 33.62 (dd, $^{1}J_{C\text{-}P}$ = 27 Hz, $^{4}J_{C\text{-}F}$ = 3 Hz P{*C*(CH_3)$_3$}), 30.21 (dd, $^{1}J_{C\text{-}P}$ = 17 Hz, $^{4}J_{C\text{-}F}$ = 4 Hz, C(*C*H_3)$_3$). **^{19}F NMR** (C_6D_6): δ -120.24 (s, 1F, C_6F_4), -125.19 (d, 1F, $^{3}J_{F\text{-}P}$ = 110 Hz, C_6F_4), -128.99 (s, 4F, *ortho*-C_6F_5), -129.68 (s, 1F, C_6F_4), -130.48 (s, 1F, C_6F_4), -142.63 (s, 2F, *para*-C_6F_5), - 160.68 (s, 4F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_6): δ 25.08 (dm, $^{3}J_{P\text{-}F}$ = 110 Hz). **UV-Vis** (Hexanes): λ_{max}= 373 nm. **Anal. Calcd.** for $C_{26}H_{18}BF_{14}P$: C, 48.93; H, 2.84. Found: C, 48.98; H, 2.98 %.

$Mes_2P(C_6F_4)B(C_6F_5)_2$ (3-14): A 20 mL vial was charged with $Mes_2PH(C_6F_4)BF(C_6F_5)_2$ (0.098 g, 0.125 mmol), toluene (10 mL) and diethyl ether (1 mL), forming a white slurry. The mixture was cooled to -35 °C and 3.0 M MeMgBr in diethyl ether (0.050 mL, 0.150 mmol) was added via syringe. Immediate formation of a clear orange solution was observed. The reaction was allowed to warm to room temperature and stirred for 12 hours. All volatiles were removed *in vacuo* and the product extracted with hexanes (3 x 5 mL) and filtered through Celite. The solvent was removed *in vacuo* to give an orange solid. Yield 78 mg (82 %). **^{1}H NMR** (C_6D_6): δ 6.67 (d, $^{4}J_{H\text{-}P}$ = 3 Hz, 4H, P(C_6H_2)$_2$), 2.29 (s, 12H, P(C_6H_2*Me-2,6*)$_2$), 2.02 (s, 6H, P(C_6H_2*Me-4*)$_2$). **^{11}B{^{1}H} NMR** (C_6D_6, 96 MHz, 300K): 55 (br). **^{13}C{^{1}H} NMR** (C_6D_6) partial: δ 148.51 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 143.36, 139.73 (quaternary, C_6H_2), 137.65 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 134.19 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 130.67 (s, C-H, C_6H_2), 127.38 (quaternary, C_6H_2), 23.01 (d, $^{3}J_{C\text{-}P}$ = 17 Hz, C_6H_2*Me-2,6*), 20.86 (s, C_6H_2*Me-4*). **^{19}F NMR** (C_6D_6): δ -129.32 (br s, 4F, *ortho*-C_6F_5), -129.90 (br s, 2F, C_6F_4), -130.82 (br s, 2F, C_6F_4), -142.96 (br s, 2F, *para*-C_6F_5), -160.59 (br s, 4F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_6, 121 MHz, 300K): δ -41.69 (t, $^{3}J_{P\text{-}F}$ = 31 Hz). **UV-Vis**

(Hexanes): λ_{max}= 455 nm. **Anal. Calcd.** for $C_{36}H_{22}BF_{14}P$: C, 56.72; H, 2.91. Found: C, 57.03; H, 3.52 %.

$Mes_2P(C_6F_4)B(C_6F_5)2(THF)$ (3-15): Dissolution of $Mes_2P(C_6F_4)B(C_6F_5)_2$ in THF afforded the species **3-15**, which was obtained as a white solid in quantitative yield after removal of all volatiles *in vacuo*. Crystals suitable for X-ray diffraction were grown from slow evaporation of a concerted THF solution at 25 °C. **^{1}H NMR** (C_6H_6): δ 6.67 (d, $^4J_{H-P}$ = 4 Hz, 4H, $P(C_6H_2)_2$), 3.35 (m, 4H, THF), 2.33 (s, 12H, $P(C_6H_2Me\text{-}2,6)_2$), 2.01 (s, 6H, $P(C_6H_2Me\text{-}4)_2$), 0.93 (m, 4H THF). **^{11}B{^{1}H} NMR** (C_6D_6): δ -2.50 (br s). **^{13}C{^{1}H} NMR** (C_6D_6) partial: δ 148.24 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 144.58 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 143.14, 139.06 (quaternary, C_6H_2), 137.50 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 130.58 (s, C-H, C_6H_2), 129.30 (quaternary, C_6H_2), 22.85 (d, $^3J_{C-P}$ = 17 Hz, $C_6H_2Me\text{-}2,6$), 20.85 (s, $C_6H_2Me\text{-}4$). **^{19}F NMR** (C_6D_6): δ -132.40 (m, 2F, C_6F_4), -133.20 (d, $^3J_{F-F}$ = 23 Hz, *ortho*-C_6F_5), -133.67 (m, 2F, C_6F_4), -155.15 (t, 2F, $^3J_{F-F}$ = 20 Hz, *para*-C_6F_5), -163.28 (t, 4F, $^3J_{F-F}$ = 23 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_6): δ -43.57 (t, $^3J_{P-F}$ = 34 Hz). **Anal. Calcd.** for $C_{40}H_{30}BF_{14}PO$: C, 57.58; H, 3.62. Found: C, 57.76; H, 3.95 %.

[^{t}Bu$_2$P(NH$_2$)(C$_6$F$_4$)B(N$_3$)(C$_6$F$_5$)$_2$] (3-16): To a stirring toluene (10 mL) solution of [^{t}Bu$_2$P(C$_6$F$_4$)BF(C$_6$F$_5$)$_2$][C$_{10}$H$_6$N$_2$(Me)$_4$H] (0.300 g, 0.34 mmol) was added a solution of Me_3SiN_3 (~ 0.045 mL, 0.34 mmol) in toluene (1 mL). The reaction was heated to 100 °C for 2 hours at which time the mixture was cooled to room temperature and all volatiles were removed *in vacuo* to give a white solid. NMR spectroscopy showed multiple products. The white solid was washed with toluene (3 x 10 mL) and recrystallized by

layering pentane on a concentrated CH_2Cl_2 solution at 25 °C. Yield 0.180 g. Major NMR signals were attributed to **3-16**, indicating water was present during reaction. Crystals of **3-16** suitable for X-Ray diffraction were grown from a layered CH_2Cl_2/pentane solution at 25 °C. **Major ^{1}H NMR** (CD_2Cl_2): δ 4.83 (s, 2H, NH_2) 1.48 (d, 18H, $^1J_{H\text{-}P}$ = 17 Hz, P{C(CH_3)$_3$}. **^{11}B {^{1}H} NMR** (CD_2Cl_2): δ -10.37 (s). **^{19}F NMR** (CD_2Cl_2): δ -123.34 (m, 1F, C_6F_4), -128.91 (m, 1F, C_6F_4), -129.67 (m, 1F, C_6F_4), -134.91 (m, 4F, *ortho*-C_6F_5), -136.97 (m, 1F, C_6F_4), -161.17 (m, 2F, *para*-C_6F_5), -166.35 (*meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 70.5 (m).

(COD)Pt(Me)(Mes)$_2$P(C_6F_4)BMe(C_6F_5)$_2$ (3-17): To a vial charged with (COD)$PtMe_2$ (0.026 g, 0.078 mmol) and C_6D_5Br (0.5 mL) was added $Mes_2P(C_6F_4)B(C_6F_5)_2$ (0.060 g, 0.078 mmol) dissolved in C_6D_5Br (0.5 mL). The mixtures was shaken for 5 minutes and transferred to an NMR tube for analysis. Quantitative formation of **3-17** was observed by NMR spectroscopy. After solvent removal under vacuum, **3-17** was obtained as a cream colored solid in 81% yield (70 mg). Crystals suitable for X-ray diffraction were grown by slowly adding pentane to the product dissolved in C_6D_5Br at 25 °C and letting the solution stand for 24 hours. **^{1}H NMR** (C_6D_5Br, -25°C): δ 7.25-7.67 (br m, 4H, P(C_6H_2)), 5.90 (br s, 1H, COD), 5.16 (br s, 1H, COD), 4.92 (br s, 2H, COD), 3.10 (br s, 3H, P(C_6H_2*Me-4*)), 2.88 (br s, 3H, P(C_6H_2*Me-4*)), 2.41-2.10 (br m, 18H, P(C_6H_2*Me-2,6*)$_2$, COD), 1.54 (br s, 2H, COD), 1.25 (br m, 3H, B*Me*), 0.44 (br s, 3H, Pt*Me*). **^{11}B {^{1}H} NMR** (C_6D_5Br): δ -14.60 (br s, B*Me*). **^{13}C {^{1}H} NMR** (C_6D_5Br) partial: δ 148.87 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 145.10 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 142.50 (br, quaternary), 141.45 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 137.30 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 130.83 (s, *para*-C_6H_2), 111.68 (br, COD), 108.01

(m, COD), 30.03 (br, COD), 29.37 (br, COD), 24.50 (br, C_6H_2*Me-4*), 20.94 (br, C_6H_2*Me-2,6*), 11.33 (br, B*Me*), 5.39 (br, Pt*Me*). **^{19}F NMR** (C_6D_5Br): δ -128.70 (m, 1F, $^3J_{F\text{-}F}$ = 20 Hz, C_6F_4), -129.28 (m, 1F, C_6F_4), -130.04 (m, 1F, C_6F_4), -132.21 (m, 1F, $^3J_{F\text{-}F}$ = 22 Hz, C_6F_4), -132.57 (m, 4F, $^3J_{F\text{-}F}$ = 24 Hz, *ortho*-C_6F_5), -163.81 (m, 2F, $^3J_{F\text{-}F}$ = 21 Hz , *para*-C_6F_5), - 166.65 (m, 4F, $^3J_{F\text{-}F}$ = 22 Hz, *meta*-C_6F_5). **^{31}P {^{1}H} NMR** (C_6D_5Br): δ -11.33 (d, $^1J_{P\text{-}Pt}$ = 3831 Hz).

Table 3.1 Selected NMR data for phosphonium borates, anionic phosphines, cationic boranes, and phosphino-boranes.

Compound	δ ^{31}P ($^{1}J_{P-H}$)	δ ^{11}B($^{1}J_{B-H}$)	^{19}F Δ_{p-m}*	δ ^{19}F (o-F, p-F, m-F)
Reference				
$B(C_6F_5)_3$[98]		59	18.2	-128.5, -143.1, -161.3
Anionic Phosphines $[R_2P(C_6F_4)BF(C_6F_5)_2][PS-H]$				
3-1 R = ^{t}Bu[a]	21.7	-0.8	4.7	-134.9, -161.5, -166.2
3-2 R = Mes[a]	-48.3	-0.7	4.8	-134.8, -161.3, -166.1
Phosphonium Borates $Mes_2PH(C_6F_4)BX(C_6F_5)_2$				
2-5 X = F	-37.7(503)	0.4	5.0	-135.8, -161.8, -166.8
3-3 X = Cl[b]	-34.3(504)	-7.6	5.4	-132.9, -161.5, -166.9
3-4 X = Br[b]	-37.9(504)	-11.5	5.7	-131.4, -161.2, -166.9
Phosphonium Borates $R_2PH(C_6F_4)BH(C_6F_5)_2$ and $R'_3P(C_6F_4)BH(C_6F_5)_2$				
3-5 R = ^{t}Bu[b]	34.0(462)	-25.2(82)	3.6	-134.1, -164.0, -167.6
3-6 R = Mes[b]	-37.9(502)	-25.2(85)	3.5	-134.1, -163.9, -167.4
3-7 R' = Cy[b]	41.0	-25.3(94)	3.5	-134.0. -164.0, -167.5
3-8 R' = ^{i}Pr[b]	52.6	-25.3(90)	3.6	-134.2, -164.1, -167.7
Cationic Borates $[R_2PH(C_6F_4)B(C_6F_5)_2][A]^{e}$ and $[R'_3P(C_6F_4)B(C_6F_5)_2][A]^{e}$				
3-9 R = ^{t}Bu[b]	35.4(460)		20.1	-126.4, -139.9, -160.0
3-10 R = Mes[b]	-37.2(508)		19.7	-126.9, -140.7, -160.4
3-11 R' = Cy[b]	45.4		20.0	-126.6, -140.3, -160.3
3-12 R' = ^{i}Pr[b]	56.1		20.1	-129.0, -142.1, -162.2
Phosphino-boranes $R_2P(C_6F_4)B(C_6F_5)_2$ and $R'_2P(C_6F_4)B(THF)(C_6F_5)_2$				
3-13 R = ^{t}Bu[a]	25.1	50	18.1	-128.9, -142.6, -160.7
3-14 R = Mes[a]	-41.7	55	17.6	-129.3, -143.0, -160.6
3-15 R' = Mes[a]	-43.6	-2.5	8.1	-133.2, -155.2, -163.3

PS = proton sponge, [A] = $B(C_6F_5)_4$ [a]C_6D_6, [b]CD_2Cl_2, [c]THF, [d]C_6D_5Br, [e]signals for $B(C_6F_5)_4$ not listed, *Chemical shift difference between *para* and *meta* resonances in ^{19}F NMR spectrum.

3.3.6 Lewis Acidity Determination

Lewis acidity determination via the Beckett/Gutmann[193] method used a procedure similar to that described by Britovsek *et al.*[141] Here, an NMR tube was charged with the Lewis acid and Et_3PO in a 3:1 ratio in dry CD_2Cl_2 and the $^{31}P\{^1H\}$ NMR spectra recorded at 27 °C. An excess of Lewis acid was used for the Gutmann–Beckett method to ensure complete formation of the Et_3PO–Lewis acid adduct. For the Childs method,[194] a NMR tube was charged with the Lewis acid and crotonaldehyde in a 1:1 ratio in dry CD_2Cl_2 and the ^1H NMR spectra recorded at -20 °C, analogous to the original report. It should be noted that attempts to use C_6D_6/CD_2Cl_2 mixtures as the solvent for Childs acidity measurements at room temperature gave irreprodrucible results.

3.3.7 X-ray Data Collection, Reduction, Solution and Refinement

Single crystals were mounted in thin-walled capillaries either under an atmosphere of dry N_2 in a glove box and flame sealed or coated in Paratone-N oil. The data were collected using the SMART software package[104] on a Siemens SMART System CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71069 Å) at 25 °C. A hemisphere of data was collected in 1448 frames with 10 second exposure times, unless otherwise noted. Data reductions were performed using the SAINT software package[105] and absorption corrections were applied using SADABS.[106] The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[107] All non-H

atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Phosphorus and nitrogen-bound hydrogen atoms were located in the electron difference map and their positions refined isotropically. For compound **3-7** disordered CH_2Cl_2 solvent molecules were removed using the 'squeeze' command in PLATON.[108, 109]

Table 3.2 Selected crystallographic data for compounds **3-2**, **3-3·CH_2Cl_2**, **3-4**.

Crystal	**3-1**	**3-3·CH_2Cl_2**	**3-4**
Formula	$C_{40}H_{37}BF_{15}N_2P$	$C_{37}H_{25}BF_{14}PCl_3$	$C_{36}H_{23}BF_{14}PBr$
Formula weight	872.50	883.70	843.23
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a(Å)	13.5325(14)	11.1136(11)	11.370(6)
b(Å)	12.9076(13)	13.22905(13)	13.9414(14)
c(Å)	23.869(3)	26.134(3)	14.1418(15)
α(°)	90	90	106.622(1)
β(°)	99.999(1)	100.2370(10)	98.290(1)
γ(°)	90	90	103.352(1)
V ($Å^3$)	4106.0(7)	3798.6(6)	2036.2(4)
Z	4	4	2
d(calc) g cm^{-1}	1.411	1.545	1.375
Abs coeff, μ, cm^{-1}	0.167	0.380	1.136
Data collected	38674	36039	19739
Data $F_o^2>3\sigma(F_o^2)$	7224	6684	7138
Variables	546	515	482
R^a	0.0548	0.0599	0.0594
$R_w{}^b$	0.1422	0.1440	0.1859
Goodness of Fit	1.045	1.008	1.061

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{½}$

Table 3.3 Selected crystallographic data for compounds **3-5**, **3-6**, **3-7**.

Crystal	**3-5**	**3-6**	**3-7**
Formula	$C_{26}H_{20}BF_{14}P$	$C_{36}H_{24}BF_{14}P$	$C_{27}H_{22}BF_{14}P$
Formula weight	640.20	764.33	654.23
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	$P2_1/n$
a(Å)	9.6218(12)	10.9443(18)	9.3212(7)
b(Å)	17.225(2)	11.6829(19)	16.4421(13)
c(Å)	18.468(2)	13.617(2)	17.8541(14)
α(°)	67.652(2)	72.560(2)	90
β(°)	76.712(3)	89.300(3)	91.0440(10)
γ(°)	88.612(2)	89.039(3)	90
V ($Å^3$)	2748(6)	1660.8(5)	2735.9(4)
Z	4	2	4
d(calc) g cm^{-1}	1.547	1.528	1.588
Abs coeff, μ, cm^{-1}	0.211	0.189	0.214
Data collected	13680	13907	25837
Data $F_o^2>3\sigma(F_o^2)$	7884	4782	4817
Variables	785	469	391
R^a	0.0548	0.1291	0.0460
$R_w{}^b$	0.1537	0.3280	0.1222
Goodness of Fit	1.044	1.001	1.065

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 3.4 Selected crystallographic data for compounds **3-8**, **3-15**, **3-16**.

Crystal	**3-8**	**3-15**	**3-16**
Formula	$C_{36}H_{34}BF_{14}P$	$C_{40}H_{20}BF_{14}PO$	$C_{26}H_{20}BF_{14}N_4P$
Formula weight	774.41	834.42	696.24
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	P-1	P-1
a(Å)	11.743(5)	8.8328(14)	11.0660(8)
b(Å)	25.780(12)	11.0137(18)	11.4485(8)
c(Å)	13.975(7)	21.073(3)	12.6338(9)
α(°)	90	100.414(2)	66.5540(19)
β(°)	113.837(7)	95.590(2)	78.9040(10)
γ(°)	90	111.122(2)	75.3460(10)
V (Å^3)	3870(3)	1851.1(5)	1413.03(17)
Z	4	2	2
d(calc) g cm^{-1}	1.329	1.497	1.636
Abs coeff, μ, cm^{-1}	0.163	0.178	0.216
Data collected	36913	17897	10479
Data $F_o^2>3\sigma(F_o^2)$	6803	6502	6917
Variables	469	520	429
R^a	0.0630	0.0461	0.0501
$R_w{}^b$	0.1564	0.1146	0.1315
Goodness of Fit	0.988	1.005	1.028

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 3.5 Selected crystallographic data for compound **3-17**.

Crystal	**3-17**
Formula	$C_{46}H_{36}BF_{14}PPt$
Formula weight	1095.65
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	9.031(5)
b(Å)	19.620(11)
c(Å)	23.802(13)
$\alpha(^o)$	90
$\beta(^o)$	95.685(9)
$\gamma(^o)$	90
V ($Å^3$)	4197(4)
Z	4
d(calc) g cm^{-1}	1.734
Abs coeff, μ, cm^{-1}	3.478
Data collected	17538
Data $F_o^2>3\sigma(F_o^2)$	2668
Variables	568
R^a	0.0476
$R_w{}^b$	0.0686
Goodness of Fit	1.102

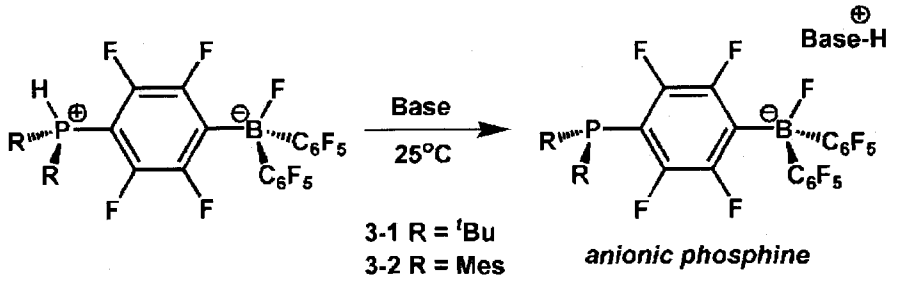
This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

3.3 Results and Discussion

3.3.1 Synthesis of Anionic Phosphines, Cationic Boranes, and Phosphino-Boranes

3.3.1.1 Anionic Phosphine Borates

The P-H moiety of the phosphonium borates described previously can be readily deprotonated giving access to anionic phosphines. The zwitterions $R_2PH(C_6F_4)BF(C_6F_5)_2$ (R = ^{t}Bu **2-4**, Mes **2-5**) react rapidly with proton sponge to give the white solids **3-1** and **3-2** in 91 % and 90 % yield, respectively (Scheme 3.1). The NMR data (Table 3.1) for **3-1** and **3-2** reveal little change in the ^{11}B NMR resonances although the ^{1}H NMR spectra confirm the deprotonation of phosphorus and the formation of protonated proton sponge. This is consistent with the observation of the N-H resonance in the ^{1}H NMR spectrum at 18 ppm and the upfield shift of the ^{31}P NMR resonance for **3-1** and **3-2** to 21.7 ppm and -48.3, respectively. In addition, the former ^{31}P NMR resonance is a doublet of doublets of doublets of doublets showing distinct coupling to the four fluorine atoms ($J_{P\text{-}F}$ = 110, 21, 7 and 5 Hz) on the C_6F_4 aryl ring (Figure 3.1). This coupling is also reflected in the ^{19}F NMR spectra where one fluorine atom is split into a distinct doublet ($^3J_{P\text{-}F}$ = 110 Hz). The large coupling constant is likely a result of a through space interaction of the P with the *ortho*-F. At 150 °C in C_6D_5Br the ^{31}P NMR signal becomes a broad singlet. While this behaviour reflects inhibited rotation about the P-aryl bond, solvent limitations precluded observation in the rapid exchange regime. In contrast, rotation of the P-C_6F_4 bond is facile at 25°C for **3-2** which is reflected in the ^{31}P NMR spectrum by the appearance of a triplet resonance ($^3J_{P\text{-}F}$ = 37 Hz).



Scheme 3.1 Synthesis of anionic phosphines. Base = proton sponge, $C_{10}H_6(NMe_2)_2$.

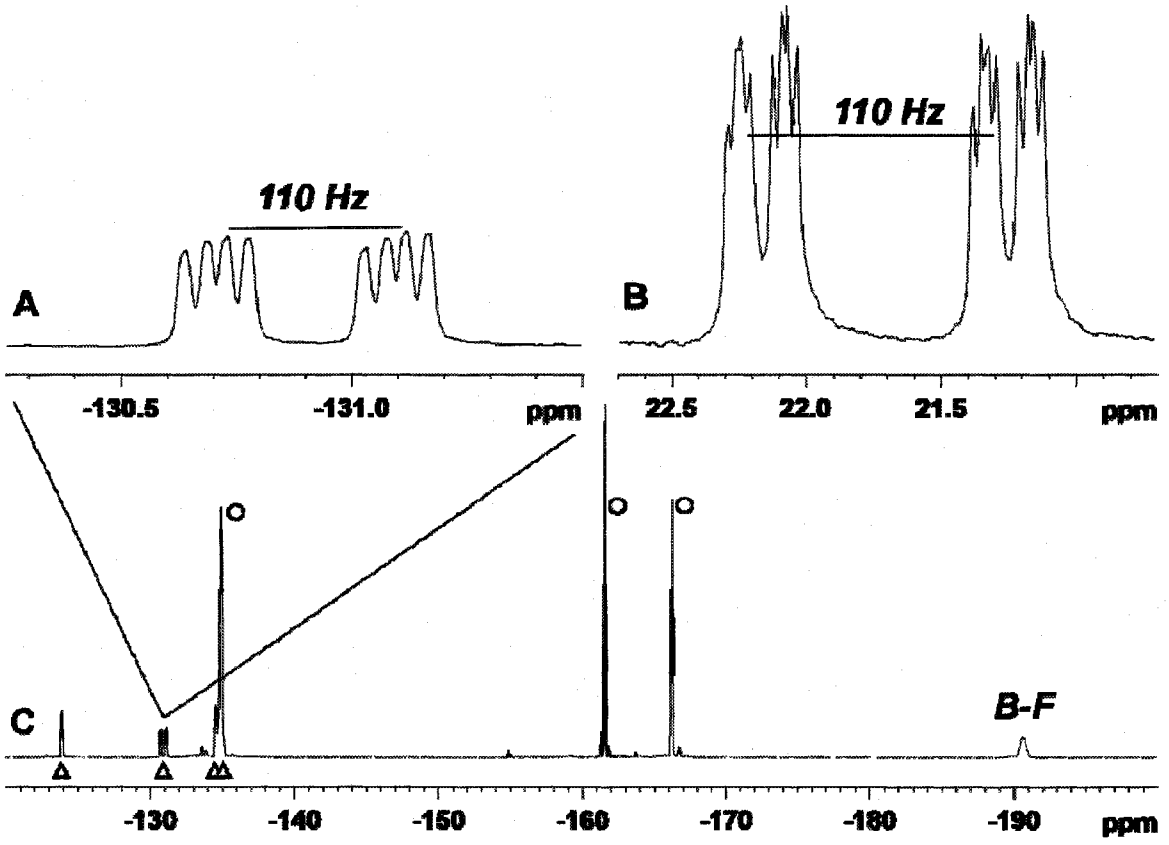


Figure 3.1 ^{19}F and $^{31}P\{^1H\}$ NMR spectra of **3-1**. (A) expanded view of the ^{19}F NMR spectrum of the C_6F_4 fluorine atom *ortho* to phosphorus. (B) $^{31}P\{^1H\}$ NMR resonance. (C) full ^{19}F NMR spectrum, O = C_6F_5, Δ = C_6F_4.

Here the phosphorus atom is coupled to two effectively equivalent fluorine atoms of the C_6F_4 aryl ring. These spectral data support the formulation of **3-1** and **3-2** as the proton-sponge salts of the phosphine-borates $[R_2P(C_6F_4)BF(C_6F_5)_2][C_{10}H_6(NMe_2)_2H]$ (R = ^{t}Bu **3-1**, Mes **3-2**) generated by deprotonation of the phosphorus center. This interpretation was further confirmed crystallographically (Table 3.2) for **3-1**. A POV-ray depiction is shown in Figure 3.2. The phosphorus center is pyramidal while the boron center remains pseudo-tetrahedral, similar to the parent phosphonium borate **2-4**. The average P-C_{alkyl} bond lengths (1.873 Å) are only slightly longer than those for **2-4** (1.849 Å), while the P-C_{aryl} bond length (1.861(3) Å) has increased from that in **2-4** (1.810(4) Å). The B-F bond length of 1.420(3) is slightly shorter than that found in **2-4** (1.441(4) Å), but is well within the average found for the series of fluoro-borate species reported in Chapter 2. The B-C bonds remain largely unchanged from **2-4**. The known ammonium cation[195-201] is positioned close to the borate moiety with a rather long NH...FB distance of 3.05(4), while several short intermolecular CH...FC contacts from 2.41(2)-2.55(2) Å were found between the methyl groups on nitrogen and the fluoroaryl rings on boron. Additionally two short intramolecular CH...FC contacts of 2.04(3) and 2.35(3) Å were observed between the *tert*-butyl groups on phosphorus and the bridging *ortho*-fluorine F(1). These distances are very short and indicate the existence of H...F hydrogen-bonding, which clearly contribute to the restricted rotation about the P-C_{aryl} bond. Interestingly, the ion pairs **3-1** and **3-2** are readily soluble in aromatic solvents whereas the parent phosphonium borates are only sparingly soluble in aromatic solvents. While ion pairs typically exhibit a lower solubility than neutral molecules, the lower solubility of the zwitterions **2-4** and **2-5** can be attributed to the ionic head-to-tail interactions observed in the solid state and several intermolecular H...F interactions, which makes the compounds

difficult to solvate. Related anionic phosphines have been previously reported but they are not fluorinated and their preparations involve complicated multi-step synthetic procedures.[154, 156, 157, 202]

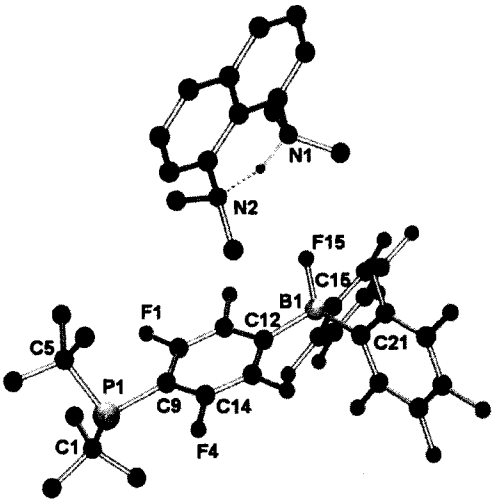
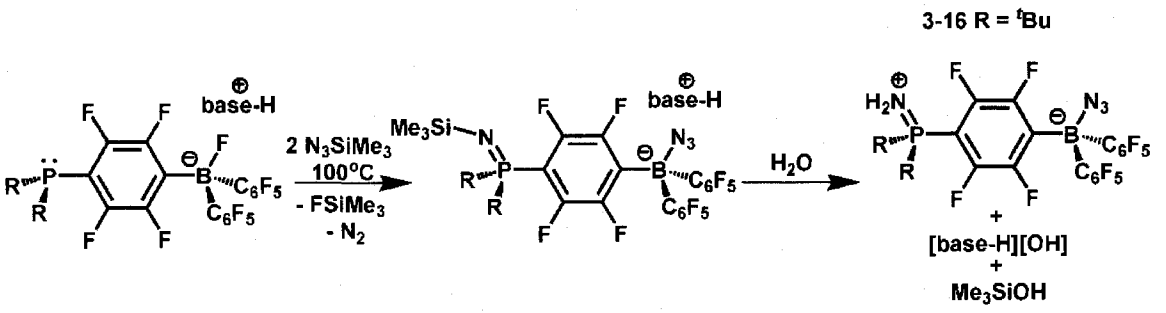


Figure 3.2 POV-ray depiction of **3-1**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Nitrogen: blue. Carbon hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **3-1**: P(1)-C(5) 1.864(4), P(1)-C(1) 1.882(4), P(1)-C(9) 1.861(3), B(1)-C(12) 1.656(4), B(1)-C(15) 1.653(4), B(1)-C(21) 1.656(4), B(1)-F(15) 1.420(3), N(1)-H 1.15(4), N(2)-H 1.49(4), C(5)-P(1)-C(1) 114.23(19), C(12)-B(1)-C(15) 112.3(2), C(12)-B(1)-F(15) 104.6(2), C(1)-P(1)-C(9)-C(14) 123.1(3), C(5)-P(1)-C(9)-C(14) 116.9(3).

The ability of phosphinimines to act as ligands for early metal olefin polymerization catalysts[203] led to the attempted oxidation of the phosphine of **3-1** via a standard Staudinger reaction. Unfortunately, treatment of **3-1** with approximately one equivalent of Me_3SiN_3 led to a mixture of products. Surprisingly, after washing the crude solid with toluene and crystallization from CH_2Cl_2 and pentanes, a white solid was isolated and identified as $^tBu_2P(NH_2)(C_6F_4)B(N_3)(C_6F_5)_2$ (**3-16**) (Scheme 3.2). The compound exhibits ^{31}P and ^{11}B NMR resonances at 70.5 ppm and -10 ppm which are indicative of phosphinimonium[204] and azidoborate[205] fragments, respectively.



Scheme 3.2 Synthesis of phosphinimonium azidoborate **3-16**.

This compound is interesting as there are only a handful of examples of azidoborates reported in the literature with this being the first zwitterionic species. The azidoborates reported are typically found to have ancillary perfluoroaryl,[205-209] aryl,[210] or azido[211-213] substituents at boron. These species consist of a $[R_3BN_3]$ anion and a corresponding spectator cation. The solid state structure of **3-16** was obtained (Table 3.4) and is shown in Figure 3.3. The molecule packs in a dimeric arrangement with head-to-tail N(4)-H...N(1) separations of approximately 2.788 Å. Also noted is the close N(4)-H...F(6)-C(7) distance of 2.480 Å. This orientation also provides parallel yet offset π-stacking of the P,B substituted arene-rings analogous to that observed for the related phosphonium fluoroborates **2-4** and **2-6**. The geometry at boron is pseudo-tetrahedral with average C-B-C and C-B-N bond angles of 111.34° and 107.55°, respectively. The B(1)-N(1) bond distance is 1.591(3) Å, while the N(1)-N(2) and N(2)-N(3) distances are 1.210(3) Å, and 1.135 (3) Å respectively. These parameters compare well to those found for the similar azidoborate $[(C_6F_5)_3BN_3][Me_4N]$,[205] while the B-N distance is slightly shorter than that found in the non-fluorinated derivative $[(C_6H_5)_3BN_3][Me_4N]$ (1.601(2) Å).[205]

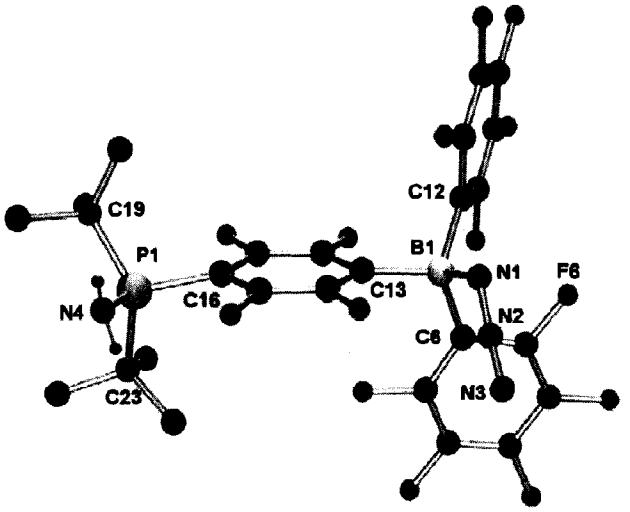


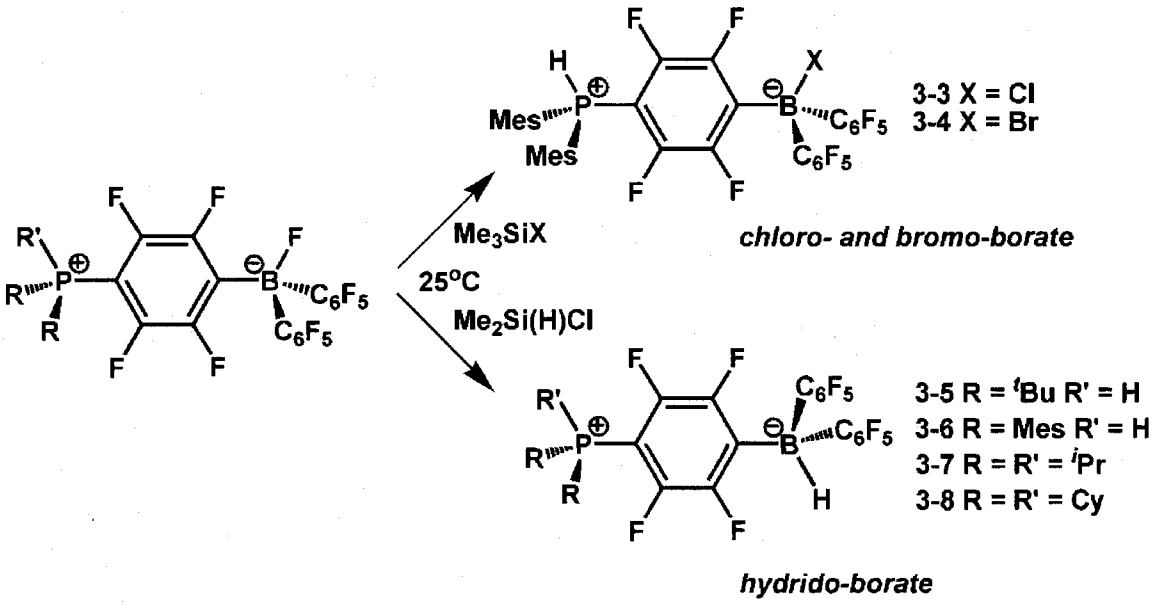
Figure 3.3 POV-ray depictions of (left) **3-1**, (right) **3-16**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Nitrogen: blue. Carbon hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **3-16** P(1)-N(4) 1.634(2), N(4)-H 0.90(4) and 0.84(4), P(1)-C(16) 1.826(2), B(1)-N(1) 1.591(3), N(1)-N(2) 1.210(3), N(2)-N(3) 1.135(3), B(1)-C(13) 1.648(3), B(1)-N(1)-N(2) 118.43(19), N(1)-N(2)-N(3) 175.9(3), B(1)-N(1)-N(2)-N(3) 176(4).

The azide unit is slightly bent with N(1)-N(2)-N(3) equal to 175.9(3)° which is typical for covalent azides and the bent B-N_3 orientation (B1-N1-N2 = 118.43(19)°) is common for all azidoborates.[205-213] The substituents at phosphorus are arranged in a distorted tetrahedral fashion with average C-P-C and C-P-N bond angles of 112.37° and 106.48°, respectively. The P(1)-N(4) bond distance of 1.634(2) Å fits within the range for similarly reported phosphinimonium cations[214, 215] and is closer to the ideal P-N double bond distance (1.57 Å) than the ideal P-N single bond distance (1.76 Å).[216] The remaining metrical parameters are unexceptional. Due to the formation of **3-16** it is apparent that oxidation of phosphorus is competitive with F for N_3 exchange. It is likely that water was present during the course of the reaction hydrolyzing the trimethylsilyl group after oxidation of phosphorus. Protonation of the resulting phosphinimine (P=NH) by trace

water gives a phosphinimonium cation and a hydroxyl anion. It is assumed the latter pairs with the proton sponge ammonium cation giving the ion pair $[C_{10}H_6(NMe_2)_2H][OH]$. Although a phosphinimine was not obtained, this result demonstrates that the present phosphine is capable of oxidation, thus there exists the possibility to synthesize anionic phosphinimines, provided there is suitable protection of the borate, which may prove useful as ancillary ligands for the generation of metal catalysts.

3.3.1.2 Fluorine Exchange

The B-F moiety of the phosphonium borates described can be modified to give both chloro and bromo derivatives. Treatment of the *bis*-mesityl compound **2-5** with Me_3SiCl or Me_3SiBr in solution gave the zwitterions $Mes_2PH(C_6F_4)BX(C_6F_5)_2$ (X = Cl **3-3**, Br **3-4**, respectively) which exist as air and moisture stable off-white solids (Scheme 3.3). The ^{19}F NMR spectra of **3-3** and **3-4** shows loss of the B-F resonances while the ^{11}B NMR spectra give singlets at -6.7 and -11.5 ppm, respectively. The upfield shift of the ^{11}B NMR resonances compared to **2-5** (δ = 0.4 ppm) is consistent with a greater electron density on boron as a consequnce of the weaker electron withdrawing abilty of Cl and Br vs. F, and additionally due to a decrease in p-type orbital overlap between B and halide going from F to Br.[217] The remaining NMR spectra of **3-3** and **3-4** are similar to those of **2-5**. The connectivies of **3-3** and **3-4** were confimed by X-ray crystallography (Table 3.2) and are shown as POV-ray depictions in Figure 3.4. The geometries are similar to those of the phosphonium borates discussed previously.



Scheme 3.3 Synthesis of phosphonium chloro-, bromo-, and hydrido-borates.

As expected, the B-Cl (1.921(5) Å) and B-Br (2.118(5) Å) bond lengths are significantly longer than the average B-F (ca. 1.439 Å) bond distances and compare well to those reported for the anions $ClB(C_6F_5)_3$[218, 219] and $BrB(CF_3)_3$.[220] In a similar fashion, hydrido borate derivates can be readily synthesized upon treament with silane. Compound **2-4** rapidly reacts with Me_2SiHCl to effect H for F exchange at boron, generating $^tBu_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-5**) as an air- and moisture-stable white solid (Scheme 3.3), although slow hydrolysis of the B-H bond is observed over extended periods of time in solution. The NMR spectra of **3-5** are similar to those of **2-4** (Table 3.1) The replacement of the B-F with a B-H fragment is verified by the doublet resonance ($^1J_{B\text{-}H}$ = 100 Hz) in the ^{11}B NMR spectrum at -25 ppm and appearance of a broad quartet in the range of 3.6 to 3.4 ppm in the ^1H NMR spectrum.

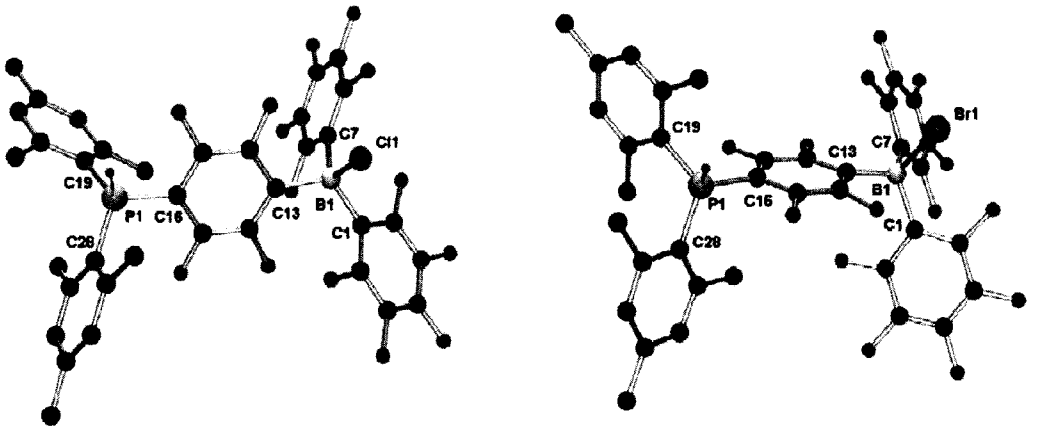


Figure 3.4 POV-ray depictions of (left) **3-3**, (right) **3-4**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Chlorine: green, Bromine: brown. Carbon hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **3-3**: P(1)-H 1.27(3), P(1)-C(19) 1.796(4), P(1)-C(28) 1.795(4), P(1)-C(16) 1.798(4), B(1)-C(13) 1.654(6), B(1)-C(1) 1.638(7), B(1)-C(7) 1.624(7), B(1)-Cl(1) 1.921(5), C(19)-P(1)-C(28) 118.32(18), C(13)-B(1)-C(7) 118.2(4), C(13)-B(1)-Cl(1) 105.6(3). **3-4** P(1)-H 1.21(6), P(1)-C(19) 1.796(4), P(1)-C(28) 1.789(4), P(1)-C(16) 1.793(4), B(1)-C(13) 1.634(6), B(1)-C(1) 1.648(6), B(1)-C(7) 1.630(6), B(1)-Br(1) 2.118(5), C(19)-P(1)-C(28) 116.5(2), C(13)-B(1)-C(7) 117.2(3), C(13)-B(1)-Br(1) 103.4(3).

The upfield shift of the ^{11}B NMR resonance compared to the F, Cl, and Br derivatives follows the observation that as the electronegativity of the subsituent at boron decreases, greater electron density is put on boron, resulting in increased chemical shielding of the ^{11}B nuclei, hence an upfield chemical shift. As mentioned previously, weaker p-type orbital overlap between B and H also contributes to the upfield chemical shift. This weaker orbital overlap is also relfected in the BH coupling constant, which is larger than the BF coupling constant, ($^1J_{B\text{-}H}$ = 100 Hz vs $^1J_{B\text{-}F}$ = 60 Hz) due to greater s-character in the former. The structure of compound **3-5** was confirmed by X-ray crystallography (Figure 3.5, Table 3.3) and has a comparable geometry to the parent fluoroborate derivative **2-4**.

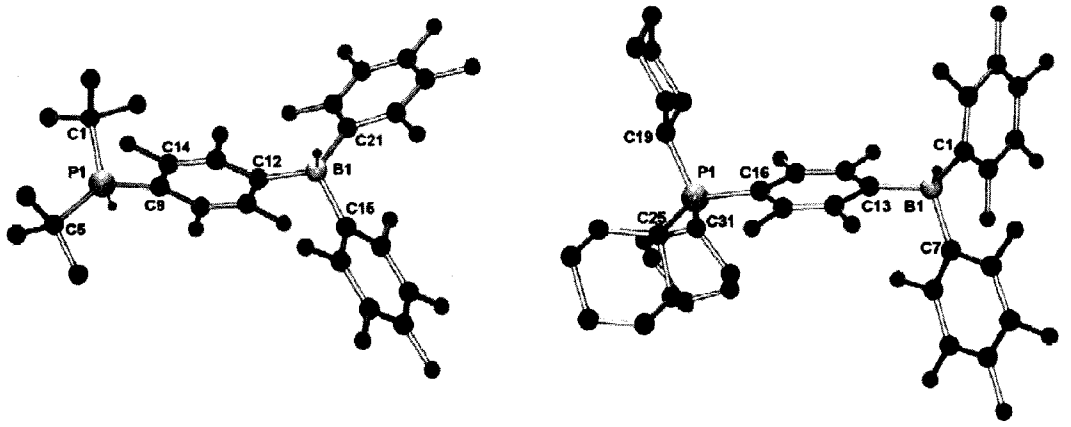


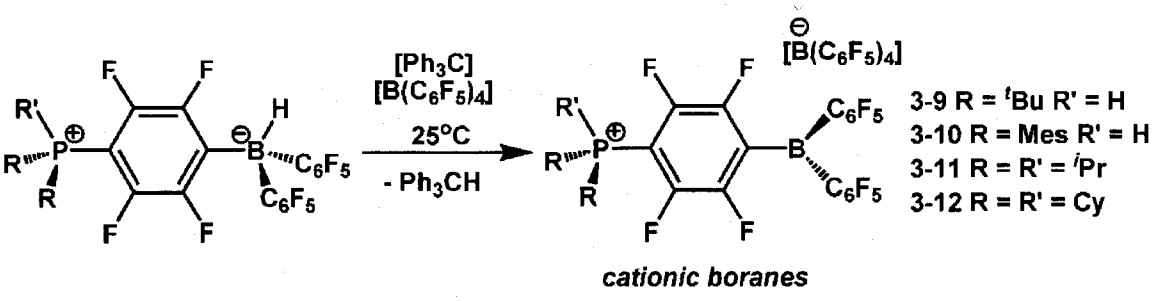
Figure 3.5 POV-ray depiction of (left) **3-5**, (right) **3-8**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green. Carbon hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **3-5**: P(1)-H 1.23(3), P(1)-C(1) 1.840(4), P(1)-C(5) 1.846(4), P(1)-C(9) 1.793(3), B(1)-C(12) 1.642(5), B(1)-C(15) 1.641(6), B(1)-C(21) 1.624(6), B(1)-H 1.19(3), C(9)-P(1)-C(1) 110.37(16), C(12)-B(1)-C(15) 112.7(3), C(21)-B(1)-C(15) 111.3(3). **3-8** P(1)-C(19) 1.813(4), P(1)-C(25) 1.831(4), P(1)-C(31) 1.823(4), P(1)-C(16) 1.825(3), B(1)-C(13) 1.642(5), B(1)-C(1) 1.648(6), B(1)-C(7) 1.628(5), B(1)-H 0.98, C(19)-P(1)-C(25) 109.5(2), C(13)-B(1)-C(7) 109.8(3), C(1)-B(1)-C(7) 112.4(3).

The PH and BH moieties are oriented trans to each other and the molecule packs in a offset head-to-tail fashion with the shortest intermolecular PH...HB distance found to be 2.60(2) Å. This distance is too long for the BH and PH fragments to be considered hydrogen bonded,[221] although the distance is overestimated as the H positions were located on the electron density map and were not standarized to vaules determined by neutron diffraction.[122] Short intramolecular contacts also exist between the *ortho*-fluorines of the C_6F_4 bridge and the PH and CH hydrogens. In a similar fashion, the hydrido borate compounds $R_2PH(C_6F_4)BH(C_6F_5)_2$ (R = Mes **3-6**) and $R_3P(C_6F_4)BH(C_6F_5)_2$ (R = ^{i}Pr **3-7**, R = Cy **3-8**) were synthesized (Scheme 3.3) and fully

characterized by multi-nuclear NMR spectroscopy, EA, and X-ray crystallography (Tables 3.1, 3.3, 3.4). A POV-ray depiction of **3-7** is shown in Figure 3.4. The hydridoborate derivates **3-5** and **3-6** are interesting compounds, as they have been shown to liberate dihydrogen. This chemistry is discussed in Chapter 5.

3.3.1.3 Cationic Phosphonium Boranes

Addition of the hydride abstractor $[Ph_3C][B(C_6F_5)_4]$ to compunds **3-5** to **3-8** provides direct high yield access to the cationic boranes $[(R_2PH)(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ (R = ^{t}Bu **3-9**, Mes **3-10**) and $[(R_3P)(C_6F_4)B(C_6F_5)_2][B(C_6F_5)_4]$ (R = ^{i}Pr **3-11**, Cy **3-12**) (Scheme 3.4). While much of the NMR spectroscopy of **3-9** to **3-12** is similar to the corresponding precursors **3-5** to **3-8** (Table 3.1), the most notable difference is the presence of a ^{11}B NMR resonance at approximately -17 ppm due to the anion $[B(C_6F_5)_4)]^-$ and the absence of the signal in the ^{11}B NMR spectra corresponding to a BH fragment (Table 3.1). In addition, a peak at 5.7 ppm for Ph_3CH is readily observed in the ^{1}H NMR of the reaction mixture. The ^{11}B NMR resonances for the three coordinate B-center of the cations were broadened into the baseline, due to the chemical shielding anisotropy of the 3-coordinate quadrupolar ^{11}B nucleus, and thus were not reported. In addition, the ^{19}F NMR peaks of the C_6F_5 units revealed gaps between *meta* and *para* F-resonances consistent with the presence of both borane and borate fragments (Figure 3.6), establishing **3-9** to **3-12** as borate salts of cationic boranes. It is noteworthy that no interaction of the very weakly coordinating $[B(C_6F_5)_4]^-$ anion[222] with the corresponding cations in **3-9** to **3-12** was detected by NMR methods in aromatic and chloroalkane solvents.



Scheme 3.4 Synthesis of cationic boranes.

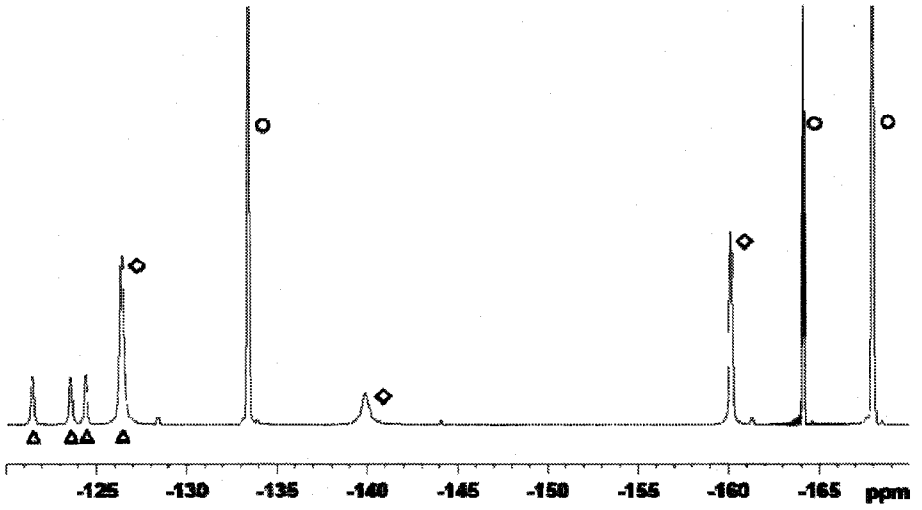
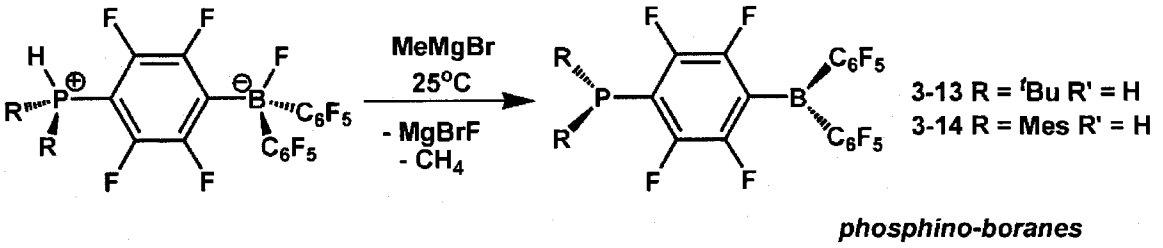


Figure 3.6 ^{19}F NMR spectrum of **3-9** [$^{t}Bu_2PH(C_6F_4)B(C_6F_5)_2$][$B(C_6F_5)_4$] O = C_6F_5 borate, Δ = C_6F_4 cationic borane, ◊ = C_6F_5 cationic borane.

Recently, Gabbai *et al.* have synthesized structurally related non-fluorinated cationic boranes which have been shown to be effective fluoride ion acceptors.[223-227] In each the case the incorperation of an R_3N^+ or a R_3P^+ moiety into the $RBMes_2$ framework, greatly enhances the Lewis acidity of the 3-coordinate boron center.

3.3.1.4 Phosphino-Boranes

The reaction of the phosphonium fluoroborates **2-4** or **2-5** with the Grignard reagent MeMgBr, results in the isolation of yellow and orange solids **3-13** and **3-14** in 56% and 82% yield, respectively (Scheme 3.5). The ^{1}H and ^{19}F NMR data confirmed the formal loss of HF to give the neutral species $R_2P(C_6F_4)B(C_6F_5)_2$ (R = ^{t}Bu **3-13**, Mes **3-14**) (Table 3.1) The ^{31}P NMR spectrum of **3-13** at 25 °C shows a signal coupled to four inequivalent F-atoms, while the ^{19}F NMR spectrum gives rise to four distinct fluorine atoms from the C_6F_4 fragment.



Scheme 3.5 Synthesis of phosphino-boranes.

These observations suggest inhibited rotation about the P-C_{ArF} bond similar to that observed in **2-4** and **3-1**. Heating to 150 °C resulted in a broadening of the NMR signals, but coupling to chemically equivalent F-atoms was not observed, consistent with a relatively high barrier to rotation. In contrast, evaluation of the parameters for a similar fluxional process was possible for **3-14**. The $^{31}P\{^{1}H\}$ NMR spectrum at 25 °C revealed a resonance coupled to two equivalent F-atoms while the corresponding ^{19}F NMR spectrum showed two broad signals attributable to the C_6F_4 ring. Upon cooling to -70 °C the ^{31}P NMR signal splits into a doublet of doublets (Figure 3.7) while the corresponding ^{19}F

NMR signals split into doublets. These observations are consistent with the change from a AA'BB'X to a ABCDX spin system resulting from slowed rotation about the P-C_{ArF} bond at low temperatures. A similar observation was made by Erker and coworkers[93] for the species $(Ph_3PC(H)Ph)(C_6F_4)BF(C_6F_5)_2$ mentioned in chapter 2. The barrier to rotation, $\Delta G^{\ddagger}$ (25°C), was found to be 44.8(3) kJ/mol using dynamic NMR simulation.[228]

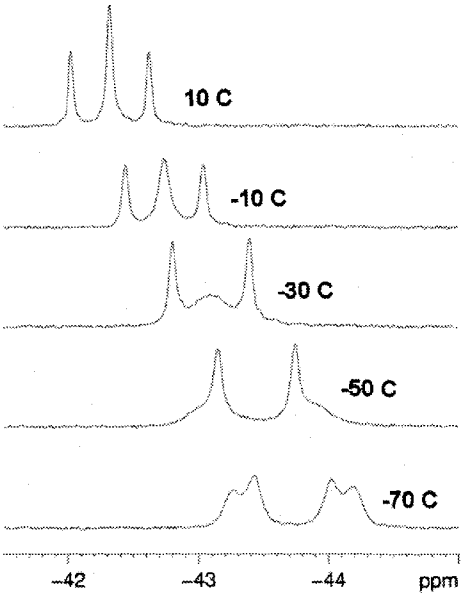


Figure 3.7 Variable-temperature $^{31}P\{^1H\}$ NMR of **3-14**. Spectra collected on a 300 MHz spectrometer. All temperatures in degress Celcius.

The corresponding barriers to P-C_{ArF} bond rotation for **3-2**, **3-10** and **2-5** were determined in a similar fashion to be 46.7(2), 52.2(1), and 52.4(3) kJ/mol, respectively, and are summarized in Table 3.6. The higher barriers to P-C_{ArF} bond rotation **3-10** and **2-5** compared to **3-2** and **3-14** can be attributed to the presence of intramolecular PH...FC interactions in the latter. This view is supported by the average close approach of the P-H proton to the *ortho*-F of the C_6F_4 linker (2.55 Å) noted in the crystal structures of **3-3**, **3-4**, and **3-6**.

Table 3.6 Barrier to rotation about the P-C_{ArF} bond of a phosphonium borate, anionic phosphine borate, cationic borane, and phosphino-borane. X = $[B(C_6F_5)_4]^-$ A = $[C_{10}H_6(NMe_2)_2H]^+$.

Compound	$\Delta G^{\ddagger}$ (25°C)
2-5 $Mes_2PH(C_6F_4)BF(C_6F_5)_2$	52.4(3)
3-10 $[Mes_2PH(C_6F_4)B(C_6F_5)_2][X]$	52.2(1)
3-2 $[Mes_2P(C_6F_4)BF(C_6F_5)_2][A]$	46.7(2)
3-14 $Mes_2P(C_6F_4)B(C_6F_5)_2$	44.8(3)

Related N-H...F-C interactions were responsible for restricted rotation in a number of amine-$B(C_6F_5)_3$ adducts.[229] It is also readily apparent that solutions of compounds **3-13** or **3-14** show no sign of aggregation via phosphorus donation to boron, even upon cooling to -77 °C in CD_2Cl_2. Accordingly, the difference in ^{19}F NMR chemical shift between the *ortho-* and *meta*-fluorine atoms of the C_6F_5 fragments on B are > 17 ppm in each case, indicative of neutral 3-coordinate boron.[128, 129, 133, 230-232] Thus, compounds **3-13** and **3-14** are also appropriately described as FLPs as the steric congestion about both the acidic and basic centers precludes traditional Lewis acid-base adduct formation. Of note is that the phosphino-boranes **3-13** and **3-14** are yellow and orange in color, respectively. Weak π-donation from phosphorus and electron acceptance by boron has been proposed for the related acetylene based phosphino-borane $Ph_2P(CC)BMes_2$[233] thus, on the basis of the intense colors of **3-13** and **3-14** in solution (λ_{max} = 373 nm **3-13**, λ_{max} = 455 nm **3-14**), it is tempting to attribute this color to an intramolecular charge transfer. The $^{31}P\{^1H\}$ NMR chemical shift for both complexes showed minimal change with temperature, an observation consistent with the persistence of a pyramidal geometry at phosphorus. Nonetheless, polarization of charge in this donor-acceptor molecule may account for the observed color.

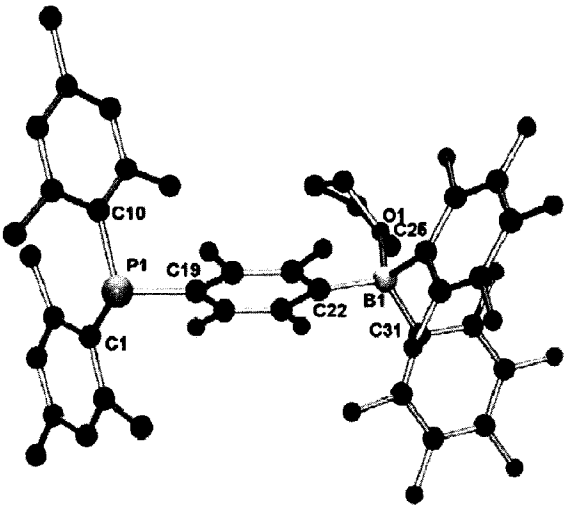
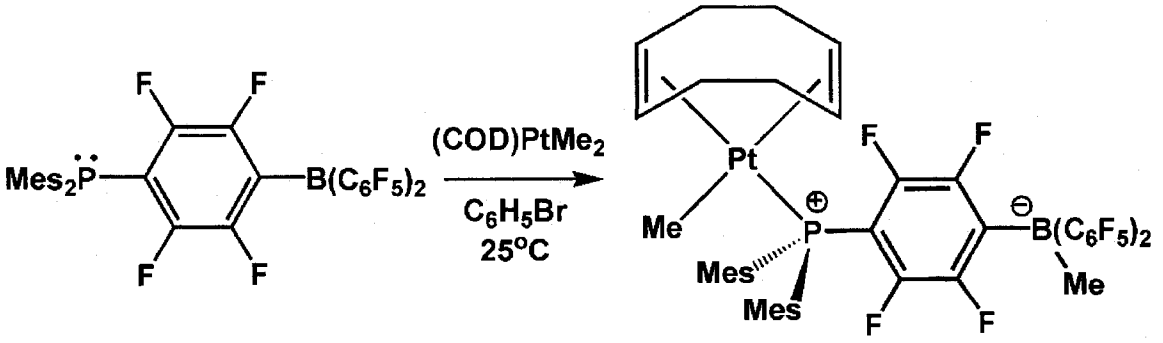


Figure 3.8 POV-ray depiction of **3-14**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Oxygen: Red, Platinum: Silver. Carbon hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **3-14**: P(1)-C(1) 1.837(3), P(1)-C(10) 1.840(3), P(1)-C(19) 1.847(2), B(1)-C(22) 1.631(3), B(1)-C(31) 1.634(3), B(1)-C(25) 1.639(4), B(1)-O(1) 1.625(3), C(1)-P(1)-C(10) 112.6(2), C(22)-B(1)-C(25) 114.4(2), C(22)-B(1)-O(1) 103.6(2).

Additionally, coordination of Lewis bases to boron rendered both species colorless. Attempts to obtain X-ray quality crystals of **3-13** and **3-14** were unsuccesful, although dissolution of **3-13** in THF gave the base coordinated compound **3-15** which readily crystallized. The ^{31}P NMR resonance of **3-15** is similar to that observed for **3-14** (Table 3.1), while the upfield shifted ^{11}B and ^{19}F NMR resonances are consistent with quaternization at boron. The solid state structure is shown in Figure 3.8 and confirms the formulation of **3-15** as $R_2P(C_6F_4)B(C_6F_5)_2(THF)$. As expected, the geometry at phosphorus is pyramidal, while the boron center is pseudo-tetrahedral. The remaining metrical parameters are unexpectional. The structurally related phosphino-borane *para*-$Ph_2P(C_6H_4)B(Mes)_2$ has previously been reported by Marder *et al.* This compound was synthesized *via* conventional methods and exhibits unique electronic properties.[233]

Attempts were made to synthesize compounds **3-13** and **3-14** directy from $B(C_6F_5)_3$ using phosphides. Unfortunately the reaction of $^tBu_2PLi$ or Mes_2PLi with $B(C_6F_5)_3$ at -35 °C or 25 °C produced a mixture of products. Resonances in the ^{31}P, ^{19}F, and ^{11}B NMR spectra indicated possible formation of $[(R_2P)B(C_6F_5)_3][Li]$, $[R_2P(C_6F_4)BF(C_6F_5)_2][Li]$, and $R_2P(C_6F_4)B(C_6F_5)_2$ with loss of LiF. It is apparent that the strong nucleophilic character of the phosphides opens several different reaction pathways that cannot be easily controlled.

The phosphino-boranes **3-13** and **3-14** are ambiphilic in nature as they contain a donor phosphine moiety and an acceptor borane moiety. Ambiphilic compounds are known in the literature[234] but their use as ligands in metal catalysis has not widely been explored. Several reports in the early 1980's described the coordination of aluminoamino-phosphines to transition metals[235-238] while recent studies have seen the use of both phosphino-borane[239-248] and -alane[249, 250] species as ligands for transition metal centers. In each case the Lewis acidic site abstracts an anionic ligand, while the Lewis basic site acts as a neutral electron donor.



Scheme 3.6 Activation of $(COD)PtMe_2$ by the phosphino-borane **3-14** to give **3-17**.

To probe the ability of the present phosphino-boranes to act as ambiphilic ligands, reaction of **3-14** with platinum dialkyls was probed. A orange bromobenzene solution of **3-14** was added to one equivalent of (COD)$PtMe_2$ at 25 °C. Immediate loss of color was observed. The ^{31}P NMR spectrum revealed a downfield shifted doublet resonace at -11.3 ppm with a ^{31}P-^{195}Pt coupling constant of 3831 Hz. The large coupling constant is consistent with phosphorus coordination to platinum.[157] The ^{11}B NMR resonance at -15 ppm along with a gap between the *meta* and *para* resonances in the ^{19}F NMR of 2.9 ppm is indicative of methyl abstraction by boron and formation of a methyl borate. The ^{1}H NMR shows resonances for the mesityl groups, while resonances attributed to cycloctadiene were slightly broadened. The platinum- and boron-methyl groups displayed chemical shifts at 0.44 and 1.25, respectively. The ^{19}F NMR spectrum also gives rise to four separate resonances for the fluorines of the C_6F_4 bridge, which indicated restricted rotation about the P-C_6F_4 bond not seen in the starting compound **3-14** or the parent phosphonium borate **2-5**. From the NMR data, the product of the reaction between **3-14** and (COD)$PtMe_2$ was formulated as the zwitterion (COD)Pt(Me)($Mes_2P(C_6F_4)BMe(C_6F_5)_2$ **3-17** (Scheme 3.6). The product is generated by methyl abstraction by boron yielding a cationic Pt center which is subsequently coordinated by phosphine. The solid-state structure of **3-17** was determined by X-ray crystallography (Table 3.5) and is shown in Figure 3.9. The X-ray analysis confirms the zwitterionic nature of **3-17** with the presence of an anionic methyl borate moiety and a phosphine-stabilized cationic platinum center. The geometry about platinum is distorted square planar while that of phosphorus and boron is pseudo-tetrahedral. The Pt(1)-P(1) bond length of 2.348(4) Å is typical for related phosphorus-platinum complexes.[158, 242]

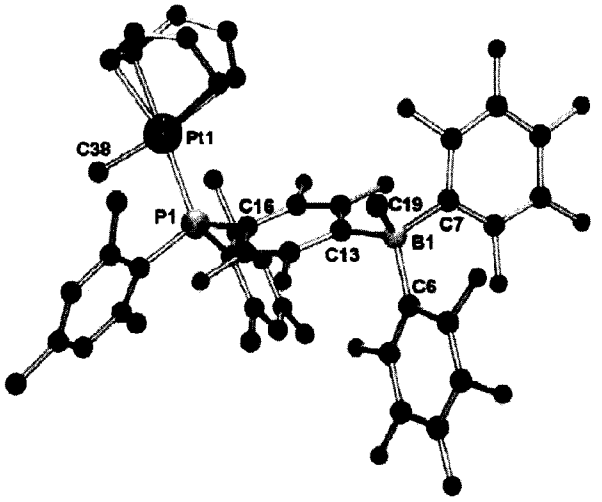


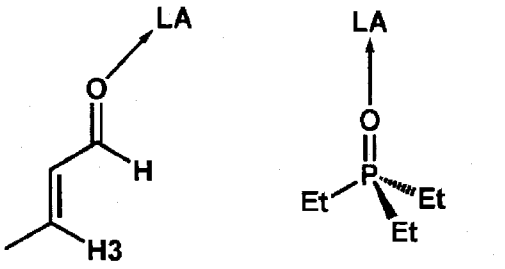
Figure 3.9 POV-ray depiction of **3-17**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Oxygen: Red, Platinum: Silver. Carbon hydrogen atoms omitted for clarity. Selected metrical parameters {distances (Å), angles (°)}: **3-17** P(1)-Pt(1) 2.348(4), P(1)-C(16) 1.866(15), Pt(1)-C(38) 2.111(8), B(1)-C(13) 1.69(2), B(1)-C(19) 1.61(3), B(1)-C(7) 1.66(3), B(1)-C(6) 1.64(2), C(38)-Pt(1)-P(1) 86.1(5), Pt(1)-P(1)-C(16) 112.0(5), C(13)-B(1)-C(19) 109.3(13), C(6)-B(1)-C(7) 110.7(14).

Addition of a second equivalent of **3-14** to **3-17** did not result in a second methyl abstraction or displacement of the cycloctadiene ligand. The formation of **3-17** demonstrates the ability of the present phosphino-boranes to act as ambiphilic ligands. This reactivity has the potential to lead to the development of a family of novel zwitterionic metal catalysts capable of C-H bond activation.[157, 158]

3.3.2 Lewis Acidity Determination

Lewis acid strength has been shown to linearly correlate with rate of catalyzed reactions in certain cases, providing the potential to predict reactivity.[193, 251] However, issues such as methodology, solvent effects and steric factors makes the construction of

an absolute Lewis acidity scale problematic.[252] Nevertheless, a number of methods to assess relative Lewis acidities, including calorimetry,[164, 194, 253, 254] reactivity[255, 256] and spectroscopic investigations[257, 258] have been developed. For fluoroarylboranes, two NMR-based methods are commonly used. Gutmann's acceptor number (AN)[259, 260] for scaling solvent polarity has been modified by Beckett *et al.*[193, 261] and further employed by Britovsek *et al.*[141] to rank the acidity of some boron-based Lewis acids (Scheme 3.6). Here, the differences in the ^{31}P NMR chemical shift of Et_3PO vs. that of the Lewis acid adduct is employed to rank the relative strength of the acids.[262] A second method, developed by Childs *et al.*[263] and computationally investigated by Laszlo,[264] utilizes crotonaldehyde as the probe and the scale is based on the relative shift of the H3- or β-proton upon Lewis acid complexation.



Childs ***Gutmann/Beckett***

Scheme 3.7 Basis of Childs and Gutmann-Beckett Lewis acidity tests.

Notably, this site is sterically remote from the locus of complexation, but electronically connected via unsaturation (Scheme 3.7). A number of groups have utilized either the Childs or Gutmann/Beckett tests to investigate the Lewis acidity of boranes and the relative scaling has been shown to predict reactivity[193, 251] or shed light on mechanistic features in catalysis.[138] In addition to these methods, equilibrium constants for

competition experiments have been used to directly compare the acidity of fluoroaryl boranes,[128, 129, 168, 173] but in such cases, the nature of the coordinating atom and the sterics of the Lewis basic probe can have an unpredictable or unexpected influence on the relative rankings.[128, 129, 141, 261]

Herein, both the Childs and Gutmann/Beckett methods have been employed both to rank the Lewis acidity of the cationic phosphonium-boranes **3-9** to **3-12** and neutral phosphino-boranes **3-13** and **3-14** relative to the parent $B(C_6F_5)_3$. The Childs test consisted of a 1:1 acid-crotonaldehyde solution in CD_2Cl_2 at -20°C while the Gutmann/Beckett test was performed with a 3:1 acid-Et_3PO ratio in CD_2Cl_2 solvent. Of note is that our values obtained for $B(C_6F_5)_3$ in both tests are essentially identical to the reported literature values.[141, 173, 265-267] All cationic complexes **3-9** to **3-12** were found to be stronger Lewis acids than $B(C_6F_5)_3$ via both methods. This is in line with the expected greater electron withdrawing effect of a cationic phosphonium group versus a fluorine atom. This was further verified by a competition study between the zwitterionic phosphonium hydridoborates **3-7** and **3-8** with $B(C_6F_5)_3$. In these cases, equimolar mixtures of **3-7** and **3-8** with $B(C_6F_5)_3$ in C_6D_5Br showed no evidence of hydride migration to $B(C_6F_5)_3$ by multi-nuclear NMR spectroscopy, even upon prolonged (16 h) heating to 110 °C. This affirms that B centers in **3-9** to **3-12** are markedly more Lewis acidic than that in $B(C_6F_5)_3$ (Figure 3.10). Conversely, the neutral phosphino-boranes **3-13** and **3-14** exhibited reduced Lewis acidity compared to $B(C_6F_5)_3$ using both methods (Figure 3.10). No accurate Childs' acidity measurement was obtained for **3-13**, as reaction with crotonaldehyde was rapid at −80 °C while for **3-14** warming above 0 °C resulted in degradation of the Lewis acid–crotonaldehyde adduct.

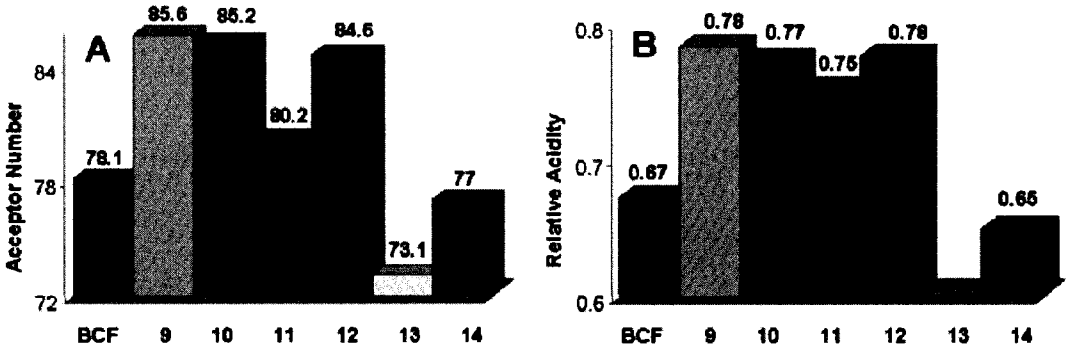


Figure 3.10 (**A**) Plot of the Gutmann acceptor number and (**B**) relative acidity (to BBr_3) as determined by the Childs method for BCF ($B(C_6F_5)_3$), cationic phosphonium boranes **3-9** to **3-12** and phosphino-boranes **3-13** and **3-14** (NB: in (B) the relative acidity of **3-13** was not determined).

This is thought to be due to an intermolecular nucleophilic attack of a P-center on the Lewis acid activated α,β-unsaturated ketone. Nonetheless, the reduced Lewis acidity is consistent with donation of the P-based lone pair into the π-system diminishing the acidity of the B center. While minor variations in the relative rankings were observed, the general trends were consistent between the methods. Similar to Beckett[193] a direct correlation between the AN values and the Childs ranking of the Lewis acids was observed for **3-9** to **3-14** and $B(C_6F_5)_3$. This stands in stark contrast to the series of boranes $B(C_6F_5)_n(OC_6F_5)_{3-n}$ where these tests gave conflicting trends.[141] The fact that the observed data parallels between the Gutmann/Beckett and Childs methods in the present Lewis acids **3-9** to **3-14** is attributable to the presence of only B-C bonds, the essentially unchanged steric environment about boron, and the variation in Lewis acidity arising from electronic changes made remote to the boron center. The relative Lewis acidities as determined by Childs method for **3-9** to **3-14** are compared to related Lewis acids in

Table 3.7. From the table it is apparent that the electron-withdrawing nature of the phosphonium moiety has a greater impact on the Lewis acidity at boron than electron donation from the phosphine moiety. Of note, phosphonium cations have recently been employed to modify the Lewis acidity of dibenzophosphaborin complexes.[268]

Table 3.7 Comparison of the Lewis acidity of compounds **3-10** to **3-14** to related Lewis acids reported in the literature.

Lewis acid	Childs Ranking	Lewis acid	Childs Ranking
BPh_3[141]	0.34	**3-11**	0.75
$AlEt_3$[139]	0.42	**3-10**	0.77
$PhB(C_6F_5)_2$[138]	0.54	**3-9**	0.78
$MeB(C_6F_5)_2$[269]	0.56	**3-12**	0.78
$MeB(C_{12}F_8)$[269]	0.64	PNB[270,*]	0.79
$(C_6F_5O)B(C_6F_5)_2$[141]	0.64	PBB[270,*]	0.85
3-13	0.65	$AlCl_3$[139]	0.82
$B(C_6F_5)_3$	0.67	BCl_3[139]	0.93
$(C_6F_5)B(C_{12}F_8)$[269]	0.70	BBr_3[139]	1.00

* Marks *et al.* reported a value of 0.77 for $B(C_6F_5)_3$ on the Childs scale, therefore the reported values for PNB and PBB may be overestimated. PNB = *tris*-(*β*-perfluoronaphthyl)borane, PBB = *tris*-(2,2',2'' perfluorobiphenyl)borane

3.4 Summary and Conclusion

In summary, phosphonium borates of the form $R_2PH(C_6F_4)BF(C_6F_5)_2$ (R = aryl or alkyl) are readily converted into anionic phosphonium borates or phosphino-boranes via facile one-step reactions. Both types of compounds offer the potential to act as phosphine ligands for transtion metals. Additionally, novel cationic phosphonium boranes are easily

synthesized from the parent compunds $R_2PH(C_6F_4)BF(C_6F_5)_2$ and $R_3P(C_6F_4)BF(C_6F_5)_2$ (R = aryl or alkyl) in a simple two step procedure. Lewis acidity tests confirmed that the cationic phosphonium-boranes are significantly more Lewis acidic than the parent borane $B(C_6F_5)_3$ while the neutral phosphino-boranes are somewhat less Lewis acidic than the $B(C_6F_5)_3$, thus this synthetic approach affords a simple means to tune the Lewis acidity of $B(C_6F_5)_3$ without a significant impact on the steric environment at boron. Both the phosphino-boranes and cationic phosphonium boranes have potential uses as Lewis acid catalysts for organic transformations.[24]

Chapter 4 FLP's and the Controlled Ring Opening of Tetrahydrofuran

4.1 Introduction

Ring opening reactions of tetrahydrofuran (THF) mediated by Lewis acidic metal centers including complexes of U,[271, 272] Sm,[273] [274]Lu,[275] La,[276] Nd,[276] Tm,[276] Y,[277] Ti, [278] Zr,[279-281] and Fe [282]are well known and have been described in the literature. In contrast, ring opening with main-group Lewis acids are less common. A boron center in a Mn-carborane complex was shown to promote THF ring opening in reactions with either PPh_3 or NEt_3.[283] Campbell and Gladfelter reported ring opening in reactions of an amine-alane adduct in THF,[284] while Letinen has reported the ring opening of THF upon treatment of $TeBr_4$ with PPh_3 in THF.[285, 286] The use of highly reducing Li reagents in the presence of BF_3 to ring open THF has also been reported.[287, 288] More recently Chivers and Schatte have reported that THF ring opening occurs in the reaction of a Te-diimide dimer with $B(C_6F_5)_3$.[289]

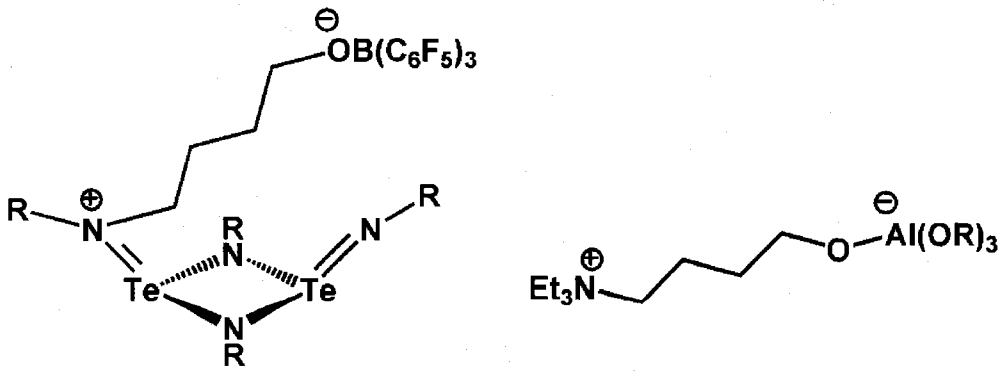


Figure 4A Examples of THF ring opening with main group compounds.

While often the isolation of these ring-opened products was not anticipated, the now numerous examples suggests the possibility that such reactions could be used in a controlled manner. The ability for sterically 'frustrated' Lewis acids and bases to undergo reactivity alternate to simple adduct formation prompted us to consider the reactions of THF and phosphorus-based nucleophiles in the presence of a Lewis acid. To that end, we have probed reactions of the Lewis acid-base adduct $(THF)B(C_6F_5)_3$ with sterically demanding phosphines and phosphides. Herein we demonstrate that such reactions effect the facile, and quantitative ring-opening of THF affording synthetic routes to zwitterionic phosphonium-borates and their corresponding lithium salts. Alternatively, these reactions can be done in tandem to provide lithium salts of phosphonium-diborate ligands. Such products have potential applications as ancillary ligands for transition metals and co-catalysts for the polymerization of olefins.

4.2 Experimental

4.2.1 General Data

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents (pentane, hexanes, toluene, and methylene chloride) were purified employing a Grubbs' type column system manufactured by Innovative Technology and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 °C under vacuum for 24 hours prior to use. Uninhibited THF was purchased from EMD and distilled from

sodium/benzophenone prior to use. Deuterated solvents were dried over sodium/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br). All common organic reagents were purified by conventional methods unless otherwise noted. ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer at 300 K unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR experiments were referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. $B(C_6F_5)_3$ was generously donated by NOVA Chemicals Corporation. Et_3P, Cy_3P, Cy_2PH, $^tBu_2PH$, and Ph_2PH were purchased from Aldrich Chemical Company and used as received. Mes_2PH was prepared as reported in the literature.[290] Mes_2PLi, $^tBu_2PLi$, and Ph_2PLi were prepared by treating the corresponding phosphine with 1 equivalent of ^{n}BuLi in toluene and collecting the precipitate. In each reaction, fresh solutions of $B(C_6F_5)_3$ and THF were prepared and used immediately as Lewis acids are known to facilitate the polymerization of THF.[289, 291]

4.2.2 Synthesis of Phosphonium Alkoxyborate Zwitterions

$(Mes)_2PH(C_4H_8O)B(C_6F_5)_3$ (4-1): To a faint yellow solution of $B(C_6F_5)_3$ (0.379 g, 0.741 mmol) in toluene (2 mL) was added THF (0.12 mL, 1.48 mmol). Dimesityl phosphine (0.200 g, 0.741 mmol) in toluene (2 mL) was added and the reaction mixture was left to stir for 72 hours at room temperature. All volatiles were removed *in vacuo* and the resulting solid was dried under vacuum for 48 hours. The final product was a tan solid.

Yield 0.497 g (79 %). Crystals suitable for X-ray diffraction were grown from a concentrated solution of product in C_6D_6 at 25 °C. **^{1}H NMR** (C_6D_6): δ 7.33 (dt, 1H, $^1J_{H\text{-}P}$ = 531 Hz, $^3J_{H\text{-}H}$ = 7 Hz, P*H*), 6.40 (d, $^4J_{H\text{-}P}$ = 4 Hz, 4H, P(C_6H_2)$_2$), 3.48 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 2.85 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.90 (s, 6H, P(C_6H_2*Me-4*)$_2$), 1.87 (s, 12H, P(C_6H_2*Me-2,6*)$_2$), 1.62 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.23 (m, 2H, $PCH_2CH_2CH_2CH_2O$). **^{11}B NMR** (C_6D_6): δ -2.79 (s). **^{13}C{^{1}H} NMR** (C_6D_6): δ 149.04 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *C*F), 146.12 (s, *para*-C_6H_2), 143.36 (d, $^2J_{C\text{-}P}$ = 11 Hz, *C*F), 139.28 (dm, $^1J_{C\text{-}F}$ = 252 Hz, *C*F), 137.52 (dm, $^1J_{C\text{-}F}$ = 257 Hz, *C*F), 132.21 (d, $^2J_{C\text{-}P}$ = 11 Hz, *meta*-C_6H_2), 125.03 (quaternary, C_6F_5), 112.07 (d, $^1J_{C\text{-}P}$ = 80 Hz, quaternary, C_6H_2), 65.56 (s, $PCH_2CH_2CH_2CH_2O$), 30.94 (s, $PCH_2CH_2CH_2CH_2O$), 24.88 (d, $^1J_{C\text{-}P}$ = 58 Hz, $PCH_2CH_2CH_2CH_2O$), 23.95 (s, $PCH_2CH_2CH_2CH_2O$), 21.80 (d, $^3J_{C\text{-}P}$ = 8 Hz, C_6H_2*Me-2,6*), 21.14 (s, C_6H_2*Me-4*). **^{19}F NMR** (C_6D_6): δ -133.94 (d, $^3J_{F\text{-}F}$ = 23 Hz, 6F, *ortho*-C_6F_5), -162.16 (s, 3F, *para*-C_6F_5), -165.91 (s, 6F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_6): δ -12.02 (s). **Anal. Calcd.** for $C_{34}H_{31}BF_{15}OP$: C, 56.23; H, 3.66. Found: C, 56.48; H, 3.83 %.

(^{t}Bu)$_2$PH(C_4H_8O)B(C_6F_5)$_3$ (4-2): To a faint yellow solution of B(C_6F_5)$_3$ (0.350 g, 0.684 mmol) in THF (4 mL) was added di-*tert*-butylphosphine (0.100 g, 0.684 mmol) via syringe and the reaction mixture was left to stir for 72 hours at room temperature. All volatiles were removed *in vacuo* and the resulting solid was dried under vacuum for 12 hours. The final product was a white solid. Yield 0.404 g (81 %). Crystals suitable for X-ray diffraction were grown from a layered THF/C_6D_6/pentane solution at 25 °C. **^{1}H NMR** (THF-d_8): δ 5.60 (dt, 1H, $^1J_{H\text{-}P}$ = 453 Hz, $^3J_{H\text{-}H}$ = 4 Hz, P*H*), 3.24 (t, 2H, $^3J_{H\text{-}H}$ = 5 Hz, $PCH_2CH_2CH_2CH_2O$), 2.64 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.99 (m, 2H,

$PCH_2CH_2CH_2CH_2O$), 1.67 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.45 (d, 18H, $^3J_{H-P}$ = 16 Hz, $P(C(CH_3)_3)_2$). **^{11}B NMR** (C_6D_6): δ -2.86 (s). **^{13}C{^{1}H} NMR** (C_6D_6): δ 149.16 (dm, $^1J_{C-F}$ = 230 Hz, *C*F), 139.28 (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 137.44 (dm, $^1J_{C-F}$ = 237 Hz, *C*F), 125.66 (quaternary, C_6F_5), 64.40 (s, $PCH_2CH_2CH_2CH_2O$), 33.59 (d, $^1J_{C-P}$ = 35.9 Hz, quaternary, $PC(CH_3)_3$), 32.79 (d, $^3J_{C-P}$ = 11 Hz, $PCH_2CH_2CH_2CH_2O$), 27.10 (s, $C(CH_3)_3$), 26.93 (m, $PCH_2CH_2CH_2CH_2O$), 14.97 (d, $^1J_{C-P}$ = 39 Hz, $PCH_2CH_2CH_2CH_2O$). **^{19}F NMR** (C_6D_6): δ -133.88 (d, $^3J_{F-F}$ = 23 Hz, 6F, *ortho*-C_6F_5), -164.78 (t, $^3J_{F-F}$ = 11 Hz, 3F, *para*-C_6F_5), -168.02 (t, $^3J_{F-F}$ = 20 Hz, 6F, *meta*-C_6F_5). **^{31}P{^{1}H}NMR** (C_6D_6): δ 50.92 (s). **Anal. Calcd.** for $C_{30}H_{27}BF_{15}OP$: C, 49.34; H, 3.73. Found: C, 48.85; H, 3.58 %.

$(Cy)_3P(C_4H_8O)B(C_6F_5)_3$ (4-3): A clear yellow solution of $B(C_6F_5)_3$ (0.200 g, 0.39 mmol) and tri-cyclohexylphosphine (0.110 g, 0.39 mmol) in THF (20 mL) was allowed to stir for 24 hours at 25 °C. All volatiles were removed *in vacuo* to give the ring opened product as a white solid. Yield 302 mg (98 %). Crystals suitable for X-ray diffraction were grown from a concentrated solution of product in CH_2Cl_2/toluene layered with pentane at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 3.21 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 2.46-2.40 (br m, 2H, $PCH_2CH_2CH_2CH_2O$), 2.23-2.15 (m, 3H, $P\{C_6H_{11}\}$), 1.89-1.80 (br m, 12H, $P\{C_6H_{11}\}$), 1.72-1.66 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.65 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.50-1.41 (br m, 6H, $P\{C_6H_{11}\}$), 1.36-1.26 (br m, 12H, $P\{C_6H_{11}\}$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -2.10 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 148.63 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 138.80 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 136.98 (dm, $^1J_{C-F}$ = 245 Hz, *C*F), 125.93 (br s, quaternary), 63.76 (s, $PCH_2CH_2CH_2CH_2O$), 32.84 (d, $^3J_{C-P}$ = 17 Hz, $PCH_2CH_2CH_2CH_2O$), 30.49 (d, $^1J_{C-P}$ = 42 Hz, $P\{C_6H_{11}\}_3$), 27.48 (s, $P\{C_6H_{11}\}_3$), 27.19 (d, $^3J_{C-P}$ = 11 Hz, $P\{C_6H_{11}\}_3$), 25.90 (s,

P{C_6H_{11}}$_3$). 21.85 (s, $PCH_2CH_2CH_2CH_2O$), 16.15 (d, $^1J_{C\text{-}P}$ = 44 Hz, $PCH_2CH_2CH_2CH_2O$). **^{19}F NMR** (CD_2Cl_2): δ -134.46 (d, 4F, $^3J_{F\text{-}F}$ = 23 Hz, *ortho*-C_6F_5), -163.78 (t, 2F, $^3J_{F\text{-}F}$ = 23 Hz , *para*-C_6F_5), -167.36 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 32.09 (s). **Anal. Calcd.** for $C_{40}H_{41}BF_{15}OP$: C, 55.57; H, 4.78. Found: C, 56.10; H, 4.98 %. **Mp:** 200-205°C.

$(Et)_3P(C_4H_8O)B(C_6F_5)_3$ (4-4): $(Et_3P)B(C_6F_5)_3$ (0.100 g, 0.16 mmol) was dissolved in THF (10 mL) and quantitatively transferred to a 50 mL reaction bomb. The solution was heated to 80 °C for 5 hours. Upon cooling all volatiles were removed *in vacuo* to give the ring opened product as a white solid. Yield 90 mg (81 %). Crystals suitable for X-ray diffraction were grown from a concentrated solution of product in CH_2Cl_2/toluene layered with pentane at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 3.23 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 2.59-2.49 (br m, 2H, $PCH_2CH_2CH_2CH_2O$), 2.11-1.99 (dq, 6H, $^3J_{H\text{-}P}$ = 12 Hz, $^3J_{H\text{-}H}$ = 8 Hz, CH_2,), 1.83 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.66 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.32-1.23 (dt, 9H, $^3J_{H\text{-}P}$ = 18 Hz, $^3J_{H\text{-}H}$ = 8 Hz, CH_3). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -2.94 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ 148.52 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 138.73 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *C*F), 137.23 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 124.94 (br s, quaternary), 63.08 (s, $PCH_2CH_2CH_2CH_2O$), 31.92 (d, $^3J_{C\text{-}P}$ = 14 Hz, $PCH_2CH_2CH_2CH_2O$), 20.22 (d, $^2J_{C\text{-}P}$ = 7 Hz, $PCH_2CH_2CH_2CH_2O$), 17.84 (d, $^1J_{C\text{-}P}$ = 47 Hz, $PCH_2CH_2CH_2CH_2O$), 12.33 (d, $^1J_{C\text{-}P}$ = 50 Hz, CH_2), 5.70 (s, CH_3). **^{19}F NMR** (CD_2Cl_2): δ -134.75 (d, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *ortho*-C_6F_5), -163.53 (m, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -167.33 (m, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 38.65 (s). **Anal. Calcd.** for $C_{28}H_{23}BF_{15}OP$: C, 47.89; H, 3.30. Found: C, 48.11; H, 3.52 %. **Mp:** 165-170°C.

4.2.3 Synthesis of Phosphine Alkoxyborate Lithium Salts

$[(Mes)_2P(C_4H_8O)B(C_6F_5)_3][Li(THF)_2]$ (4-5): To a faint yellow solution of $B(C_6F_5)_3$ (0.582 g, 1.14 mmol) in THF (5 mL) was added dropwise an orange solution of Mes_2PLi (0.306 g, 1.11 mmol) in THF (5 mL). The reaction mixture immediately went colorless followed by a gradual color change to red. The reaction mixture was allowed to stir for 12 hours, at which time all volatiles were remove *in vacuo*. Pentane (5 mL) was added and the reaction stirred for 10 minutes. All volatiles were removed *in vacuo* and the reaction dried under vacuum for 24 hours yielding the product as a tan solid. Yield 0.844 g (80 %). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 6.75 (s, 4H, $P(C_6H_2)_2$), 3.72 (s, 8H, THF), 3.22 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 2.33 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 2.20 (s, 18H, $P(C_6H_2Me\text{-}2,4,6)_2$), 1.85 (s, 8H, THF), 1.49 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.14 (m, 2H, $PCH_2CH_2CH_2CH_2O$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -3.10 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ 148.39 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 142.18 (d, $^2J_{C\text{-}P}$ = 13 Hz, *ortho*-C_6H_2), 139.67 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 138.13 (s, *para*-C_6H_2), 137.33 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 130.35 (s, *meta*-C_6H_2), 122.53, 117.96 (quaternary, C_6F_5, C_6H_2), 68.86 (s, THF), 65.56 (s, $PCH_2CH_2CH_2CH_2O$), 33.37 (d, $^2J_{C\text{-}P}$ = 14 Hz, $PCH_2CH_2CH_2CH_2O$), 28.19 (d, $^1J_{C\text{-}P}$ = 14.3 Hz, $PCH_2CH_2CH_2CH_2O$), 25.94 (s, THF), 23.92 (s, $PCH_2CH_2CH_2CH_2O$), 23.21 (d, $^3J_{C\text{-}P}$ = 14 Hz, $C_6H_2Me\text{-}2,6$), 20.99 (s, $C_6H_2Me\text{-}4$). **^{19}F NMR** (CD_2Cl_2): δ -137.55 (d, $^3J_{F\text{-}F}$ = 20 Hz, 6F, *ortho*-C_6F_5), -161.03 (t, $^3J_{F\text{-}F}$ = 20 Hz, 3F, *para*-C_6F_5), -165.63 (t, $^3J_{F\text{-}F}$ = 20 Hz, 6F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ -21.44 (s). **Anal. Calcd.** for $C_{48}H_{46}BF_{15}LiO_3P$: C, 57.39; H, 4.62. Found: C, 57.57; H, 5.25 %.

$[(Ph)_2P(C_4H_8O)B(C_6F_5)_3][Li(THF)_2]$ (4-6): To a faint yellow solution of $B(C_6F_5)_3$ (0.200 g, 0.391 mmol) in toluene (2 mL) was added THF (0.16 mL, 1.97 mmol). Ph_2PLi (0.075 g, 0.390 mmol) in toluene (2 mL) and THF (0.16 mL, 1.97 mmol) was added and the reaction mixture was left to stir for 24 hours at room temperature. All volatiles were removed *in vacuo* and the resulting cream-colored solid was washed with Et_2O (2 mL) and pentane (2 mL) and then dried under vacuum for 24 hours. Yield 0.188 g (62 %). **^{1}H NMR** (C_6D_6): δ 7.28 (m, 4H, $P(C_6H_6)_2$), 7.05 (m, 6H, $P(C_6H_6)_2$), 3.38 (t, $^3J_{H-H}$ = 7 Hz, 2H, $PCH_2CH_2CH_2CH_2O$), 3.25 (m, 8H, THF), 1.85 (t, $^3J_{H-H}$ = 7 Hz, 2H, $PCH_2CH_2CH_2CH_2O$), 1.42 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.26 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.19 (s, 8H, THF). **^{11}B{^{1}H} NMR** (C_6D_6): δ -2.66 (s). **^{13}C{^{1}H} NMR** (C_6D_6): δ 148.66 (dm, $^1J_{C-F}$ = 232 Hz, *C*F), 139.59 (dm, $^1J_{C-F}$ = 237 Hz, *C*F), 137.22 (dm, $^1J_{C-F}$ = 249 Hz, *C*F), 133.41, 132.75, 131.57, 128.81 (quaternary, C_6H_6), quaternary C_6F_5 could not be located, 68.37 (s, THF), 65.13 (s, $PCH_2CH_2CH_2CH_2O$), 31.96 (d, $^3J_{C-P}$ = 10 Hz, $PCH_2CH_2CH_2CH_2O$), 27.59 (d, $^1J_{C-P}$ = 10 Hz, $PCH_2CH_2CH_2CH_2O$), 25.15 (s, THF), 22.56 (d, $^2J_{C-P}$ = 15 Hz, $PCH_2CH_2CH_2CH_2O$), **^{19}F NMR** (C_6D_6): δ -137.51 (d, $^3J_{F-F}$ = 14 Hz, 6F, *ortho*-C_6F_5), -159.11 (t, $^3J_{F-F}$ = -20 Hz, 3F, *para*-C_6F_5), -164.20 (t, $^3J_{F-F}$ = 20 Hz, 6F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_6): δ -18.86 (s). **Anal. Calcd.** for $C_{42}H_{32}BF_{15}LiO_3P$: C, 54.93; H, 3.51. Found: C, 55.77; H, 4.01 %.

$[(^tBu)_2P(C_4H_8O)B(C_6F_5)_3][Li(THF)_2]$ (4-7): *Method A*: The species $(^tBu)_2PH(C_4H_8O)B(C_6F_5)_3$ (0.207 g, 0.283 mmol) was dissolved in THF (5 mL) and cooled to -35 °C. To this reaction mixture was added *tert*-butyllithium in hexanes (0.18 mL, 0.301 mmol) via syringe. The mixture turned pale yellow and then colorless. The

reaction was allowed to warm to room temperature over 30 minutes at which time the solution turned from colorless to pale yellow. The reaction was stirred for a further 2 hours. All volatiles were removed *in vacuo* and the resulting white solid was dried under vacuum for 12 hours. Yield 0.180 g (73 %). *Method B*: $^{t}Bu_2PLi$ (0.100 g, 0.657 mmol) was dissolved in THF (4 mL) and cooled to -78 °C in a dry ice / acetone bath. A solution of $B(C_6F_5)_3$ (0.340 g, 0.664 mmol) in THF (2 mL) was then added to the phosphide via syringe over the course of 15 minutes. The yellow solution was warmed to room temperature over the course of 6 hours and then further stirred at room temperature overnight. All volatiles were removed *in vacuo* to give a white sticky solid. Hexanes (10 mL) was added and removed *in vacuo* three times. The resulting off-white solid was dried under vacuum overnight. Yield 0.350 g (65 %).**^{1}H NMR** (THF-d_8): δ 4.02 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 3.60 (s, 8H, THF), 2.18 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.84 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.90 (s, 8H, THF), 1.75 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.46 (d, 18H, $^{3}J_{H\text{-}P}$ = 11 Hz, $P(C(CH_3)_3)_2$). **^{1}H NMR** (C_6D_6): δ 3.55 (s, 8H, THF), 3.45 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.75 (s, 8H, THF), 1.40 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.29 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.08 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 0.96 (d, 18H, $^{3}J_{H\text{-}P}$ = 11 Hz, $P(C(CH_3)_3)_2$). **^{11}B{^{1}H} NMR** (THF-d_8): δ -2.85 (s). **^{13}C{^{1}H} NMR** (THF-d_8): δ 149.25 (dm, $^{1}J_{C\text{-}F}$ = 235 Hz, *C*F), 139.20 (dm, $^{1}J_{C\text{-}F}$ = 242 Hz, *C*F), 137.21 (dm, $^{1}J_{C\text{-}F}$ = 244 Hz, *C*F), 126.61 (quaternary, *C*F), 64.47 (s, $PCH_2CH_2CH_2CH_2O$), 35.41 (d, $^{1}J_{C\text{-}P}$ = 30 Hz, quaternary $P(C(CH_3)_3)_2$), 31.78 (d, $^{3}J_{C\text{-}P}$ = 20 Hz, $PCH_2CH_2CH_2CH_2O$), 30.42 (d, $^{2}J_{C\text{-}P}$ = 9 Hz, $P(C(CH_3)_3)_2$), 28.31 (d, $^{1}J_{C\text{-}P}$ = 26 Hz, $PCH_2CH_2CH_2CH_2O$), 22.38 (d, $^{2}J_{C\text{-}P}$ = 20 Hz $PCH_2CH_2CH_2CH_2O$). **^{19}F NMR** (THF-d_8): δ -136.65 (m, 6F, *ortho*-C_6F_5), -159.61 (t,

$^{3}J_{F\text{-}F}$ = 20 Hz, 3F, *para*-C_6F_5), -164.10 (s, 6F, *meta*-C_6F_5). **$^{31}P\{^{1}H\}$ NMR** (THF-d_8): δ 27.36 (s).

[(^{t}Bu)$_2$P(C_4H_8O)B(C_6F_5)$_3$][Li] (4-8): The species (^{t}Bu)$_2$PH(C_4H_8O)B(C_6F_5)$_3$ (0.200 g, 0.274 mmol) was slurried in toluene (8 mL) and cooled to -35 °C. To this mixture was added *tert*-butyllithium in hexanes (0.16 mL, 0.274 mmol) via syringe. The reaction was allowed to warm to room temperature over 30 minutes at which time all solids dissolved. The reaction was stirred for a further 2 hours. All volatiles were removed *in vacuo* and the resulting solid was dried under vacuum for 12 hours. The final product was isolated as an off-white solid. Yield 0.180 g (89 %). **^{1}H NMR** (Toluene-d_8, 500 MHz): δ 3.18 (br s, 2H, $PCH_2CH_2CH_2\mathit{CH_2}O$), 1.35 (m, 2H, $P\mathit{CH_2}CH_2CH_2CH_2O$), 1.30 (m, 2H, $PCH_2CH_2\mathit{CH_2}CH_2O$), 0.95 (m, 2H, $PCH_2\mathit{CH_2}CH_2CH_2O$), 0.88 (d, 18H, $^{3}J_{H\text{-}P}$ = 11.60 Hz, $P(C(\mathit{CH_3})_3)_2$). **^{11}B NMR** (Toluene-d_8): δ -2.91 (s). **$^{13}C\{^{1}H\}$ NMR** (Toluene-d_8): δ 148.94 (dm, $^{1}J_{C\text{-}F}$ = 235 Hz, C*F*), 140.11 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, C*F*), 137.98 (dm, $^{1}J_{C\text{-}F}$ = 238 Hz, C*F*), 126.02 (quaternary, C*F*), 64.06 (s, $PCH_2CH_2CH_2\mathit{CH_2}O$), 31.74 (d, $^{1}J_{C\text{-}P}$ = 32 Hz, quaternary $P(\mathit{C}(CH_3)_3)_2$), 30.86 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, $PCH_2CH_2\mathit{CH_2}CH_2O$), 29.46 (d, $^{2}J_{C\text{-}P}$ = 10 Hz, $P(C(\mathit{CH_3})_3)_2$), 22.73 (d, $^{1}J_{C\text{-}P}$ = 17 Hz, $P\mathit{CH_2}CH_2CH_2CH_2O$), 19.55 (s, $PCH_2\mathit{CH_2}CH_2CH_2O$). **$^{19}F$ NMR** (Toluene-d_8): δ -139.24 (s, 6F, *ortho*-C_6F_5), -158.26 (t, $^{3}J_{F\text{-}F}$ = 20 Hz, 3F, *para*-C_6F_5), -163.31 (t, $^{3}J_{F\text{-}F}$ = 20 Hz, 6F, *meta*-C_6F_5). **^{7}Li NMR** (Toluene-d_8): δ 1.25-0.51 (dm, $J_{Li\text{-}P}$ = 77 Hz). **$^{31}P\{^{1}H\}$ NMR** (Toluene-d_8): δ 26.65 (q, $J_{P\text{-}Li}$ = 73 Hz).

4.2.4 Synthesis of Phosphonium bis-Alkoxyborate Lithium Salts

$[(Mes)_2P\{C_4H_8OB(C_6F_5)_3\}_2][Li(THF)_4]$ (4-9): To a faint yellow solution of $B(C_6F_5)_3$ (0.200 g, 0.391 mmol) in THF (5 mL) was added dropwise an orange solution of Mes_2PLi (0.054 g, 0.195 mmol) in THF (5 mL). The reaction mixture immediately went colorless followed by a gradual color change to red. The reaction mixture was allowed to stir for 12 hours, at which time all volatiles were remove *in vacuo*. Pentane (5 mL) was added and the reaction stirred for 10 minutes. All volatiles were removed *in vacuo* and the reaction dried under vacuum for 24 hours yielding the product as a tan solid. Yield 0.844 g (80 %). **^{1}H NMR** (CD_2Cl_2): δ 6.99 (d, $^4J_{H\text{-}P}$ = 4 Hz, 4H, $P(C_6H_2)_2$), 3.69 (s, 16H, THF), 3.15 (m, 4H, $PCH_2CH_2CH_2CH_2O$), 2.75 (m, 4H, $PCH_2CH_2CH_2CH_2O$), 2.32 (s, 6H, $P(C_6H_2Me\text{-}4)_2$), 2.17 (s, 12H, $P(C_6H_2Me\text{-}2,6)_2$), 1.85 (s, 16H, THF), 1.48 (m, 4H, $PCH_2CH_2CH_2CH_2O$), 1.36 (m, 4H, $PCH_2CH_2CH_2CH_2O$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -2.99 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ 148.40 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 145.77 (s, *para*-C_6H_2), 142.24 (d, $^2J_{C\text{-}P}$ = 10 Hz, *ortho*-C_6H_2), 139.26 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 137.29 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 133.45 (d, $^3J_{C\text{-}P}$ = 9.50 Hz, *meta*-C_6H_2), 123.42 (quaternary, C_6F_5), 117.06 (d, $^1J_{C\text{-}P}$ = 88.34 Hz, quaternary, C_6H_2), 68.71 (s, THF), 64.78 (s, $PCH_2CH_2CH_2CH_2O$), 32.32 (d, $^2J_{C\text{-}P}$ = 13 Hz, $PCH_2CH_2CH_2CH_2O$), 27.20 (d, $^1J_{C\text{-}P}$ = 44.8 Hz, $PCH_2CH_2CH_2CH_2O$), 25.94 (s, THF), 23.51 (d, $^3J_{C\text{-}P}$ = 14 Hz, $C_6H_2Me\text{-}2,6$), 21.22 (s, $C_6H_2Me\text{-}4$), 20.96 (s, $PCH_2CH_2CH_2CH_2O$). **^{19}F NMR** (CD_2Cl_2): δ -136.08 (s, 12F, *ortho*-C_6F_5), -161.82 (s, 6F, *para*-C_6F_5), -166.00 (m, 12F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 30.87 (s). **Anal. Calcd.** for $C_{79}H_{70}B_2F_{30}LiO_6P$: C, 54.06; H, 4.07. Found: C, 53.58; H, 3.89 %.

[(^{t}Bu)$_2$P{$C_4H_8OB(C_6F_5)_3$}$_2$}][Li] (4-10): To a faint yellow solution of $B(C_6F_5)_3$ (0.673 g, 1.314 mmol) in THF (2 mL) was added lithium ^{t}Bu$_2$PLi (0.100 g, 0.657 mmol) in THF (4 mL) and the reaction mixture was left to stir for 12 hours at room temperature. All volatiles were removed *in vacuo* and the resulting white solid was dried under vacuum for 24 hours. Yield 0.776 g (89 %). Crystals suitable for X-ray diffraction were grown from a layered THF/pentane solution at 25 °C. **^{1}H NMR** (THF-d_8): δ 3.22 (t, 4H, $^3J_{H-H}$ = 5 Hz, $PCH_2CH_2CH_2CH_2O$), 2.51 (m, 4H, $PCH_2CH_2CH_2CH_2O$), 1.92 (m, 4H, $PCH_2CH_2CH_2CH_2O$), 1.65 (m, 2H, $PCH_2CH_2CH_2CH_2O$), 1.35 (d, 18H, $^3J_{H-P}$ = 14.3 Hz, $P(C(CH_3)_3)_2$). **^{11}B{^{1}H} NMR** (THF-d_8): δ -2.90(s). **^{13}C{^{1}H} NMR** (THF-d_8): δ 149.18 (dm, $^1J_{C-F}$ = 246 Hz, *C*F), 139.20 (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 137.47(dm, $^1J_{C-F}$ = 245 Hz, *C*F), 126.22 (quaternary, C_6F_5), 64.49 (s, $PCH_2CH_2CH_2CH_2O$), 35.29 (d, $^1J_{C-P}$ = 38.1 Hz, quaternary, $PC(CH_3)_3$), 33.42 (d, $^3J_{C-P}$ = 12.2 Hz, $PCH_2CH_2CH_2CH_2O$), 27.54(s, $C(CH_3)_3$), 26.56 (m, $PCH_2CH_2CH_2CH_2O$), 17.83 (d, $^1J_{C-P}$ = 39.62 Hz, $PCH_2CH_2CH_2CH_2O$). **^{19}F NMR** (THF-d_8): δ -133.88 (d, $^3J_{F-F}$ = 23 Hz, 12F, *ortho*-C_6F_5), -165.17 (t, $^3J_{F-F}$ = 11 Hz, 6F, *para*-C_6F_5), -168.24 (t, $^3J_{F-F}$ = 20 Hz, 12F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (THF-d_8): δ 45.26 (s). **Anal. Calcd.** for $C_{52}H_{34}B_2F_{30}LiO_2P$: C, 47.30; H, 2.60. Found: C, 47.58; H, 2.89 %.

4.2.5 Displacement of THF from $B(C_6F_5)_3$ by Secondary Phosphines

$(Cy_2PH)B(C_6F_5)_3$ and $(Ph_2PH)B(C_6F_5)_3$: The solid $B(C_6F_5)_3$ (0.050 g, 0.098 mmol) was dissolved in THF (10 mL) and stirred for 5 minutes. The appropriate phosphine (Cy_2PH: 0.020 g, 0.099 mmol, Ph_2PH: 0.018 g, 0.099 mmol) in THF (1 mL) was then added via

syringe and the reaction mixture stirred for 6 hours at room temperature. All volatiles were removed *in vacuo* to give the corresponding phosphine-borane adducts which are known in the literature.[103]

Table 4.1 Selected NMR data for phosphonium alkoxyborates, phosphine alkoxyborates, and phosphonium bis-alkoxyborates.

Compound	δ ^{31}P ($^{1}J_{P-H}$)	δ ^{11}B	^{19}F Δ_{p-m}*	δ ^{19}F (o-F, p-F, m-F)
Starting Materials				
$B(C_6F_5)_3$		59	18.2	-128.5, -143.1, -161.3
Et_3P [a]	-19.1			
Cy_3P [a]	11.1			
Mes_2PH [a]	-92.7 (230)			
$^{t}Bu_2PH$ [a]	20.1 (200)			
Mes_2PLi [b]	-61.5			
$^{t}Bu_2PLi$ [b]	42.8			
Ph_2PLi [b]	-21.1			
Phosphonium Alkoxyborates				
4-1 (Mes)	-12.0 (531)	-2.8	3.8	-133.9, -162.3, -165.9
4-2 (^{t}Bu)	50.9 (453)	-2.9	3.2	-133.9, -164.8, -168.0
4-3 (Cy)	32.1	-2.1	3.8	-133.9, -163.8, -167.6
4-4 (Et)	38.7	-2.9	3.8	-134.8, -163.5, -167.3
Phosphine Alkoxyborates				
4-5 (Mes)	-21.4	-3.1	4.6	-137.6, -161.0, -165.6
4-6 (Ph)	-18.9	-2.7	5.1	-137.5, -159.1, -164.2
4-7 (^{t}Bu)	27.4	-2.9	4.5	-136.7, -159.6, -164.1
4-8 (^{t}Bu)	26.7	-2.9	5.0	-139.4, -158.3, -163.3
Phosphonium bis-Alkoxyborates				
4-9 (Mes)	30.9	-3.0	4.2	-136.1, -161.8, -166.0
4-10 (^{t}Bu)	45.3	-2.9	3.0	-133.9, -165.2, -168.2

[a] C_6D_6, [b] THF, * Chemical shift difference between the *para* and *meta* resonances in the ^{19}F NMR spectrum

4.2.6 X-ray Data Collection, Reduction, Solution and Refinement

Single crystals were mounted in thin-walled capillaries either under an atmosphere of dry N_2 in a glove box and flame sealed or coated in Paratone-N oil. The data were collected using the SMART software package[104] on a Siemens SMART System CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71069 Å) at 25 °C. A hemisphere of data was collected in 1448 frames with 10 second exposure times unless otherwise noted. Data reductions were performed using the SAINT software package[105] and absorption corrections were applied using SADABS.[106] The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[107] All non-H atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Phosphorus-bound hydrogen atoms were located in the electron difference map and their positions refined isotropically.

Table 4.2 Selected crystallographic data for compounds **4-1**, **4-2**, **4-3**.

Crystal	**4-1**	**4-2**	**4-3**
Formula	$C_{34}H_{31}BF_{15}OP$	$C_{30}H_{27}BF_{15}OP$	$C_{28}H_{23}BF_{15}OP$
Formula weight	1010.7	730.3	702.3
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	C2/c	P-1
a(Å)	16.3017(14)	15.4885(31)	10.3288(17)
b(Å)	15.3950(13)	21.5739 (31)	12.0825(20)
c(Å)	19.3950(13)	19.9793 (33)	13.0835(21)
α(°)	90.0	90.0	94.234(2)
β(°)	103.134(1)	111.543(3)	105.527(2)
γ(°)	90.0	90.0	106.696(2)
V (Å^3)	4778.70(13)	6209.66(81)	1486.64(17)
Z	4	8	2
d(calc) g cm^{-1}	1.40	1.56	1.57
Abs coeff, μ, cm^{-1}	0.155	0.204	0.210
Data collected	45396	29758	4394
Data $F_o^2>3\sigma(F_o^2)$	8404	5475	1202
Variables	643	437	415
R^a	0.058	0.042	0.043
$R_w{}^b$	0.136	0.110	0.106
Goodness of Fit	0.978	1.011	1.075

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

Table 4.3 Selected crystallographic data for compounds **4-4**, **4-5**, **4-10**.

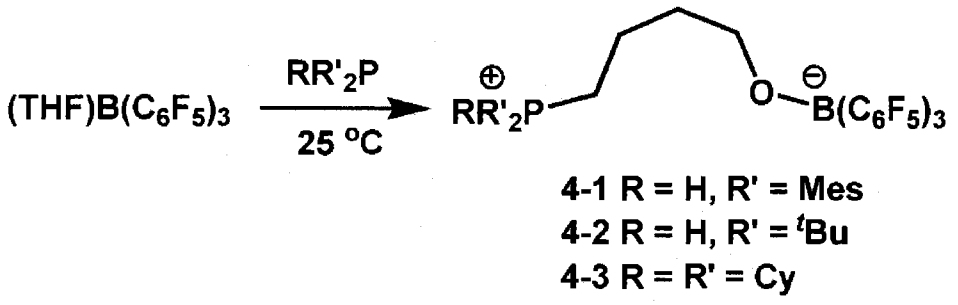
Crystal	**4-4**	**4-5**	**4-10**
Formula	$C_{40}H_{41}BF_{15}OP$	$C_{48}H_{46}BF_{15}O_3PLi$	$C_{52}H_{34}B_2F_{30}O_2PLi$
Formula weight	864.5	1076.7	1359.4
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a(Å)	12.2670(39)	21.1866(48)	12.8410(90)
b(Å)	13.0763(42)	12.7005(29)	15.686(11)
c(Å)	24.4486(78)	21.5301(49)	27.97(2)
$\alpha(^o)$	90.0	90.0	90.0
$\beta(^o)$	90.0	109.807(3)	94.046(12)
$\gamma(^o)$	90.0	90.0	90.0
V ($Å^3$)	3921.73(22)	5450.59(66)	6021.58(90)
Z	4	4	4
d(calc) g cm^{-1}	1.46	1.31	1.50
Abs coeff, μ, cm^{-1}	0.174	0.142	0.179
Data collected	37516	51615	47536
Data $F_o^2>3\sigma(F_o^2)$	6900	9598	8644
Variables	523	674	794
R^a	0.047	0.069	0.127
$R_w{}^b$	0.074	0.170	0.388
Goodness of Fit	0.985	0.988	0.990

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).

$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$

4.3 Results and discussion

In the selection of suitable phosphorus-based nucleophiles we noted that reaction of $(THF)B(C_6F_5)_3$ with the secondary phosphines Ph_2PH and Cy_2PH leads to the expected and known ligand exchange products $(R_2PH)B(C_6F_5)_3$ (R = Cy, Ph)[103] liberating THF at room temperature. However, the analogous reaction employing the sterically demanding phosphine Mes_2PH does not proceed in this fashion. Rather, reaction of $B(C_6F_5)_3$, THF and Mes_2PH afforded the THF ring opened phosphonium borate **4-1** in 79% yield after a 72 h reaction at 25 °C and appropriate work-up.



Scheme 4.1 Ring opening reactions of THF with sterically demanding phosphines to give zwitterionic phosphonium alkoxyborates.

The ^{11}B NMR spectrum revealed a single resonance at -2.8 ppm indicative of a four-coordinate boron center while the ^{31}P NMR spectrum gave rise to a downfield shifted doublet at -12.0 ppm with a P-H coupling constant of 531 Hz, supporting phosphonium formation (Table 4.1). ^{1}H NMR data showed methylene resonances at 3.48, 2.85, 1.62 and 1.23 ppm as well as resonances attributable to the mesityl groups and a PH. These spectroscopic data confirm the presence of the $B(C_6F_5)_3$ and $HPMes_2$ fragments in **4-1** as well as a ring opened THF molecule.

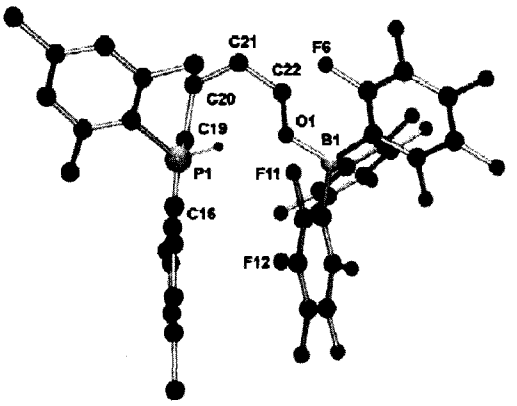


Figure 4.1 POV-ray depiction of **4-1**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Oxygen: red, Hydrogen: light gray. Selected metrical parameters {distances (Å), angles (°)}: **4-1**: P(1)-H 1.289(2), P(1)-C(19) 1.804(3), C(19)-C(20) 1.530(5), C(20)-C(21) 1.518(5), C(21)-C(22) 1.505(4), O(1)-C(22) 1.415(4), B(1)-O(1) 1.459(4), P(1)-C(19)-C(20) 114.0(3), B(1)-O(1)-C(22) 117.9(2), P(1)-C(19)-C(20)-C(21) 65.99(4), O(1)-C(22)-C(21)-C(20) 75.86(4).

Recrystallization afforded X-ray quality crystals that provided confirmation of the formulation of **4-1** as the zwitterionic phosphonium-borate $[Mes_2PH(C_4H_8O)B(C_6F_5)_3]$ (Figure 4.1, Scheme 4.1). The THF ring opening reaction product exhibits an O(1)-B(1) bond length of 1.459(4) Å and a P(1)-C(19) bond length of 1.804(3) Å. The B-O bond distance is slightly longer than the reported value of 1.444(4) Å for the related compound ^{t}BuNTe(μ-N^{t}Bu)$_2$TeN(^{t}Bu)$(CH_2)_4OB(C_6F_5)_3$[289] and shorter than that found in the anion $\{HOB(C_6F_5)_3\}^-$ (B-O = 1.480 (11)).[292] The P(1)-C(19) bond distance is typical for phosphonium-alkyl linkages. The remaining metric parameters within the molecule are unexceptional. In a similar fashion, the reaction of ^{t}Bu$_2$PH with $(THF)B(C_6F_5)_3$ afforded the analogous zwitterionic ring-opened product $[^t Bu_2PH(C_4H_8O)B(C_6F_5)_3]$ **4-2** as confirmed by both spectroscopic and crystallographic data (Figure 4.2, Scheme 4.1).

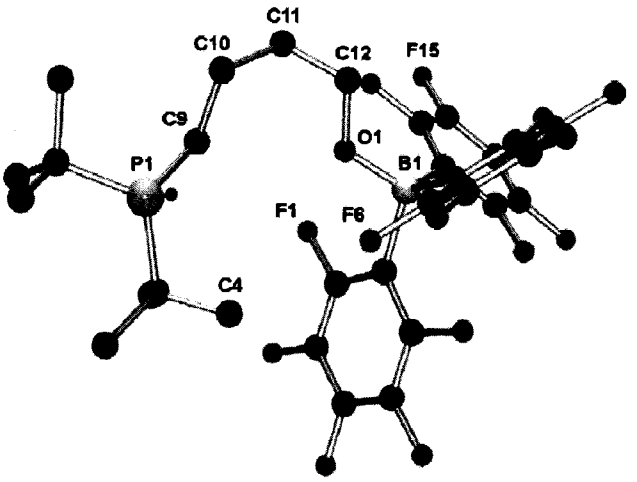


Figure 4.2 POV-ray depiction of **4-2**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Oxygen: red, Hydrogen: light gray. Selected metrical parameters {distances (Å), angles (°)}: **4-2**: P(1)-H 1.242(2), P(1)-C(9) 1.815(2), C(9)-C(10) 1.525(4), C(10)-C(11) 1.524(3), C(11)-C(12) 1.511(3), O(1)-C(22) 1.416(3), B(1)-O(1) 1.459(3), P(1)-C(9)-C(10) 117.21(18), B(1)-O(1)-C(22) 118.64(17), P(1)-C(9)-C(10)-C(11) 158.14(19), O(1)-C(22)-C(21)-C(20) 67.512(27).

Here the ^{31}P NMR doublet resonance is shifted downfield 30.8 ppm from the parent phosphine while the ^{11}B NMR signal at -2.9 ppm again supports the presence of a borate functionality (Table 4.1). The ^{1}H NMR and ^{1}H-^{1}H COSY NMR clearly show the 4 methylene resonances of the ring opened THF ring, the doublet resonance of the ^{t}Bu groups, and the P-*H* resonance which exists as a doublet of triplets due to proton coupling to phosphorus and an adjacent C*H*$_2$ (Figure 4.3 and Figure 4.4). Analogous to secondary phosphines, tertiary phosphines can act as suitable nucleophiles for the controlled ring opening of THF. The addition of Cy_3P to a solution of $B(C_6F_5)_3$ in THF results in the formation of the zwitterion **4-3** $[Cy_3P(C_4H_8O)B(C_6F_5)_3]$ over the course of 24 hours at room temperature (Scheme 4.1). Product formation was confirmed by spectroscopic and crystallographic data (Table 4.1, Figure 4.5).

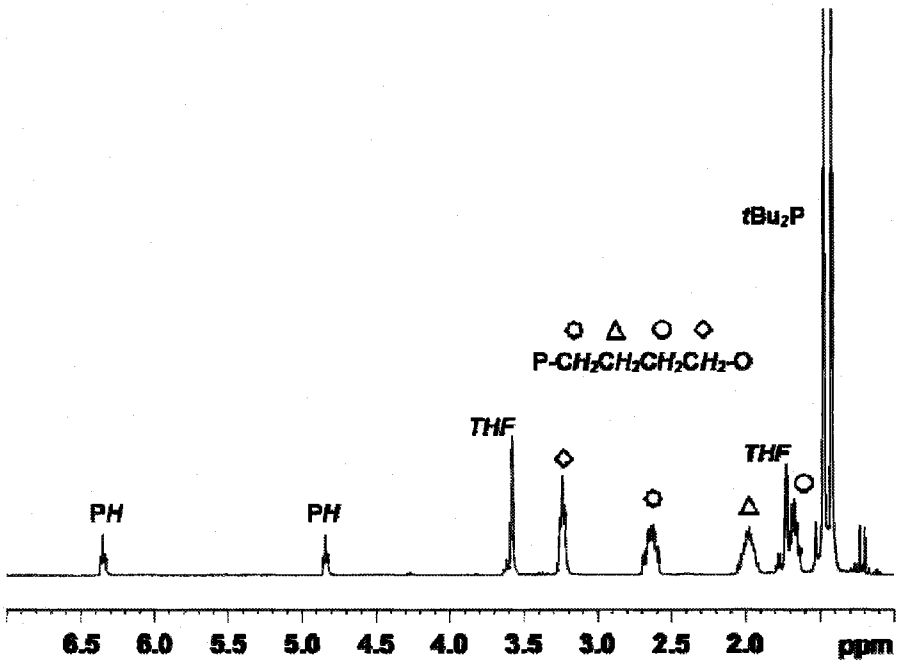


Figure 4.3 ^{1}H NMR spectrum of $^{t}Bu_2PH(C_4H_8O)B(C_6F_5)_3$.

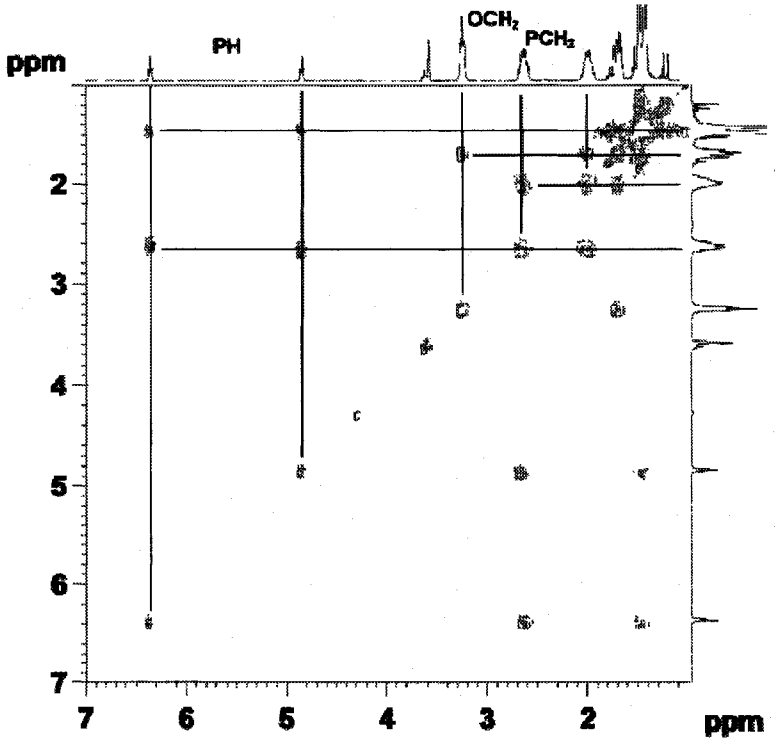


Figure 4.4 ^{1}H-^{1}H COSY 2D NMR spectrum of $^{t}Bu_2PH(C_4H_8O)B(C_6F_5)_3$.

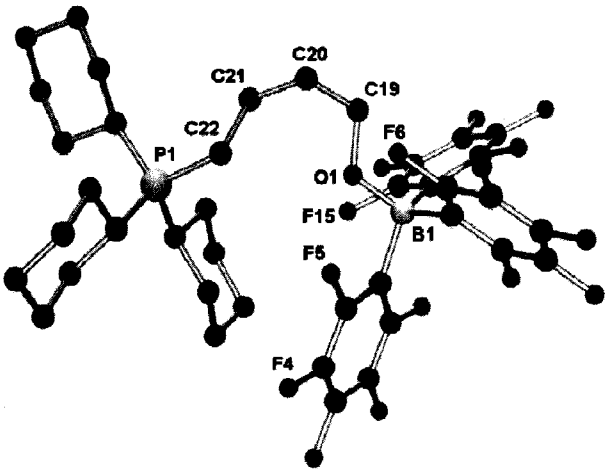
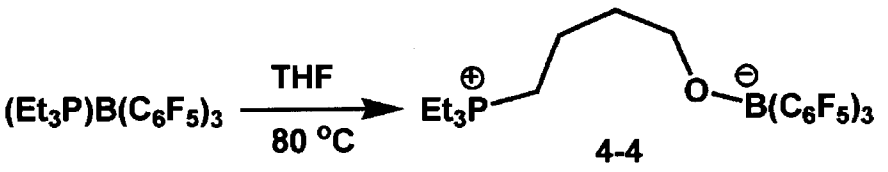


Figure 4.5 POV-ray depiction of **4-3**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Oxygen: red. Selected metrical parameters {distances (Å), angles (o)}: 4-3: P(1)-C(22) 1.799(4), C(22)-C(21) 1.531(5), C(21)-C(20) 1.515(5), C(20)-C(19) 1.482(5), O(1)-C(19) 1.414(4), B(1)-O(1) 1.444(5), P(1)-C(22)-C(21) 118.8(3), B(1)-O(1)-C(19) 117.8(3), P(1)-C(22)-C(21)-C(20) 177.4(3), O(1)-C(19)-C(20)-C(21) 55.8(5).

It should be noted that the reaction time for the synthesis of compounds **4-1**, **4-2**, and **4-3** can be decreased from 24-72 hours to roughly 6 hours upon heating the reaction mixtures to 80 °C. Additionally, through the use of heat, zwitterionic THF ring opened compounds can be synthesized from phosphine-$B(C_6F_5)_3$ adducts. The adduct $(Et_3P)B(C_6F_5)_3$ was dissolved in THF and heated to 80 °C for 6 hours giving a white solid in 81% yield after appropriate workup. The product was identified as $[Et_3P(C_4H_8O)B(C_6F_5)_3]$ (**4-4**, Scheme 4.2) by NMR spectroscopy (Table 4.1) and X-ray crystallography (Figure 4.6). The ability of phosphine-$B(C_6F_5)_3$ adduct to thermally undergo THF ring opening can allow for a wide range of zwitterionic species to be synthesized.



Scheme 4.2 Ring opening reaction of THF with a phosphine-$B(C_6F_5)_3$ adduct.

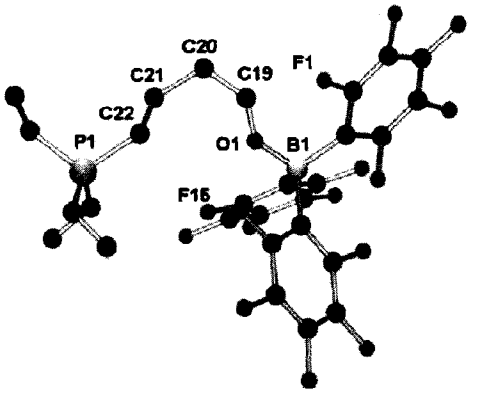


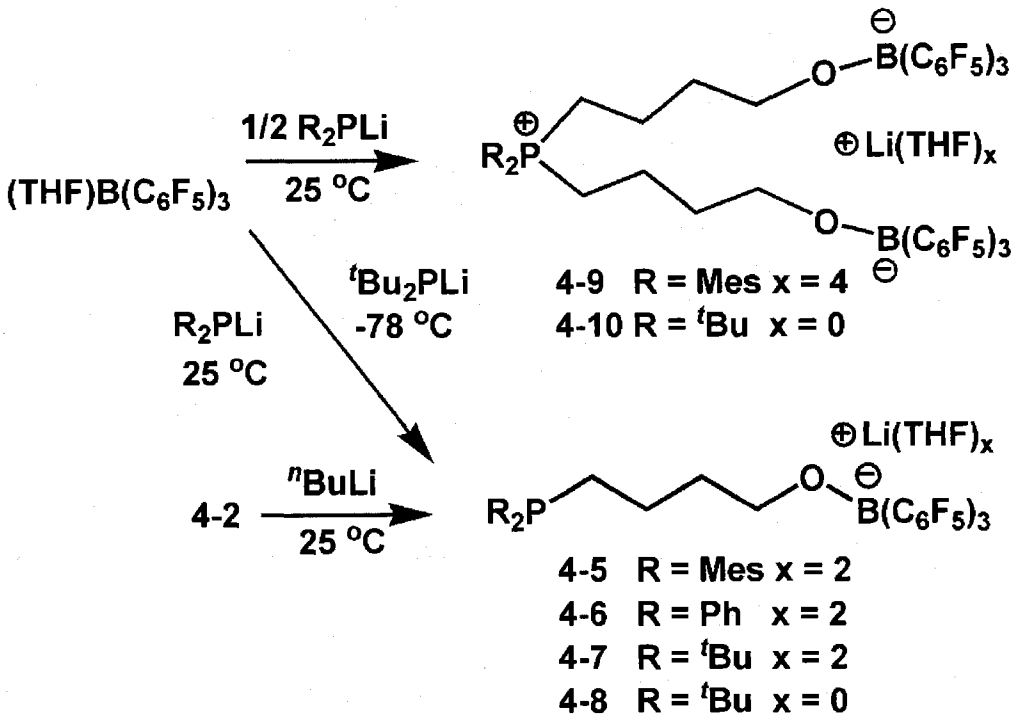
Figure 4.6 POV-ray depiction of **4-4**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Oxygen: red. Selected metrical parameters {distances (Å), angles (°)}: **4-4**: P(1)-C(22) 1.803(15), C(22)-C(21) 1.266(14), C(21)-C(20) 1.551(17), C(20)-C(19) 1.393(16), O(1)-C(19) 1.153(13), B(1)-O(1) 1.415(18), P(1)-C(22)-C(21) 125.8(16), B(1)-O(1)-C(19) 135.5(17), P(1)-C(22)-C(21)-C(20) 180.0(10), O(1)-C(19)-C(20)-C(21) 6(3).

In a related experiment, however, the adduct Et_2PH-$B(C_6F_5)_3$ showed no reactivity towards THF at 80 °C. Presumably Et_2PH forms a relatively stronger adduct with $B(C_6F_5)_3$ than Et_3P due to a reduced steric strain, which ultimately disfavors phosphine dissociation preventing the reaction from taking place.

Examining the solid-state structures of compounds **4-1** to **4-4** it is interesting to note that in each case, the positively charged phosphonium fragment is positioned towards the negatively charged borate fragment. This gives rise to intramolecular P-O and

P-B distances ranging from 3.25-4.28 Å and 4.42-5.86 Å, respectively. These are considerably shorter contacts than the intermolecular P-O and P-B atom distances ranging from 6.698-9.138 Å and 6.682-7.750 Å, respectively, in **4-1** to **4-4**. A similar observation was made for a THF ring opened (aryloxy)alane.[284] Zwitterions **4-1** to **4-4** exhibited very low solubility in alkane, chlorloalkane, aryl, and aryl halide solvents and high solubility in THF. They are also tolerant to air and moisture as samples left open to the atmosphere for several days showed no degradation by NMR spectroscopy.

Related anionic phosphine-borates are readily synthesized via the reaction of $(THF)B(C_6F_5)_3$ with an appropriate lithium phosphide (R_2PLi, R = Mes, Ph) at room temperature in THF. Subsequent workup gave the products **4-5** and **4-6** in 80 % and 62 % yield, respectively. Multinuclear NMR spectroscopy confirmed the formulation of **4-5** and **4-6** as $[R_2P(C_4H_8O)B(C_6F_5)_3Li(THF)_2]$ (R = Mes, **4-5**, R = Ph, **4-6**) (Table 4.3, Scheme 4.3). The ^{31}P NMR spectra of both compounds show singlet resonances that are shifted downfield from the parent lithium phosphide. In the case of **4-5**, the ^{31}P NMR resonance is shifted 9.4 ppm upfield from the corresponding phosphonium derivative (**4-1**) in part owning to an increased electron density at P. The ^{1}H NMR spectra of **4-5** and **4-6** each show four distinct methylene resonances typical of a ring opened THF molecule while the ^{11}B and ^{19}F NMR spectra confirm the formation of a 4-coordinate anionic borate center. The ^{1}H NMR spectra also reveals that two additional molecules of THF are retained in the complexes. The solid-state structure of **4-5** (Figure 4.7) was determined by a single crystal X-ray crystallographic study. In analogy with **4-1** to **4-4**, THF ring opening resulted in the formation of an anionic four coordinate B center with a B-O bond length of 1.484(5) Å.



Scheme 4.3 Ring opening reactions of THF with sterically demanding phosphines and phosphides to give phosphine alkoxyborates and phosphonium bis-alkoxylborates.

However, the concurrently formed P-C bond affords a neutral and pendant diarylalkylphosphine moiety with a P(1)-C(22) bond of 1.849(4) Å which is approximately 0.045 Å longer than the P-C alkyl bond in **4-1**. Countering the anionic charge of the borate is a Li cation. The Li center is pseudo-tetrahedral as it is coordinated to two THF molecules, the alkoxide oxygen and an *ortho*-F from one of the C_6F_5 groups on B. The Li-O distances range between 1.891(10) Å to 1.967(10) Å, while the Li-F approach is 2.015(9) Å. These Li-F contacts do not exist in solution as all three C_6F_5 rings remain equivalent, even at -70 °C as observed by ^{19}F NMR spectroscopy. Compared to the structure of **4-1**, the phosphine moiety in **4-5** is not oriented towards the negatively charged borate end, which results in the alkyl chain adopting a more typical linear zigzag arrangement.

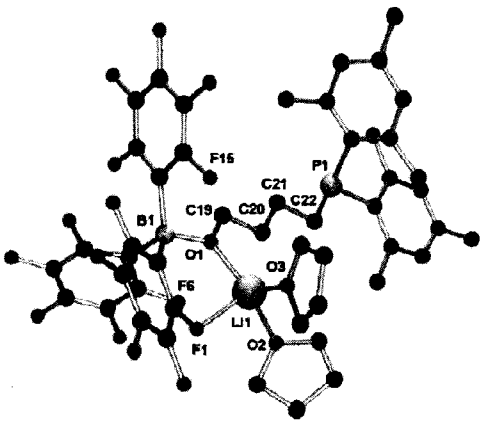
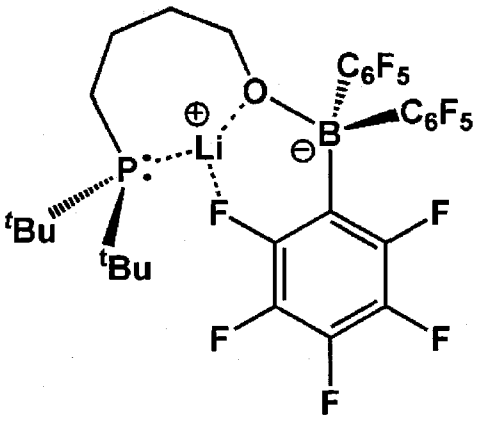


Figure 4.7 POV-ray depiction of **4-5**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: Yellow-green, Oxygen: red, Lithium: gray. Selected metrical parameters {distances (Å), angles (°)}: **4-5**: P(1)-C(22) 1.849(4), C(22)-C(21) 1.515(6), C(21)-C(20) 1.525(6), C(20)-C(19) 1.496(6), O(1)-C(19) 1.433(5), B(1)-O(1) 1.484(5), Li(1)-O(1) 1.913(9), Li(1)-O(2) 1.967(10), Li(1)-O(3), 1.891(10), Li(1)-F(1), 2.015(9), P(1)-C(22)-C(21) 110.8(3), B(1)-O(1)-C(19) 115.5(3), O(1)-Li(1)-F(1) 88.2(3), O(1)-Li(1)-O(2) 138.2(5), P(1)-C(22)-C(21)-C(20) 179.0(3), O(1)-C(19)-C(20)-C(21) 173.4(5), C(20)-C(19)-O(1)-Li(1), 0.6(9) C(19)-O(1)-Li(1)-F(1) 148.1(7).

This can be attributed to a reduced electrostatic interaction between the P and B moieties as the P center of this molecule is neutral, as opposed to positively charged in **4-1**. Peters has reported related phosphine-borate complexes where a phenyl group links a phosphine and a phenylborate moiety.[154] Interestingly, the reaction of $^{t}Bu_2PLi$ with $(THF)B(C_6F_5)_3$ gave a mixture of mono and bis THF ring opened (*vide infra*) products that could not be separated. Cooling to 0 °C and changing the order of addition gave similar results. Only by cooling a THF solution of $^{t}Bu_2PLi$ to -78 °C and slowly adding $(THF)B(C_6F_5)_3$ was the phosphine-borate **4-7** cleanly synthesized using a lithium phosphide.



Scheme 4.4 One possible Li atom coordination environment for species **4-8**.

Alternatively, compound **4-7** and the base free derivative **4-8** were generated by deprotonation of **4-2** with an alkyl lithium reagent in THF or toluene, respectively (Scheme 4-3). The formulation of **4-7** and **4-8** as $[^tBu_2P(C_4H_8O)B(C_6F_5)_3Li(THF)_x]$ (x = 0 or 2) was confirmed by multinuclear NMR spectroscopy (Table 4.3). The ^1H, ^{11}B, and ^{19}F NMR spectra of both species show the expected resonances for a ring opened THF molecule and an anionic boron center. However, the ^{31}P NMR spectra of **4-7** and **4-8** are markedly different. Both compounds exhibit a single resonance, at 27.4 and 26.7 ppm, respectively, which are shifted upfield from the parent lithium phosphide and the corresponding phosphonium borate **4-2** (Table 4.3). Unlike the ^{31}P NMR resonance for **4-7** which is a singlet, the ^{31}P NMR resonance of **4-8** is a quartet ($^1J_{P\text{-}Li}$ = 73 Hz) due to coupling to a spin 3/2 ^7Li nuclei. The corresponding ^7Li NMR spectrum shows a doublet with a Li-P coupling constant of 77 Hz. Thus, in the absence of THF, the tertiary phosphine binds to the Li counterion filling one of its coordination sites. The room temperature ^{19}F NMR spectra show all C_6F_5 to be equivalent, but upon cooling to -70 °C in toluene the *ortho*-fluorine resonance broadens out into the baseline. This indicates a

possible interaction of the *ortho*-F atom with the Li cation. In THF, no such interactions are observed at low temperature as THF occupies all of the Li cations coordination sites. It is likely that the Li atom in **4-8** is chelated by the P and O atoms and an *ortho*-fluorine of a C_6F_5 ring (Scheme 4.4). Unfortunately, X-ray quality crystals of **4-7** or **4-8** could not be obtained. Given the formation of **4-5** to **4-8**, it was proposed that such phosphines should be capable of initiating a second ring-opening.

The reaction of $(THF)B(C_6F_5)_3$ and Mes_2PLi was repeated with the adjusted stoichiometry of 2:1. Following a similar work-up procedure the product **4-9** was isolated in 80 % yield (Scheme 4.3). While the ^{11}B NMR chemical shift of -3.0 ppm is similar to that seen in **4-5**, the ^{31}P NMR chemical shift of 30.9 ppm observed for **4-9** is markedly downfield of the corresponding resonance for **4-5** (Table 4.3). This latter observation suggests the formation of a phosphonium center. The difference in the ^{31}P NMR chemical shifts of the phosphonium centers in **4-9** and **4-1** can be attributed to the increased steric and electronic effects of an alkyl substituent vs. a hydrogen atom. The ^{19}F NMR spectrum gave resonances at -136.1, -161.8 and -166.0 ppm, typical of the anionic $OB(C_6F_5)_3$ fragment. The ^{1}H NMR data for **4-9** are consistent with ring opening of THF as methylene resonances are observed at 3.2, 2.8, 1.5 and 1.4 ppm, although the integration is consistent with a 1:1 ratio of mesityl:methylene chain fragments. In addition, resonances at 3.69 and 1.85 ppm were attributed to four THF molecules coordinated to Li. Based on these data, **4-9** was formulated as $[Mes_2P(C_4H_8OB(C_6F_5)_3)_2]$ $[Li(THF)_4]$. Unfortunately attempts to obtain X-ray quality crystals of **4-9** were unsuccessful and thus this formulation was not confirmed crystallographically. Following a similar procedure, the analogous reaction of a 2:1 ratio of $(THF)B(C_6F_5)_3$ and $^tBu_2PLi$ was performed. The resulting white solid **4-10** was isolated in 89 % yield.

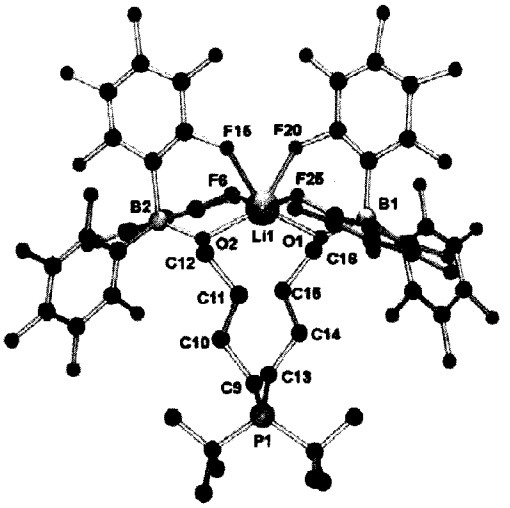


Figure 4.8 POV-ray depiction **4-10**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: Yellow-green, Oxygen: red, Lithium: gray. Selected metrical parameters {distances (Å), angles (°)}: **4-10**: P(1)-C(13) 1.804(12), P(1)-C(9) 1.775(11), O(1)-C(16) 1.447(12), O(2)-C(12) 1.466(12), O(1)-B(1) 1.542(16), O(2)-B(2) 1.513(15), O(1)-Li(1) 2.050(19), O(2)-Li(1) 2.053(19), Li(1)-F(6) 2.02(2), Li(1)-F(15) 2.240(19), Li(1)-F(20) 2.20(2), Li(1)-F(25) 2.10(2).

The NMR data for **4-10** were similar to that reported for **4-9** with an ^{11}B NMR signal at -2.9 ppm and a ^{31}P NMR resonance at 45.3 ppm consistent with the presence of both borate and phosphonium fragments. In a similar fashion the ^{1}H NMR data were consistent with THF ring opening affording two methylene chains on P. In contrast to **4-9**, compound **4-10** does not contain coordinated THF according to the ^{1}H NMR spectrum. The resulting formulation for **4-10** based on these data is $[^{t}Bu_2P(C_4H_8O)B(C_6F_5)_3)_2][Li]$. Crystals of $[^{t}Bu_2P(C_4H_8O)B(C_6F_5)_3)_2][Li]$ were grown from a THF/benzene/pentane solution at 25 °C (Figure 4.8, Scheme 4.3). Although the crystal quality of **4-10** is not the best, the data does confirm the formulation and establish the connectivity. Two butoxide chains link the cationic phosphonium center to two anionic borate fragments. The lithium counterion is coordinated to the two oxygen atoms and interacts with four fluorine atoms

on the boron bound aryl rings. This results in a distorted octahedral coordination sphere for the lithium atom. The Li-O distances average 2.052(19) Å while the Li-F interactions range from 2.02(2) Å to 2.240(19) Å. Again low-temperature ^{19}F NMR spectroscopy in THF showed all C_6F_5 rings to be equivalent down to -70 °C indicating that in solution THF coordinates to the Li cation. Unfortunately, due to the low solubility of **4-10**, dynamic NMR spectra could not be obtained in a non-coordinating solvent.

4.4 Summary and Conclusions

Mechanistically, it is thought that the ring opening of THF occurs via coordination of the THF oxygen to the electrophilic boron[293] center polarizing the oxygen-carbon bonds, rendering the α-carbon susceptible to nucleophilic attack[289] by a phosphine or phosphide. Clearly the formation of **4-1** to **4-10** demonstrates that the size and strength of the nucleophile dictate reactivity. Sterically demanding phosphines effect the ring opening of THF in (THF)$B(C_6F_5)_3$ whereas less sterically demanding phosphines form simple donor-acceptor adducts with $B(C_6F_5)_3$ at room temperature. High temperatures are required for phosphine-$B(C_6F_5)_3$ adducts to ring open THF, as high temperatures favor adduct dissociation and subsequent THF ring opening. Aryl and alkyl phosphides can effectively ring open THF yielding phosphine borates which in turn can ring open further equivalents of $B(C_6F_5)_3$-activated THF. It should be noted that in the absence of $B(C_6F_5)_3$, phosphorus based nucleophiles have been shown to react with THF. The reaction of THF with $[Et_2P]Li$ was reported in 1959 to give an uncharacterized product upon standing in THF solution for prolonged periods.[294] Subsequently in 1968, the ring opening of THF by $[Me_2P]Li$ in refluxing THF was reported.[295] Phosphorus trihalides and THF in the

presence of HgX_2 has also been shown to give moderate yields of ring-opened phosphorus acid esters.[296] In each case the reaction was either unexpected or the product not fully characterized. The quantitative nature of the reported reactions affords the opportunity to examine the ability of phosphonium-borate zwitterions act as protic activators for early metal pre-catalysts and the coordination chemistry of new anionic phosphine and anionic-phosphonium-dialkoxide ligands. This work, as well as the diverse reactions of Lewis acid adducts and sterically demanding nucleophiles in ligand synthesis and metal coordination, will continue to be an area of interest in the Stephan research group.

Chapter 5 Reversible, Metal-Free Hydrogen Activation

5.1 Introduction

As mentioned in Chapter 1, the ability to reversibly activate H_2 is an important chemical process only capable at transition metal centers. While metal-free compounds have been developed that can either liberate or activate H_2, no progress has been made in the design and synthesis of systems capable of both. This chapter details the unprecedented reactivity of 'frustrated' Lewis pairs towards H_2. The phosphonium-hydridoborate species $R_2PH(C_6F_4)BH(C_6F_5)_2$ undergoes thermally induced loss of H_2 to generate the corresponding phosphino-boranes $R_2P(C_6F_4)B(C_6F_5)_2$, which can subsequently activate H_2. These findings marked the first ever reported metal-free systems to both activate and liberate H_2 gas. Additionally the reactivity of FLP's towards Si-H, O-H, S-H, and S-S bonds is explored.

5.2 Experimental

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents (pentane, hexanes, toluene, and methylene chloride) were purified employing a Grubbs' type column system manufactured by Innovative Technology and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 °C under vacuum for 24 hours prior to use. Uninhibited THF was purchased from EMD and distilled from

sodium/benzophenone prior to use. Deuterated solvents were dried over sodium/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br) and vacuum distilled prior to use. Hydrogen and deturerium gas were purchased from Praxair and passed through a Dririte gas drying unit prior to use. H_2O was distilled and de-oxygenated prior to use. All common organic reagents were purified by conventional methods unless otherwise noted. ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer at 300 K unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR experiments were referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute vaules. DEPT and 2-D $^1H/^{13}C$ correlation experiments were completed for assignment of the carbon atoms. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. $B(C_6F_5)_3$ was generously donated by NOVA Chemicals Corporation. All phosphines were purchased from Aldrich or Strem and used as received unless otherwise noted. Paratone-N oil was purchased from Hampton Research. Me_2SiClD was prepared as reported,[297] while Mes_2PD prepared from Mes_2PCl and $LiAlD_4$.

5.2.1 General Procedures for the Liberation and Activation of H_2

General procedure for the heating of $R'RPH(C_6F_4)BH(C_6F_5)_2$ and $[R''_3PH][HB(C_6F_5)_3]$ R'= R= Mes (3-6) , R'= R= ^{t}Bu (3-5), R' = ^{t}Bu, R = Mes (5-1), R' = ^{t}Bu, R = Ph (5-2), R'' = ^{t}Bu (5-5), R'' = Mes (5-6). These reactions were performed in a similar fashion and thus only one preparation is detailed. A sealable J-

Young NMR tube was charged with $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (35 mg, 0.046 mmol) and C_6D_5Br (1.142 g) and sealed forming a 0.060 M solution. The sample was inserted into a NMR spectrometer pre-heated to 150 °C and allowed to reach thermal equilibrium over 2 minutes. The reaction was monitored by ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopy for 2 hours. For all species except **3-6**, additional heating experiments were conducted by attaching the J-Young NMR tube to a N_2/vacuum manifold and placing it in a temperature controlled silicon oil bath. Depending on the experiments, the sample was open or closed to a constant pressure (1 atm) stream of N_2. Before collecting NMR data all samples were cooled to 25 °C.

General procedure for the reaction of $R'RP(C_6F_4)B(C_6F_5)_2$ with H_2 R'= R= Mes (3-6) , R'= R= ^{t}Bu (3-5), R' = ^{t}Bu, R = Mes (5-3), R' = ^{t}Bu, R = Ph (5-4). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A sealable J-Young NMR tube was charged with $Mes_2P(C_6F_4)B(C_6F_5)_2$ (3-14) (30 mg, 0.039 mmol) and toluene (0.75 mL) and sealed, which formed an orange solution. The sample was subjected to a freeze-pump-thaw procedure using liquid N_2 in order to degas the solution. The sample was exposed to a constant pressure (1 atm) stream of hydrogen gas for 2 minutes at -196 °C. The NMR sample was sealed, warmed to room temperature (generating a pressure of ~3.5 atm), and vigorously shaken resulting in complete loss of the orange color within 10 minutes. Immediate NMR indicated conversion of **3-14** to **3-6**.

5.2.2 Synthesis of Phosphonium Hydridoborates

(^{t}Bu)(Mes)PH(C_6F_4)BH(C_6F_5)$_2$ (5-1): To a slurry of (^{t}Bu)(Mes)PH(C_6F_4)BF(C_6F_5)$_2$ (0.500g, 0.694 mmol) in dichloromethane (10 mL) was added Me_2SiHCl (0.77 mL, 6.94 mmol) via syringe. The reaction was allowed to stir for 12 hours at room temperature. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 483 mg (99 %). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane / pentane solution at 25 °C. **^{1}H NMR** ($THF\text{-}d_8$): δ 8.22 (d, 1H, $^1J_{H\text{-}P}$ = 467 Hz, P*H*), 7.22 (d, $^4J_{H\text{-}P}$ = 5 Hz, 2H, P(C_6H_2)), 3.92 (q, $^1J_{H\text{-}B}$ = 85 Hz, B*H*), 2.48 (br s, 6H, P(C_6H_2*Me-2,6*), 2.32 (s, 3H, P(C_6H_2*Me-4*), 1.62 (d, 9H, $^3J_{H\text{-}P}$ = 21 Hz, P{$C(CH_3)_3$}). **^{11}B NMR** ($THF\text{-}d_8$): δ -24.67 (d, $^1J_{B\text{-}H}$ = 85 Hz). **^{13}C{^{1}H} NMR** ($THF\text{-}d_8$) partial: δ 150.26 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 149.17 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 147.88 (s, *para-*C_6H_2), 146.52 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 145.01 (d, $^2J_{C\text{-}P}$ = 11 Hz, *ortho-*C_6H_2), 139.03 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *C*F), 137.31 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 132.52 (d, $^3J_{C\text{-}P}$ = 11 Hz, *meta-*C_6H_2), 111.84 (d, $^1J_{C\text{-}P}$ = 80 Hz, P-C_6H_2), 37.58 (d, $^1J_{C\text{-}P}$ = 40 Hz, P{*C*$(CH_3)_3$}), 26.40 (s, C(*C*$H_3)_3$), 22.67 (d, $^3J_{C\text{-}P}$ = 8 Hz, C_6H_2*Me-2,6*), 21.29 (s, C_6H_2*Me-4*). **^{19}F NMR** ($THF\text{-}d_8$): δ -128.67 (s, 2F, C_6F_4), -131.09 (s, 2F, C_6F_4), -133.52 (m, 4F, *ortho-*C_6F_5), -165.37 (m, 2F, *para-*C_6F_5), -168.45 (m, 4F, *meta-*C_6F_5). **^{31}P{^{1}H} NMR** ($THF\text{-}d_8$): δ -2.85 (m). **Anal. Calcd.** for $C_{31}H_{22}BF_{14}P$: C, 53.02; H, 3.16. Found: C, 52.87; H, 3.18 %.

(^{t}Bu)(Ph)PH(C_6F_4)BH(C_6F_5)$_2$ (5-2): To a solution of (^{t}Bu)(Ph)PH(C_6F_4)BF(C_6F_5)$_2$ (0.300g, 0.442 mmol) dissolved in dichloromethane (10 mL) was added $(CH_3)_2SiHCl$ (0.49 mL, 4.42 mmol) via syringe. The reaction was allowed to stir for 12 hours at room

temperature, during which time a precipitate formed. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 260 mg (89 %). **^{1}H NMR** (CD_2Cl_2): δ 7.96-7.88 (m, 3H, P(C_6H_5)), 7.78-7.72 (m, 2H, P(C_6H_5)), 7.20 (br d, 1H, $^{1}J_{H-P}$ = 480 Hz, P*H*), 3.67 (q, $^{1}J_{H-B}$ = 92 Hz, B*H*), 1.55 (d, 9H, $^{3}J_{H-P}$ = 21 Hz, P{C(CH_3)$_3$}). **^{11}B NMR** (CD_2Cl_2): δ -24.85 (d, $^{1}J_{B-H}$ = 94 Hz). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.84 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 148.66 (dm, $^{1}J_{C-F}$ = 240 Hz, *C*F), 145.10 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 138.60 (dm, $^{1}J_{C-F}$ = 240 Hz, *C*F), 136.99 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 136.93 (s, C_6H_5), 134.46 (d, $^{3}J_{C-P}$ = 11 Hz, C_6H_5), 131.39 (d, $^{2}J_{C-P}$ = 14 Hz, C_6H_5), 112.64 (d, $^{1}J_{C-P}$ = 78 Hz, P-C_6H_5), 35.05 (d, $^{1}J_{C-P}$ = 42 Hz, P{*C*(CH_3)$_3$}), 26.13 (s, C(*C*H_3)$_3$). **^{19}F NMR** (CD_2Cl_2): δ -127.71 (s, 2F, C_6F_4), -131.39 (m, 2F, C_6F_4), -134.04 (d, 4F, $^{3}J_{F-F}$ = 23 Hz, *ortho*-C_6F_5), -163.81 (t, 2F, $^{3}J_{F-F}$ = 20 Hz, *para*-C_6F_5), -167.44 (t, 4F, $^{3}J_{F-F}$ = 23 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 20.15 (m). **Anal. Calcd.** for $C_{28}H_{16}BF_{14}P$: C, 50.94; H, 2.24. Found: C, 50.20; H, 1.94 %.

$Cy_2PH(C_6F_4)BH(C_6F_5)_2$ (5-9): To a slurry of $Cy_2PH(C_6F_4)BF(C_6F_5)_2$ (0.200g, 0.282 mmol) in dichloromethane (10 mL) was added Me_2SiHCl (0.31 mL, 0.282 mmol) via syringe. The reaction was allowed to stir for 12 hours at room temperature. All volatiles were removed *in vacuo* to give the product as a white solid. Yield 150 mg (78 %). **^{1}H NMR** (THF-d_8): δ 7.04 (d, 1H, $^{1}J_{H-P}$ = 495 Hz, P*H*), 3.40 (q, $^{1}J_{H-B}$ = 88 Hz, B*H*), 3.00 (m, 2H, P{C_6H_{11}}$_2$), 2.31-2.16 (br m, 20H, P{C_6H_{11}}$_2$). **^{11}B{^{1}H} NMR** (THF-d_8): δ -24.58 (br). **^{13}C{^{1}H} NMR** (THF-d_8) partial: δ 149.39 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 148.36 (dm, $^{1}J_{C-F}$ = 240 Hz, *C*F), 146.05 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 139.40 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 137.00 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 129.50, 121.99, 86.90 (quaternary), 33.40 (d, $^{1}J_{C-P}$ = 40

Hz, P{C_6H_{11}}$_2$), 28.20 (s, P{C_6H_{11}}$_2$), 28.05 (s, P{C_6H_{11}}$_2$), 26.95 (s, P{C_6H_{11}}$_2$), 26.09 (d, $^3J_{C\text{-}P}$ = 15 Hz, P{C_6H_{11}}$_2$), 25.17 (s, P{C_6H_{11}}$_2$). **^{19}F NMR** (THF-d_8): δ -128.27 (s, 2F, C_6F_4), -133.29 (d, 4F, $^3J_{F\text{-}F}$ = 22 Hz, *ortho*-C_6F_5), -133.8 (s, 2F, C_6F_4), -163.31 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5), -167.98 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (THF-d_8): δ 9.91 (m). **Anal. Calcd.** for $C_{30}H_{24}BF_{14}P$: C, 52.05; H, 3.49. Found: C, 51.88; H, 3.75 %.

5.2.3 Synthesis of Phosphino-Boranes

Synthesis of $Mes_2P(C_6F_4)B(C_6F_5)_2$ (3-14) through H_2 liberation: A 50 mL glass bomb was charged with $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (0.200 g, 0.262 mmol) and bromobenzene (20 mL), which formed a white slurry. The bomb was heated to 150 °C for 5 hours. At 90 minute intervals, the sample was cooled to 25 °C, briefly opened to dynamic vacuum, to remove H_2, and repressurized with N_2. The resulting deep orange solution was cooled to room temperature and all volatiles were removed *in vacuo*. The red residue was taken up in pentane (10 mL), sonicated for 10 minutes, and filtered to give a white solid and a deep orange filtrate. The solid was identified as starting material. The filtrate was reduced to 5 mL, transferred to a 25 mL vial, and all volatiles removed *in vacuo*. The resulting orange solid was dried under vacuum for 12 hours. Yield 0.150 g (75 %).

(^{t}Bu)(Mes)P(C_6F_4)B(C_6F_5)$_2$ (5-3): A 20 mL vial was charged with (^{t}Bu)(Mes)PH(C_6F_4)BF(C_6F_5)$_2$ (0.500 g, 0.69 mmol), toluene (10 mL) and diethyl ether (1 mL), which formed a white slurry. The mixture was cooled to -35 °C and 3.0 M

MeMgBr in diethyl ether (0.23 mL, 0.76 mmol) was added via syringe. Vigorous gas evolution and immediate formation of a clear orange solution was observed. The reaction was allowed to warm to room temperature and stirred for 12 hours. All volatiles were removed *in vacuo* and the product extracted with hexanes (3 x 20 mL) and filtered through Celite. The solvent was removed *in vacuo* to give an orange solid. Yield 378 mg (78 %).**^{1}H NMR** (CD_2Cl_2): δ 6.94 (m, 2H, P(C_6H_2)), 2.38 (br s, 6H, P(C_6H_2*Me-2,6*), 2.27 (s, 3H, P(C_6H_2*Me-4*), 1.35 (d, 9H, $^{3}J_{H-P}$ = 15 Hz, P{$C(CH_3)_3$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ 59.14 (br s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 148.27 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 145.92 (dm, $^{1}J_{C-F}$ = 230 Hz, *C*F), 145.00 (dm, $^{1}J_{C-F}$ = 240 Hz, *C*F), 144.89 (d, $^{2}J_{C-P}$ = 11 Hz, C_6H_2), 140.57 (s, C_6H_2), 137.91 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 130.28 (m, *meta*-C_6H_2), 114.97 (br m, P-C_6H_2), 35.16 (d, $^{1}J_{C-P}$ = 25 Hz, P{*C*$(CH_3)_3$}), 29.60 (d, $^{2}J_{C-P}$ = 18 Hz, C(*C*$H_3)_3$), 24.84 (d, $^{3}J_{C-P}$ = 16 Hz, C_6H_2*Me-2,6*), 21.09 (s, C_6H_2*Me-4*). **^{19}F NMR** (CD_2Cl_2): δ -131.93 (m, 2F, C_6F_4), -132.46 (m, 4F, *ortho*-C_6F_5), -133.29 (m, 2F, C_6F_4), -149.07 (m, 2F, *para*-C_6F_5), -165.23 (m, 4F, *meta*-C_6F_5), **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ -1.95 (t, $^{3}J_{P-F}$ = 22 Hz). **Anal. Calcd.** for $C_{31}H_{20}BF_{14}P$: C, 53.17; H, 2.88. Found: C, 54.05; H, 3.12 %.

(^{t}Bu)(Ph)P(C_6F_4)B(C_6F_5)$_2$ (5-4): A 20 mL vial was charged with (^{t}Bu)(Ph)PH(C_6F_4)BF(C_6F_5)$_2$ (0.500 g, 0.76 mmol), toluene (10 mL) and diethyl ether (1 mL), which formed a white slurry. The mixture was cooled to -35 °C and 3.0 M MeMgBr in diethyl ether (0.25 mL, 0.76 mmol) was added via syringe. Vigorous gas evolution and immediate formation of a clear yellow solution was observed. The reaction was allowed to warm to room temperature and stirred for 12 hours. All volatiles were removed *in vacuo* and the product extracted with hexanes (3 x 20 mL) and filtered through celite. The

solvent was removed *in vacuo* to give a yellow-orange solid. Yield 394 mg (81 %). **^{1}H NMR** (CD_2Cl_2): δ 7.60-7.56 (m, 2H, P(C_6H_5)), 7.38-7.36 (m, 3H, P(C_6H_5)), 1.33 (d, 9H, $^{3}J_{H-P}$ = 14 Hz, P{$C(CH_3)_3$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ 57.77 (br s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 148.60 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 148.00 (dm, $^{1}J_{C-F}$ = 245 Hz, *C*F), 145.22 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 140.85 (dm, $^{1}J_{C-F}$ = 240 Hz, *C*F), 138.14 (dm, $^{1}J_{C-F}$ = 250 Hz, *C*F), 133.70 (d, $^{2}J_{C-P}$ = 20 Hz, C_6H_5), 129.34 (s, C_6H_5), 128.89 (d, $^{3}J_{C-P}$ = 6 Hz, C_6H_5), 125.17, 119.98, 113.88 (quaternary), 33.02 (d, $^{1}J_{C-P}$ = 20 Hz, P{*C*$(CH_3)_3$}), 29.13 (d, $^{1}J_{C-P}$ = 16 Hz, C(*C*$H_3)_3$). **^{19}F NMR** (CD_2Cl_2): δ -129.69 (m, 2F, C_6F_4), -131.85 (d, 4F, $^{3}J_{F-F}$= 20 Hz, *ortho*-C_6F_5), -133.22 (m, 2F, C_6F_4), -148.09 (br m, 2F, *para*-C_6F_5), -164.98 (t, 4F, $^{3}J_{F-F}$= 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 4.16 (t, $^{3}J_{P-F}$= 35 Hz). **Anal. Calcd.** for $C_{28}H_{14}BF_{14}P$: C, 51.10; H, 2.14. Found: C, 51.55; H, 2.78 %.

5.2.4 Activation of Hydrogen with Phosphines and Boranes

[^{t}Bu$_3$PH][HB(C$_6$F$_5$)$_3$] (5-5): Solid $B(C_6F_5)_3$ (0.506 g, 0.99 mmol) and $^{t}Bu_3P$ (0.200 g, 0.99 mmol) were added to a 50 mL Schlenk flask and dissolved in toluene (20 mL), which formed a colorless solution. The solution was purged with H_2 via a stainless steel needle for 30 minutes during which time a white precipitate formed. The reaction was allowed to stir under a static atmosphere of H_2 for 12 hours. The reaction was then concentrated to half of the original volume and hexanes (10 mL) was added to promote precipitation. The mixture was filtered, washed with hexanes (2 x 5 mL) and dried *in vacuo*. The product was collected as a white solid. Yield 0.635 g (90 %). Crystals suitable for X-ray diffraction were grown from a layered bromobenzene/pentane solution at 25 °C.

^{1}H NMR (C_6D_5Br): δ 4.99 (d, 1H, $^{1}J_{H\text{-}P}$ = 454 Hz, P*H*), 4.18 (q, 1H, $^{1}J_{H\text{-}B}$ = 100 Hz, B*H*), 1.01 (d, 18H, $^{3}J_{H\text{-}P}$ = 16 Hz, P{C(CH_3)$_3$}). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -25.76 (s). **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 148.40 (dm, $^{1}J_{C\text{-}F}$ = 235 Hz, *ortho*-C_6F_5), 137.68 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *para*-C_6F_5), 136.59 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *meta*-C_6F_5), 36.56 (d, $^{1}J_{C\text{-}P}$ = 28 Hz, P{*C*(CH_3)$_3$}), 29.18 (s, PC(*C*H_3)$_3$). **^{19}F NMR** (C_6D_5Br): δ -131.74 (br m, 6F, *ortho*-C_6F_5), -162.89 (br m, 3F, *para*-C_6F_5), -165.75 (br m, 6F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 56.56 (s). **Anal. Calcd.** for $C_{30}H_{29}BF_{15}P$: C, 50.30; H, 4.08. Found: C, 49.94; H, 4.02 %.

[Mes_3PH][$HB(C_6F_5)_3$] (5-6): Solid $B(C_6F_5)_3$ (0.500 g, 0.98 mmol) and Mes_3P (0.380 g, 0.98 mmol) were added to a 50 mL Schlenk flask and dissolved in toluene (20 mL), which formed a violet solution. The solution was purged with H_2 via a stainless steel needle for 30 minutes during which time the solution turned colorless and a white precipitate formed. The reaction was allowed to stir under a static atmosphere of H_2 for 12 hours. The reaction was then concentrated to half of the original volume and hexanes (10 mL) was added to promote precipitation. The mixture was filtered, washed with hexanes (2 x 5 mL) and dried *in vacuo*. The product was collected as a white solid. Yield 0.65 g (74 %). Crystals suitable for X-ray diffraction were grown from a layered bromobenzene/pentane solution at 25 °C. **^{1}H NMR** (C_6D_5Br): δ 7.91 (d, 1H, $^{1}J_{H\text{-}P}$ = 480 Hz, P*H*), 6.58 (d, $^{4}J_{H\text{-}P}$ = 10 Hz, 4H, P(C_6H_2)$_3$), 4.10 (q, 1H, $^{1}J_{H\text{-}B}$ = 112 Hz, B*H*), 1.95 (s, 9H, P(C_6H_2Me-*4*)$_3$), 1.87 (s, 9H, P(C_6H_2Me-*2*)$_3$), 1.62 (s, 9H, P(C_6H_2Me-*6*)$_3$). **^{11}B {^{1}H} NMR** (C_6D_5Br): δ -25.47 (s). **^{13}C {^{1}H} NMR** (C_6D_5Br) partial: δ 148.65 (dm, $^{1}J_{C\text{-}F}$ = 244 Hz, *ortho*-C_6F_5), 148.25 (dm, $^{1}J_{C\text{-}F}$ = 244 Hz, *para*-C_6F_5), 146.99 (d, $^{4}J_{C\text{-}P}$ = 2.78 Hz, *para*-C_6H_2), 143.08 (d, $^{2}J_{C\text{-}P}$ = 102 Hz, *ortho*-C_6H_2), 136.67 (dm, $^{1}J_{C\text{-}F}$ = 246 Hz, *meta*-

C_6F_5), 132.95 (d, $^3J_{C\text{-}P}$ = 11 Hz, *meta*-C_6H_2), 111.06 (d, $^1J_{C\text{-}P}$ = 83 Hz, P-C_6H_2), 21.83 (m, C_6H_2*Me-6*), 21.27 (s, C_6H_2*Me-4*), 20.84 (d, $^3J_{C\text{-}P}$ = 10 Hz, C_6H_2*Me-2*). **^{19}F NMR** (C_6D_5Br): δ -132.77 (d, 6F, $^3J_{F\text{-}F}$ = 22 Hz, *ortho*-C_6F_5), -164.13 (t, 3F, $^3J_{F\text{-}F}$ = 22 Hz, *para*-C_6F_5), -166.95 (t, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P {^{1}H} NMR** (C_6D_5Br): δ -27.53 (s). **Anal. Calcd.** for $C_{45}H_{35}BF_{15}P$: C, 59.89; H, 3.91. Found: C, 59.63; H, 3.42 %.

[^{t}Bu$_3$PH][HB(C$_6$H$_5$)$_3$] (5-7): Solid BPh_3 (0.500 g, 2.06 mmol) and ^{t}Bu$_3$P (0.418 g, 2.07 mmol) were added to a 50 mL Schlenk flask and dissolved in toluene (10 mL), which formed a faint yellow solution. Note: It is imperative that BPh_3 is extremely pure prior to use. The solution was vigoursly purged with H_2 for 60 minutes during which time a white precipitate formed. The reaction was allowed to stir under a static atmosphere of H_2 for 24 hours. The reaction was then concentrated to half of the original volume and hexanes (10 mL) was added to promote precipitation. The mixture was filtered, the solid was washed with hexanes (2 x 5 mL) and dried *in vacuo*. The product was collected as a white solid. Yield 0.298 g (33 %). **^{1}H NMR** (CD_2Cl_2): δ 8.15 (m, 3H, Ph), 7.68 (m, 3H, Ph), 7.40 (m, 3H, Ph), 7.38 (m, 3H, Ph), 7.06 (m, 3H, Ph), 4.28 (d, 1H, $^1J_{H\text{-}P}$ = 435 Hz, P*H*), 2.34 (br s, 1H, B*H*), 1.26 (d, 27H, $^1J_{H\text{-}P}$ = 15 Hz, P{C(CH$_3$)$_3$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -6.88 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 135.35 (s, Ph), 132.30 (s, Ph), 130.11 (s, Ph), 127.78 (s, Ph), 126.99 (s, Ph), 37.61 (d, $^3J_{C\text{-}P}$ = 28 Hz, P{*C*(CH$_3$)$_3$}), 30.34 (s, PC(*C*H$_3$)$_3$). **^{31}P{^{1}H} NMR** (CD_2Cl_2): δ 58.35 (s).

5.2.6 Liberation of H_2 in the Presence of MesCN

$Mes_2P(C_6F_4)B(C_6F_5)_2$(MesCN) (5-8): To a 20 mL vial charged with $Mes_2P(C_6F_4)B(C_6F_5)_2$ (0.100 g, 0.131 mmol) and toluene (10 mL) was added MesCN (0.020 g, 0.138 mmol) in toluene (5 mL) via syringe. Upon addition of MesCN there was a color change from orange to colorless. The reaction was allowed to stir for 30 minutes at room temperature. All volatiles were removed *in vacuo* yielding a white solid. Yield 105 mg (88 %). Alternative synthesis: A J-Young NMR tube was charged with $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (0.058 g, 0.076 mmol), MesCN (0.011 g, 0.076 mmol), and C_6D_5Br (0.75 mL). The solution was heated to 150 °C for 15 minutes. NMR confirmed quantitative product formation. The sample was transferred to a pre-weighed vial and all volatiles removed under vacuum to give a white solid. Yield 51 mg (86 %). **^{1}H NMR** (C_6D_5Br): δ 6.74 (d, 4H, $^4J_{H\text{-}P}$ = 3 Hz, $P(C_6H_2)_2$), 6.52 (s, 2H, $NC(C_6H_2)$), 2.29 (m, 12H, $P(C_6H_2Me\text{-}2,6)_2$), 2.14 (m, 12H, $P(C_6H_2Me\text{-}4)_2$, 2.11 (s, 6H, $NC(C_6H_2Me\text{-}2,6)$), 2.07 (s, 3H, $NC(C_6H_2Me\text{-}4)$). **$^{11}B\{^1H\}$ NMR** (C_6D_5Br): -9.26 (br s). **$^{13}C\{^1H\}$ NMR** (C_6D_5Br) partial: δ 148.24 (dm, $^1J_{C\text{-}F}$ = 244 Hz, C_6F_5), 147.98 (quaternary, $NC(C_6H_2)$), 147.05 (dm, $^1J_{C\text{-}F}$ = 247 Hz, C_6F_4), 146.33 (quaternary, $NC(C_6H_2)$), 142.48 (quaternary, $P(C_6H_2)_2$), 140.33 (dm, $^1J_{C\text{-}F}$ = 235 Hz, C_6F_5), 138.49 (quaternary, $P(C_6H_2)_2$), 136.95 (dm, $^1J_{C\text{-}F}$ = 240 Hz, C_6F_5), 130.11 (s, C-H, $P(C_6H_2)_2$), 128.00 (s, C-H, $NC(C_6H_2)$), 122.20 (quaternary, N≡C), 117.76 (quaternary, $NC(C_6H_2)$), 114.99 (quaternary, $NC(C_6H_2)$), 22.61 (d, $^3J_{C\text{-}P}$ = 17 Hz, $P(C_6H_2Me\text{-}2,6)_2$), 21.80 (s, $NC(C_6H_2Me\text{-}4)$), 20.85 (s, $P(C_6H_2Me\text{-}4)_2$), 19.49 (s, $NC(C_6H_2Me\text{-}2,6)$). **^{19}F NMR** (C_6D_5Br): δ -132.37 (br s, 2F, C_6F_4), -133.62 (m, 4F, *ortho*-C_6F_5), -133.93 (br s, 2F, C_6F_4), -156.12 (m, 2F, *para*-C_6F_5), -163.26 (m,

4F, *meta*-C_6F_5). **$^{31}P\{^1H\}$ NMR** (C_6D_5Br): δ -47.49 (t, $^3J_{P-F}$ = 34 Hz). **Anal. Calcd.** for $C_{46}H_{33}BF_{14}NP$: C, 60.88; H, 3.67; N, 1.54. Found: C, 61.44; H, 3.87; N, 1.79 %.

^{t}Bu$_2$P(C$_6$F$_4$)B(MesCN)(C$_6$F$_5$)$_2$ (5-10): A J-Young NMR tube was charged with ^{t}Bu$_2$PH(C$_6$F$_4$)BH(C$_6$F$_5$)$_2$ (0.049 g, 0.076 mmol), MesCN (0.011 g, 0.076 mmol), and C_6D_5Br (0.075 mL) and sealed. The mixture was heated to 150 °C for 270 minutes. Complete liberation of H_2 and quantitative formation of **5-10** was observed. The sample was transferred to a pre-weighed vial and all volatiles removed *in vacuo* to give a white solid. Yield 52 mg (85 %). **^{1}H NMR** (C_6D_5Br): δ 6.51 (s, 2H, NC(C_6H_2)), 2.15 (s, 6H, NC(C_6H_2*Me-2,6*)), 2.07 (s, 3H, NC(C_6H_2*Me-4*)). 1.25 (d, 18H, $^3J_{H-P}$ = 12 Hz, P{C(CH_3)$_3$}). **$^{11}B\{^1H\}$ NMR** (C_6D_5Br): δ -9.66 (br). **$^{13}C\{^1H\}$ NMR** (C_6D_5Br) partial: δ 148.83 (quaternary, NC(C_6H_2)), 148.28 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 145.86 (quaternary, NC(C_6H_2)), 140.13 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 137.54 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 129.62 (s, C-H, NC(C_6H_2)), 122.21 (quaternary, N≡*C*), 115.61 (quaternary, NC(C_6H_2)), 103.22 (quaternary, BC), 32.97 (d, $^1J_{C-P}$ = 30Hz, P{*C*(CH_3)$_3$}), 30.67 (d, $^2J_{C-P}$ = 18Hz, C(*C*H_3)$_3$). 22.30 (s, NC(C_6H_2*Me-4*)), 19.98 (s, NC(C_6H_2*Me-2,6*)). **^{19}F NMR** (C_6D_5Br): δ -122.28 (m, 1F, C_6F_4), -128.36 (ddd, 1F, $^3J_{F-P}$ = 109 Hz, $^3J_{F-F}$ = 24 Hz, $^4J_{F-F}$ = 15 Hz, C_6F_4), -133.52 (m, 1F, C_6F_4), -133.73 (dd, 1F, $^3J_{F-F}$ = 24 Hz, $^4J_{F-F}$ = 15 Hz, C_6F_4), -133.96 (m, 4F, $^4J_{F-F}$ = 24 Hz, $^3J_{F-F}$ = 10 Hz, *ortho*-C_6F_5), -155.50 (t, 2F, $^4J_{F-F}$ = 22 Hz, *para*-C_6F_5), -167.44 (td, 4F, $^3J_{F-F}$ = 23 Hz, $^3J_{F-F}$ = 10 Hz, *meta*-C_6F_5). **$^{31}P\{^1H\}$ NMR** (C_6D_5Br): δ 22.06 (dd, $^3J_{PF}$ = 109 Hz, $^3J_{PF}$ = 22 Hz).

(^{t}Bu)(Mes)P(C_6F_4)B(C_6F_5)$_2$(MesCN) (5-11): A J-Young NMR tube was charged with (^{t}Bu)(Mes)PH(C_6F_4)BH(C_6F_5)$_2$ (0.054 g, 0.076 mmol), MesCN (0.011 g, 0.076 mmol), and C_6D_5Br (0.075 mL) and sealed. The mixture was heated to 150 °C for 65 minutes. Complete liberation of H_2 and quantitative formation of **5-11** was observed. The sample was transferred to a pre-weighed vial and all volatiles removed *in vacuo* to give a white solid. Yield 55 mg (92 %). **^{1}H NMR** (C_6D_5Br): δ 6.77 (s, 2H, P(C_6H_2)$_2$), 6.50 (s, 2H, NC(C_6H_2)), 2.48 (m, 12H, P(C_6H_2*Me-2,6*)$_2$), 2.28 (m, 12H, P(C_6H_2*Me-4*)$_2$, 2.11 (s, 6H, NC(C_6H_2*Me-2,6*)), 2.06 (s, 3H, NC(C_6H_2*Me-4*)), 1.29 (d, 9H, $^1J_{H\text{-}P}$ = 12 Hz, P{C(CH_3)$_3$}). **^{11}B{^{1}H} NMR** (C_6D_5Br): -8.29 (br s). **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 148.34 (quaternary, NC(C_6H_2)), 148.24 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 145.99 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 145.53 (quaternary, NC(C_6H_2)), 142.26 (quaternary, P(C_6H_2)$_2$), 140.61 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 138.29 (quaternary, P(C_6H_2)$_2$), 137.41 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *C*F), 130.07 (s, C-H, P(C_6H_2)$_2$), 128.18 (s, C-H, NC(C_6H_2)), 122.05 (quaternary, N≡*C*), 117.18 (quaternary, P(C_6H_2)$_2$), 115.12 (quaternary, NC(C_6H_2)), 110.73 (quaternary, NC(C_6H_2)), 34.22 (d, $^1J_{C\text{-}P}$ = 27 Hz, P{*C*(CH_3)$_3$}), 29.51 (d, $^2J_{C\text{-}P}$ = 18 Hz, C(*C*H_3)$_3$), 22.00 (s, P(C_6H_2*Me-2,6*)$_2$), 21.53 (s, NC(C_6H_2*Me-4*)), 20.57 (s, P(C_6H_2*Me-4*)$_2$), 19.70 (s, NC(C_6H_2*Me-2,6*)). **^{19}F NMR** (C_6D_5Br): δ -129.48 (m, 2F, C_6F_4), -133.66 (m, 4F, *ortho*-C_6F_5), -134.12 (m, 2F, C_6F_4), -156.20 (m, 2F, *para*-C_6F_5), -163.32 (m, 4F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ -7.22 (t, $^3J_{P\text{-}F}$ = 25 Hz).

(^{t}Bu)(Ph)PH(C_6F_4)B(MesCN)(C_6F_5)$_2$ (5-12): A J-Young NMR tube was charged with (^{t}Bu)(Ph)PH(C_6F_4)BH(C_6F_5)$_2$ (0.050 g, 0.076 mmol), MesCN (0.011 g, 0.076 mmol), and C_6D_5Br (0.075 mL) and sealed. The mixture was heated to 150 °C for 30 minutes.

Complete liberation of H_2 and quantitative formation of **5-12** was observed. The sample was transferred to a pre-weighed vial and all volatiles removed *in vacuo* to give a white solid. Yield 55 mg (90 %). **^{1}H NMR** (C_6D_5Br): δ 7.61 (m, 2H, P(C_6H_5)), 7.17 (m, 3H, P(C_6H_5)), 6.55 (s, 2H, NC(C_6H_2)), 2.13 (s, 6H, NC(C_6H_2*Me-2,6*)), 2.06 (s, 3H, NC(C_6H_2*Me-4*)). 1.55 (d, 9H, $^3J_{H-P}$ = 14 Hz, P{C(CH_3)$_3$}). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -9.53 (br). **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 149.84 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 149.77 (quaternary, NC(C_6H_2)), 148.66 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 146.62 (quaternary, NC(C_6H_2)), 145.10 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 138.60 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 136.99 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 136.93 (s, C_6H_5), 134.46 (d, $^3J_{C-P}$ = 11 Hz, C_6H_5), 131.39 (d, $^2J_{C-P}$ = 14 Hz, C_6H_5), 130.12 (s, C-H, NC(C_6H_2)), 122.80 (quaternary, N≡*C*), 115.97 (quaternary, NC(C_6H_2)), 112.64 (d, $^1J_{C-P}$ = 78 Hz, P-C_6H_5), 103.79 (quaternary, BC), 35.05 (d, $^1J_{C-P}$ = 42 Hz, P{*C*(CH_3)$_3$}), 26.13 (s, C(*C*H_3)$_3$). 22.47 (s, NC(C_6H_2*Me-4*)), 20.34 (s, NC(C_6H_2*Me-2,6*)). **^{19}F NMR** (C_6D_5Br): δ -127.13 (m, 2F, C_6F_4), -131.11 (m, 2F, C_6F_4), -133.46 (d, 4F, $^4J_{F-F}$ = 22 Hz, *ortho*-C_6F_5), -155.96 (td, 2F, $^4J_{F-F}$ = 21 Hz, $^3J_{F-F}$ = 10 Hz *para*-C_6F_5), - 167.44 (td, 4F, $^3J_{F-F}$ = 22 Hz, , $^3J_{F-F}$ = 10 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 0.25 (t, $^3J_{PF}$ = 37 Hz).

$Cy_2P(C_6F_4)B(MesCN)(C_6F_5)_2$ (5-13): A J-Young NMR tube was charged with $Cy_2PH(C_6F_4)BH(C_6F_5)_2$ (0.054 g, 0.076 mmol), MesCN (0.011 g, 0.076 mmol), and C_6D_5Br (0.75 mL) and sealed. The mixture was heated to 150 °C for 135 minutes. Complete liberation of H_2 and quantitative formation of **5-13** was observed. The sample was transferred to a pre-weighed vial and all volatiles removed *in vacuo* to give a white solid. Yield 54 mg (83 %). **^{1}H NMR** (C_6D_5Br): δ 6.51 (s, 2H, NC(C_6H_2)), 3.00 (m, 2H,

P{C_6H_{11}}$_2$), 2.44 (s, 6H, NC(C_6H_2*Me-2,6*)), 2.40 (s, 3H, NC(C_6H_2*Me-4*)), 1.95 (br, 2H, P{C_6H_{11}}$_2$), 1.71 (br, 4H, P{C_6H_{11}}$_2$), 1.59 (br, 4H, P{C_6H_{11}}$_2$), 1.21 (br m, 10H, P{C_6H_{11}}$_2$). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -10.11 (br s). **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 148.93 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 148.72 (quaternary, NC(*C*$_6$H$_2$)), 148.39 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 145.90 (quaternary, NC(*C*$_6$H$_2$)), 140.76 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 137.68 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 129.64 (s, C-H, NC(*C*$_6$H$_2$)), 122.36 (quaternary, N≡*C*), 115.54 (quaternary, NC(*C*$_6$H$_2$)), 111.03 (quaternary), 33.54 (m, P{*C*$_6$H$_{11}$}$_2$), 31.68 (m, P{*C*$_6$H$_{11}$}$_2$), 30.58 (m, P{*C*$_6$H$_{11}$}$_2$), 27.35 (s, P{*C*$_6$H$_{11}$}$_2$), 27.18 (s, P{*C*$_6$H$_{11}$}$_2$), 26.60 (s, P{*C*$_6$H$_{11}$}$_2$), 22.34 (s, NC(C_6H_2*Me-4*)), 20.87 (s, NC(C_6H_2*Me-2,6*)). **^{19}F NMR** (C_6D_5Br): δ -130.33 (m, 2F, C_6F_4), -133.37 (m, 2F, C_6F_4), -133.60 (m, 4F, $^4J_{F\text{-}F}$ = 24 Hz, $^3J_{F\text{-}F}$ = 10 Hz, *ortho*-C_6F_5), -156.16 (t, 2F, $^3J_{F\text{-}F}$ = 22 Hz , *para*-C_6F_5), -167.95 (m, 4F, $^4J_{F\text{-}F}$ = 24 Hz, $^3J_{F\text{-}F}$ = 10 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ -5.09 (t, $^3J_{P\text{-}F}$ = 36 Hz).

(MesCN)B(C_6F_5)$_3$ (5-14): To a 20 mL vial charged with B(C_6F_5)$_3$ (0.100 g, 0.195 mmol) and toluene (10 mL) was added MesCN (0.028 g, 0.195 mmol) in toluene (5 mL) via syringe. The reaction was allowed to stir for 30 minutes at room temperature. All volatiles were removed *in vacuo* to give a white solid. Yield 115 mg (91 %). **^{1}H NMR** (CD_2Cl_2): δ 7.09 (s, 2H, NC(C_6H_2)), 2.44 (s, 6H, NC(C_6H_2*Me-2,6*)), 2.40 (s, 3H, NC(C_6H_2*Me-4*)). **^{11}B{^{1}H} NMR** (CD_2Cl_2): -10.62 (br s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 149.77 (quaternary, NC(*C*$_6$H$_2$)), 148.60 (dm, $^1J_{C\text{-}F}$ = 244 Hz, *C*F), 146.62 (quaternary, NC(*C*$_6$H$_2$)), 140.90 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 137.97 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 130.12 (s, C-H, NC(*C*$_6$H$_2$)), 128.80 (quaternary, N≡*C*), 115.97 (quaternary, NC(*C*$_6$H$_2$)), 103.79 (quaternary, B-C), 22.47 (s, NC(C_6H_2*Me-4*)), 20.34 (s, NC(C_6H_2*Me-2,6*)). **^{19}F NMR**

(CD_2Cl_2): δ -134.38 (dd, 6F, $^4J_{FF}$ = 24 Hz, $^3J_{FF}$ = 10 Hz, *ortho*-C_6F_5), -157.67 (t, 3F, $^3J_{FF}$ = 22 Hz, *para*-C_6F_5), -164.77 (dt, 6F, $^3J_{FF}$ = 24 Hz, $^3J_{FF}$ = 10 Hz, *meta*-C_6F_5).

5.2.7 Deuterium Labelled Compounds

[Mes_3PD][$DB(C_6F_5)_3$] (5-6$_{PDBD}$): Solid $B(C_6F_5)_3$ (0.025 g, 0.049 mmol) and Mes_3P (0.019 g, 0.049 mmol) were added to a sealable J-Young NMR tube and dissolved in C_6H_5Br (1.0 mL) giving a violet solution. The sample was de-gassed using the freeze-pump-thaw method. The NMR tube was exposed to a constant flow of deuterium gas at 77 K, followed by warming to room temperature, and vigorous shaking for 5 minutes. Addition of deuterium gas was repeated to ensure maximum gas pressure. The sample was left to stand approximately 3 hours. **^{2}H NMR** (C_6H_5Br): δ 7.5 (d, 1D, $^1J_{D\text{-}P}$ = 74 Hz, P*D*), 3.80 (br s, 1D). **^{11}B{^{1}H} NMR** (C_6H_5Br): δ -25.5 (br s). **^{31}P{^{1}H} NMR** (C_6H_5Br): δ -28.1 (t, $^1J_{P\text{-}D}$ = 74 Hz, P*D*).

$Mes_2PD(C_6F_4)BF(C_6F_5)_2$ (3-6$_{PDBF}$): Prepared in same fashion as **2-5** using Mes_2PD. **^{2}H NMR** (CH_2Cl_2): δ 7.75 (d, $^1J_{D\text{-}P}$ = 77 Hz, P*D*). **^{31}P{^{1}H} NMR** (CH_2Cl_2): δ -37.53 (tt, $^3J_{P\text{-}D}$ = 77 Hz, $^3J_{P\text{-}F}$ = 9 Hz, *P*D).

$Mes_2PD(C_6F_4)BH(C_6F_5)_2$ (3-6$_{PDBH}$): Prepared from **3-6$_{PDBF}$** using Me_2SiClH in the same fashion as **3-6**. **^{2}H NMR** (CH_2Cl_2): δ 7.78 (d, $^1J_{D\text{-}P}$ = 77 Hz, P*D*). **^{31}P {^{1}H} NMR** (CH_2Cl_2): δ -37.49 (tt, $^3J_{P\text{-}D}$ = 77 Hz, $^3J_{P\text{-}F}$ = 9 Hz, *P*D).

$Mes_2PH(C_6F_4)BD(C_6F_5)_2$ ($3\text{-}6_{PHBD}$): Prepared from **2-5** using Me_2SiClD in the same fashion as **3-6**. **^2H NMR** (CH_2Cl_2): δ 3.48 (br, B*D*). **^{11}B NMR** (CH_2Cl_2): δ -25.4 (br). **$^{31}P\{^1H\}$ NMR** (CH_2Cl_2): δ -37.40 (m, $^3J_{P\text{-}F}$ = 8 Hz).

$Mes_2PD(C_6F_4)BD(C_6F_5)_2$ ($3\text{-}6_{PDBD}$): Prepared from **$3\text{-}6_{PDBF}$** using Me_2SiClD in the same fashion as **3-6** or by reaction of **3-14** with D_2. **^2H NMR** (CH_2Cl_2): δ 7.76 (d, $J_{D\text{-}P}$ = 77 Hz, P*D*), 3.50 (br, B*D*). **^{11}B NMR** (CH_2Cl_2): δ -25.36 (br). **$^{31}P\{^1H\}$ NMR** (CH_2Cl_2): δ -37.49 (tt, $^3J_{P\text{-}D}$ = 77 Hz, $^3J_{P\text{-}F}$ = 9 Hz, *P*D).

$^tBu_2PH(C_6F_4)BD(C_6F_5)_2$ ($3\text{-}5_{PHBD}$): Prepared from **2-4** using Me_2SiClD in the same fashion as **$3\text{-}6_{PHBD}$**. **^2H NMR** (CH_2Cl_2): δ 3.75 (br, B*D*). **^{11}B NMR** (CH_2Cl_2): δ -25.43 (br).

5.2.8 Activation of H_2O with Phosphines and $B(C_6F_5)_3$

$[Mes_3PH][HOB(C_6F_5)_3]$ (5-15): Solid $B(C_6F_5)_3$ (0.200 g, 0.39 mmol) and Mes_3P (0.152 g, 0.39 mmol) were added to a 50 mL Schlenk flask and dissolved in toluene (20 mL) giving a violet solution. To this solution was added distilled and de-oxygenated water via syringe (7 μL, 0.39 mmol) at room temperature. The reaction mixture was stirred vigorously for 5 minutes at which time the mixture became colorless and a white precipitate formed. After stirring for a further 20 minutes the solid re-dissolved and subsequently oiled out of solution. All volatiles were removed *in vacuo* to give a white solid. Pentane (10 mL) was added forming a white slurry which was stirred for 60

minutes. All volatiles were removed *in vacuo* and the resulting white solid was dried under vacuum for 24 hours. Yield 0.340 g (95 %). **^{1}H NMR** (CD_2Cl_2): δ 8.27 (d, 1H, $^1J_{H-P}$ = 480 Hz, P*H*), 7.17 (br s, 3H, P(C_6H_2)$_3$), 7.08 (br s, 3H, P(C_6H_2)$_3$), 5.01 (br s, 1H, BO*H*), 2.38 (s, 9H, P(C_6H_2*Me-4*)$_3$), 2.30 (s, 9H, P(C_6H_2*Me-2*)$_3$), 2.02 (s, 9H, P(C_6H_2*Me-6*)$_3$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -3.74 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 148.52 (dm, $^1J_{C-F}$ = 245 Hz, *C*F), 147.82 (s, *para*-C_6H_2), 144.86 (m, *ortho*-C_6H_2), 143.32 (m, *ortho*-C_6H_2), 139.16 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 137.19 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 133.71 (d, $^3J_{C-P}$ = 10 Hz, *meta*-C_6H_2), 132.42 (d, $^3J_{C-P}$ = 11 Hz, *meta*-C_6H_2), 112.03 (d, $^1J_{C-P}$ = 83 Hz, P-C_6H_2), 22.46 (m, $C_6H_2Me_3$), 21.72 (s, $C_6H_2Me_3$), 21.21 (m, $C_6H_2Me_3$). **^{19}F NMR** (CD_2Cl_2): δ -136.42 (d, 6F, $^3J_{F-F}$ = 23 Hz, *ortho*-C_6F_5), -162.94 (br s, 3F, *para*-C_6F_5), -166.96 (t, 6F, $^3J_{F-F}$ = 21 Hz, *meta*-C_6F_5). **^{31}P NMR** (CD_2Cl_2): δ -26.86 (d, $^1J_{P-H}$ = 480 Hz, P*H*). **^{1}H NMR** (CD_2Cl_2, 203 K): δ 8.17 (d, 1H, $^1J_{H-P}$ = 482 Hz, P*H*), 8.10 (br s, 1H, BO*H*), 7.09 (d, 3H, $^4J_{H-P}$ = 5 Hz, P(C_6H_2)$_3$), 6.99 (d, 3H, $^4J_{H-P}$ = 5 Hz, P(C_6H_2)$_3$), 2.30 (s, 9H, P(C_6H_2*Me-4*)$_3$), 2.24 (s, 9H, P(C_6H_2*Me-2*)$_3$), 1.89 (s, 9H, P(C_6H_2*Me-6*)$_3$). **^{19}F NMR** (CD_2Cl_2, 203 K): δ -136.94 (d, 6F, $^3J_{F-F}$ = 22 Hz, *ortho*-C_6F_5), -162.76 (br s, 3F, *para*-C_6F_5), -166.66 (d, 6F, $^3J_{F-F}$ = 22 Hz, *meta*-C_6F_5). **Anal. Calcd.** for $C_{45}H_{35}BF_{15}PO$: C, 58.84; H, 3.84. Found: C, 59.78; H, 4.56 %.

[Mes$_3$PH][HO{B(C$_6$F$_5$)$_3$}$_2$] (5-16): An NMR tube was charged with [Mes$_3$PH][HOB(C$_6$F$_5$)$_3$] (0.040 g, 0.044 mmol), B(C$_6$F$_5$)$_3$ (0.022 g, 0.044 mmol), and CD_2Cl_2 (0.75 mL). The NMR tube was vigorously shaken for 1 minute to ensure all solids dissolved. NMR confirmed immediate and quantitative product formation. Removing all volatiles *in vacuo* gave the product as a white solid in 72% yield (45 mg).

Crystals suitable for X-ray diffraction were obtained by adding a small amount of pentane to a concentrated CH_2Cl_2 of product and letting it stand 24 hours at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 8.25 (d, 1H, $^1J_{H\text{-}P}$ = 480 Hz, P*H*), 7.17 (br s, 3H, P(C_6H_2)$_3$), 7.08 (br s, 3H, P(C_6H_2)$_3$), 6.34 (br s, 1H, BO*H*), 2.38 (s, 9H, P(C_6H_2*Me-4*)$_3$), 2.29 (s, 9H, P(C_6H_2*Me-2*)$_3$), 2.02 (s, 9H, P(C_6H_2*Me-6*)$_3$). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -0.45 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2) partial: δ 148.23 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 147.90 (s, *para*-C_6H_2), 144.08 (m, *ortho*-C_6H_2), 143.30 (m, *ortho*-C_6H_2), 140.30 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 137.08 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 133.81 (d, $^3J_{C\text{-}P}$ = 11 Hz, *meta*-C_6H_2), 132.38 (d, $^3J_{C\text{-}P}$ = 11 Hz, *meta*-C_6H_2), 111.99 (d, $^1J_{C\text{-}P}$ = 80 Hz, P-C_6H_2), 22.46 (m, $C_6H_2Me_3$), 21.72 (s, $C_6H_2Me_3$), 21.54 (m, $C_6H_2Me_3$). **^{19}F NMR** (CD_2Cl_2): δ -133.84 (br s, 6F, *ortho*-C_6F_5), -160.02 (t, 3F, $^3J_{F\text{-}F}$ = 21 Hz, *para*-C_6F_5), -166.06 (t, 6F, $^3J_{F\text{-}F}$ = 23 Hz, *meta*-C_6F_5). **^{31}P NMR** (CD_2Cl_2): δ -26.85 (d, $^1J_{P\text{-}H}$ = 480 Hz, P*H*). **^{1}H NMR** (CD_2Cl_2, 203 K): δ 8.14 (d, 1H, $^1J_{H\text{-}P}$ = 480 Hz, P*H*), 7.09 (d, 3H, $^4J_{H\text{-}P}$ = 5 Hz, P(C_6H_2)$_3$), 6.99 (d, 3H, $^4J_{H\text{-}P}$ = 5 Hz, P(C_6H_2)$_3$), 6.58 (t, $J_{H\text{-}F}$ = 18 Hz 1H, BO*H*), 2.30 (s, 9H, P(C_6H_2*Me-4*)$_3$), 2.24 (s, 9H, P(C_6H_2*Me-2*)$_3$), 1.90 (s, 9H, P(C_6H_2*Me-6*)$_3$). **^{19}F NMR** (CD_2Cl_2, 203 K): δ -127.17 (t, 1F, $^3J_{F\text{-}F}$ = 32 Hz, C*F*), -127.17 (d, 1F, $^3J_{F\text{-}F}$ = 24 Hz, C*F*), -129.27 (t, 1F, $^3J_{F\text{-}F}$ = 28 Hz, C*F*), -130.80 (t, 1F, $^3J_{F\text{-}F}$ = 28 Hz, C*F*), -135.58 (s, 1F, C*F*), -137.80 (t, 1F, $^3J_{F\text{-}F}$ = 34 Hz, C*F*), -155.32 (t, 1F, $^3J_{F\text{-}F}$ = 20 Hz, C*F*), -155.98 (t, 1F, $^3J_{F\text{-}F}$ = 30 Hz, C*F*), -157.22 (t, 1F, $^3J_{F\text{-}F}$ = 24 Hz, C*F*), -160.53 (t, 1F, $^3J_{F\text{-}F}$ = 22 Hz, C*F*), -162.16 (m, 2F, $^3J_{F\text{-}F}$ = 18 Hz, C*F*), -162.78 (t, 1F, $^3J_{F\text{-}F}$ = 20 Hz, C*F*), -162.95 (t, 1F, $^3J_{F\text{-}F}$ = 18 Hz, C*F*), -163.68 (t, 1F, $^3J_{F\text{-}F}$ = 25 Hz, C*F*). **Anal. Calcd.** for $C_{63}H_{35}B_2F_{30}PO$: C, 52.90; H, 2.47. Found: C, 54.10; H, 3.10 %.

5.2.9 Liberation of H_2 in the Presence of R_3PO

General procedure for the heating of $R_2PH(C_6F_4)BH(C_6F_5)_2$ R = ^{t}Bu (5-5), R = Mes (5-6) in the presence of R_3PO and MesCN. These reactions were performed in a similar fashion and thus only one preparation is detailed. A sealable J-Young NMR tube was charged with $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (0.035 g, 0.046 mmol), Ph_3PO (0.014 g, 0.050 mmol), MesCN (0.007 g, 0.048 mmol) and C_6D_5Br (1.142 g) and sealed forming a 0.060 M phosphonium borate solution. The sample was inserted into a NMR spectrometer pre-heated to 100 °C and allowed to reach thermal equilibrium over 2 minutes. The reaction was monitored by ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopy until complete H_2 loss was observed (See table 5.9 for experiment times).

$Mes_2P(C_6F_4)B(C_6F_5)_2(Et_3PO)$ (5-17): A J-Young NMR tube was charged with $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (0.050 g, 0.066 mmol), Et_3PO (0.09 g, 0.068 mmol), and bromobenzene (0.75 mL). The solution was heated to 150 °C for 30 minutes. NMR confirmed quantitative product formation. The sample was transferred to a pre-weighed vial and all volatiles were removed under vacuum to give a white solid. Yield 48 mg (82 %). **^1H NMR** (C_6D_5Br): δ 6.73 (d, 4H, $^4J_{H\text{-}P}$ = 4 Hz, $P(C_6H_2)_2$), 2.27 (s, 12H, $P(C_6H_2Me\text{-}2,6)_2$), 2.14 (s, 6H, $P(C_6H_2Me\text{-}4)_2$), 1.51 (m, 6H, Et), 0.91 (m, 9H, Et). **$^{11}B\{^1H\}$ NMR** (C_6D_5Br): -2.1 (br s). **$^{13}C\{^1H\}$ NMR** (C_6D_5Br) partial: δ 148.40 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 147.24 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 143.02 (quaternary, $P(C_6H_2)_2$), 141.39 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 139.77 (quaternary, $P(C_6H_2)_2$), 137.20 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 130.87 (*C*-H, $P(C_6H_2)_2$), 121.15 (quaternary), 23.11 (d, $^2J_{C\text{-}P}$ = 17 Hz, $P(C_6H_2Me\text{-}2,6)_2$), 21.26 (s,

P(C_6H_2*Me-4*)$_2$), 17.97 (d, $^1J_{C\text{-}P}$ = 67 Hz, PEt), 5.35 (s, PEt). **^{19}F NMR** (C_6D_5Br): δ -132.77 (m, 4F, *ortho*-C_6F_5), -133.17 (m, 2F, C_6F_4), -133.25 (m, 2F, C_6F_4), -158.12 (m, 2F, *para*-C_6F_5), -164.10 (m, 4F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 77.08 (s, Et_3PO), -48.30 (t, $^3J_{P\text{-}F}$ = 27 Hz).

^{t}Bu$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$(Et$_3$PO) (5-18): A J-Young NMR tube was charged with ^{t}Bu$_2$PH(C$_6$F$_4$)BH(C$_6$F$_5$)$_2$ (0.050 g, 0.078 mmol), Et_3PO (0.011 g, 0.080 mmol), and bromobenzene and sealed. The mixture was heated to 150 °C for 60 minutes. Complete liberation of H_2 and quantitative formation of **5-18** was observed. The sample was transferred to a pre-weighed vial and all volatiles removed under vacuum to give a white solid. Yield 50 mg (83 %). **^{1}H NMR** (C_6D_5Br): δ 1.52 (m, 6H, Et), 1.11 (d, 18H, $^3J_{H\text{-}P}$ = 13 Hz, P{C(CH$_3$)$_3$}), 0.93 (m, 9H, Et).**^{11}B{^{1}H} NMR** (C_6D_5Br): δ -2.51 (br). **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 150.05 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 148.50 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 146.98 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 139.12 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 137.10 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 121.34 (quaternary), 32.97 (d, $^1J_{C\text{-}P}$ = 29 Hz, P{*C*(CH$_3$)$_3$}), 30.67 (d, $^2J_{C\text{-}P}$ = 26 Hz, C(*C*H$_3$)$_3$), 17.22 (d, $^1J_{C\text{-}P}$ = 66 Hz, PEt), 4.88 (d, $^2J_{C\text{-}P}$ = 5 Hz, PEt). **^{19}F NMR** (C_6D_5Br): δ -122.51 (m, 1F, C_6F_4), -128.95 (ddd, 1F, $^3J_{F\text{-}P}$ = 107 Hz, $^3J_{F\text{-}F}$ = 25 Hz, $^4J_{F\text{-}F}$ = 14 Hz, C_6F_4), -133.60 (m, 2F, C_6F_4), -134.28 (m, 4F, *ortho*-C_6F_5), -158.35 (t, 2F, $^4J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -164.24 (m, 4F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 76.15 (s, PEt), 21.35 (dd, $^3J_{PF}$ = 108 Hz, $^3J_{PF}$ = 26 Hz, P^{t}Bu).

Mes$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$(Ph$_3$PO) (5-19): To a 20 mL vial charged with Mes$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (0.100 g, 0.131 mmol) and toluene (5 mL) was added Ph_3PO (0.040

g, 0.143 mmol) in toluene (5 mL) via syringe. Upon addition of Ph_3PO there was a color change from orange to colorless. The reaction was allowed to stir for 30 minutes at room temperature. All volatiles were removed *in vacuo* yielding a white solid. Yield 135 mg (98 %). **^{1}H NMR** (C_6D_5Br): δ 7.90 (m, 6H, Ph), 7.61 (m, 3H, Ph), 7.39 (m, 6H, Ph), 6.93 (d, 4H, $^4J_{H\text{-}P}$ = 3 Hz, P(C_6H_2)$_2$), 2.49 (s, 12H, P(C_6H_2*Me-2,6*)$_2$), 2.35 (s, 6H, P(C_6H_2*Me-4*)$_2$). **^{11}B {^{1}H} NMR** (C_6D_5Br): -1.2 (br s). **^{13}C {^{1}H} NMR** (C_6D_5Br) partial: δ 148.50 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 144.26 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 142.87 (quaternary, P(C_6H_2)$_2$), 136.66 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 134.12 (*C*-H, Ph), 132.81 (*C*-H, Ph), 132.37 (*C*-H, Ph), 130.50 (*C*-H, P(C_6H_2)$_2$), 129.10 (*C*-H, Ph), 128.63 (*C*-H, Ph), 23.02 (d, $^3J_{C\text{-}P}$ = 15 Hz, P(C_6H_2*Me-2,6*)$_2$), 21.30 (s, P(C_6H_2*Me-4*)$_2$), **^{19}F NMR** (C_6D_5Br): δ -132.48 (m, 4F, *ortho*-C_6F_5), -133.23 (m, 2F, C_6F_4), -133.39 (m, 2F, C_6F_4), -158.15 (m, 2F, *para*-C_6F_5), -164.29 (m, 4F, *meta*-C_6F_5). **^{31}P {^{1}H} NMR** (C_6D_5Br): δ 45.51, (s, Ph_3PO), -48.30 (t, $^3J_{P\text{-}F}$ = 27 Hz Mes_2P).

5.2.10 Activation of PhSSPh and HSPh

^{t}Bu$_2$(PhS)P(C_6F_4)B(SPh)(C_6F_5)$_2$ (5-20): A 20 mL vial was charged with ^{t}Bu$_2$P(C_6F_4)B(C_6F_5)$_2$ (0.200 g, 0.31 mmol) and toluene forming an orange solution. To this solution was added PhSSPh (0.070 g, 0.32 mmol) in toluene (5 mL) dropwise at room temperature. An immediate a color change from orange to faint yellow was observed. The reaction was stirred at room temperature for 1 hour. All volatiles were removed *in vacuo* to give an off-yellow solid. Yield 205 mg (76 %). Note: Addition of PhSSPh to an NMR scale sample of ^{t}Bu$_2$P(C_6F_4)B(C_6F_5)$_2$ in C_6D_5Br showed formation of **5-20** to be facile at -

30 °C. **^{1}H NMR** (C_6D_5Br): δ 7.86 (d, 2H, $^3J_{H-H}$ = 7 Hz, Ph), 7.78 (d, 2H, $^3J_{H-H}$ = 7 Hz, Ph), 7.54 (d, 2H, $^3J_{H-H}$ = 8 Hz, Ph), 7.43 (m, 2H, Ph), 7.21 (t, 2H, $^3J_{H-H}$ = 8 Hz, Ph), 1.34 (d, 18H, $^3J_{H-P}$ = 19 Hz, P{C(CH_3)$_3$}). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -9.76. **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 149.84 (dm, $^1J_{C-F}$ = 254 Hz, *C*F), 148.56 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 146.32 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 142.07 (s, PS*Ph*), 139.35 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 137.41 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 135.17 (s, PS*Ph*), 133.67 (s, BS*Ph*), 131.72 (s, PS*Ph*), 128.71 (d, $^2J_{C-P}$ = 120 Hz, quaternary, PS*Ph*), 127.91 (s, BS*Ph*), 124.64 (s, BS*Ph*), 45.16 (d, $^1J_{C-P}$ = 22 Hz, P{*C*(CH_3)$_3$}), 28.58 (s, C(*C*H_3)$_3$). **^{19}F NMR** (C_6D_5Br): δ -123.93 (br s, 3F, C_6F_4), -130.35 (br s, 1F, C_6F_4), -130.89 (m, 4F, $^3J_{F-F}$ = 20 Hz, *ortho*-C_6F_5), -161.04 (m, 2F, $^3J_{F-F}$ = 17 Hz, *para*-C_6F_5), -165.36 (m, 4F, $^3J_{F-F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 76.16 (s). **Anal. Calcd.** for $C_{38}H_{28}BF_{14}PS_2$: C, 53.29; H, 3.29. Found: C, 54.05; H, 3.85 %.

^{t}Bu$_2$P(S)(C_6F_4)B(C_6F_5)$_2$ (5-21): [Method A] A 20 mL vial was charged with ^{t}Bu$_2$P(C_6F_4)B(C_6F_5)$_2$ (0.132 g, 0.21 mmol), S_8 (0.007 g, 0.027 mmol), and toluene (10 mL) forming a yellow slurry. The reaction was stirred at room temperature for 12 hours. The reaction mixture was filtered through Celite and all volatiles were removed *in vacuo* to give a sticky yellow solid. The product was slurried in hexanes and stirred for 30 minutes and the solvent removed *in vacuo* to give an off-yellow powder. Yield 120 mg (87 %). **[Method B]** A J-Young NMR tube was charged with ^{t}Bu$_2$PH(C_6F_4)BH(C_6F_5)$_2$ (0.029 g, 0.045 mmol), S_8 (0.010 g, 0.039 mmol), and C_6D_5Br (0.75 mL) forming a slurry. The NMR tube was sealed and heated to 150 °C for 10 minutes. During this time vigorous bubbling was observed (H_2 elimination), all solids dissolved, and the reaction became

intense yellow in color. The reaction was cooled and NMR confirmed 100 % product formation and no coordination of the excess S_8 to boron. **^{1}H NMR** (C_6D_5Br): δ 1.31 (d, 18H, $^{1}J_{H\text{-}P}$ = 17 Hz, P{C(CH_3)$_3$}. **^{11}B{^{1}H} NMR** (C_6D_5Br): Signal broadened into baseline. **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 148.87 (dm, $^{1}J_{C\text{-}F}$ = 251 Hz, *C*F), 144.89 (dm, $^{1}J_{C\text{-}F}$ = 257 Hz, *C*F), 137.72 (dm, $^{1}J_{C\text{-}F}$ = 257 Hz, *C*F), 113.82 (quaternary) 33.62 (d, $^{1}J_{C\text{-}P}$ = 39 Hz, P{*C*(CH_3)$_3$}), 27.67 (s, C(*C*H_3)$_3$). **^{19}F NMR** (C_6D_5Br): δ -119.44 (s, 1F, C_6F_4), -125.38 (s, 1F, C_6F_4), -126.74 (s, 1F, C_6F_4), 127.78 (s, 4F, *ortho*-C_6F_5), -130.01 (s, 1F, C_6F_4), -144.49 (s, 2F, *para*-C_6F_5), -160.46 (s, 4F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (C_6D_5Br): δ 85.91 (s).

[^{t}Bu$_3$(PhS)P][B(SPh)(C_6F_5)$_3$] (5-22): To a 50 mL reaction bomb was added $^{t}Bu_3P$ (0.081 g, 0.401 mmol), $B(C_6F_5)_3$ (0.200 g, 0.391 mmol), and toluene (10 mL). Immediately to this solution was added PhSSPh (0.085 g, 0.399 mmol) in toluene (1 mL) via syringe. The reaction was sealed under nitrogen and allowed to stir for 6 hours at which time the product precipitated out of solution as a yellow oil. All volatiles were then removed *in vacuo* to give a white solid. Yield 305 mg (84 %). Note: Addition of PhSSPh to an NMR scale sample of $^{t}Bu_3P$ and $B(C_6F_5)_3$ in C_6D_5Br showed formation of **5-22** to be facile at -30°C. **^{1}H NMR** (CD_2Cl_2): δ 7.89 (m, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 7.57 (m, 1H, $^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 7.49 (m, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 7.09 (m, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 6.88 (m, 3H, $^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 1.67 (d, 27H, $^{3}J_{H\text{-}P}$ = 16 Hz, P{C(CH_3)$_3$}). **^{11}B {^{1}H} NMR** (CD_2Cl_2): δ -9.95 (s). **^{13}C {^{1}H} NMR** (CD_2Cl_2) partial: δ 148.56 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 142.72 (s, PS*Ph*), 138.96 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 138.48 (s, PS*Ph*), 137.11 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 133.43 (s, BS*Ph*), 131.30 (s, PS*Ph*), 128.94 (d, $^{2}J_{C\text{-}P}$ = 110 Hz, quaternary, PS*Ph*), 127.72

(s, BS*Ph*), 124.02 (s, BS*Ph*), 46.46 (d, $^{1}J_{C\text{-}P}$ = 15 Hz, P{*C*(CH_3)$_3$}), 30.96 (s, C(*C*H_3)$_3$). **^{19}F NMR** (CD_2Cl_2): δ -131.70 (d, 6F, $^{3}J_{F\text{-}F}$ = 23 Hz, *ortho*-C_6F_5), -163.65 (t, 3F, $^{3}J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -167.56 (m, 6F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P NMR** (CD_2Cl_2): δ 85.71 (s).

^{t}Bu$_2$PH(C_6F_4)B(SPh)(C_6F_5)$_2$ (5-23): A 20 mL vial was charged with ^{t}Bu$_2$P(C_6F_4)B(C_6F_5)$_2$ (0.100 g, 0.16 mmol) and toluene (5 mL) forming a orange solution. To this solution was added HSPh (0.017 g, 16 uL, 0.32 mmol) in toluene (5 mL) dropwise at room temperature. Immediately a color change was observed from orange to colorless. The reaction was stirred at room temperature for 1 hour. All volatiles were removed *in vacuo* to give a white solid. Yield 96 mg (82 %). **^{1}H NMR** (C_6D_5Br): δ 7.63 (m, 1H, $^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 7.30 (m, 1H, Ph), 7.24 (m, 2H, Ph), 7.10 (m, 1H, $^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 6.13 (d, 1H, $^{1}J_{H\text{-}P}$ = 480 Hz), 1.34 (d, 18H, $^{3}J_{H\text{-}P}$ = 19 Hz, P{C(CH_3)$_3$}). **^{11}B{^{1}H} NMR** (C_6D_5Br): δ -9.53 (s). **^{13}C{^{1}H} NMR** (C_6D_5Br) partial: δ 151.10 (dm, $^{1}J_{C\text{-}F}$ = 260 Hz, *C*F), 149.80 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 146.25 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 140.13 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 138.34 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 134.92 (s, Ph), 128.96 (s, Ph), 125.70 (s, Ph), 36.51 (d, $^{1}J_{C\text{-}P}$ = 30 Hz, P{*C*(CH_3)$_3$}), 28.25 (s, C(*C*H_3)$_3$). **^{19}F NMR** (C_6D_5Br): δ -123.95 (m, 2F, $^{3}J_{F\text{-}F}$ = 25 Hz, C_6F_4), -127.36 (m, 1F, $^{3}J_{F\text{-}F}$ = 17 Hz, C_6F_4), -130.50 (s, 4F, $^{3}J_{F\text{-}F}$ = 23 Hz, *ortho*-C_6F_5), -132.77 (m, 1F, $^{3}J_{F\text{-}F}$ = 25 Hz, C_6F_4), -160.81 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -165.38 (m, 4F, $^{3}J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P NMR** (C_6D_5Br): δ 32.41 (d, $^{1}J_{P\text{-}H}$ = 486 Hz). **Anal. Calcd.** for $C_{32}H_{24}BF_{14}PS_2$: C, 51.36; H, 3.23. Found: C, 52.04; H, 3.60 %.

[^{t}Bu$_3$PH][B(SPh)(C$_6$F$_5$)$_3$] (5-24): To a 50 mL reaction bomb was added ^{t}Bu$_3$P (0.040 g, 0.200 mmol), B(C$_6$F$_5$)$_3$ (0.100 g, 0.195 mmol), and toluene (10 mL). Immediately to this solution was added HSPh (0.20 mL, 2.00 mmol) via syringe. The reaction was sealed under nitrogen and allowed to stir for 6 hours at which time a pale yellow oil precipitated out of solution. All volatiles were then removed *in vacuo* to give a white solid. Yield 135 mg (84 %). Crystals suitable for X-ray diffraction were grown via slow diffusion of pentane into a concentrated CH_2Cl_2 solution of **5-24** at 25 °C. **^{1}H NMR** (CD_2Cl_2): δ 7.10 (d, 2H, $^3J_{H\text{-}H}$ = 9 Hz, Ph), 6.91 (m, 3H, $^3J_{H\text{-}H}$ = 8 Hz, Ph), 5.65 (d, 1H, $^1J_{H\text{-}P}$ = 442 Hz, P*H*), 1.59 (d, 27H, $^3J_{H\text{-}P}$ = 17 Hz, P{C(CH$_3$)$_3$}). **^{11}B{^{1}H} NMR** (CD_2Cl_2): δ -9.29 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ 148.34 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 139.13 (dm, $^1J_{C\text{-}F}$ = 255 Hz, *C*F), 137.26 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *C*F), 133.08 (s, Ph), 128.09 (s, Ph), 124.64 (s, Ph), 123.51 (br, quaternary), 37.97 (d, $^1J_{C\text{-}P}$ = 28 Hz, P{*C*(CH$_3$)$_3$}), 30.38 (s, C(*C*H$_3$)$_3$). **^{19}F NMR** (CD_2Cl_2): δ -131.89 (d, 6F, $^3J_{F\text{-}F}$ = 23 Hz, *ortho*-C$_6$*F*$_5$), -163.14 (t, 3F, $^3J_{F\text{-}F}$ = 22 Hz, *para*-C$_6$*F*$_5$), -167.39 (m, 6F, $^3J_{F\text{-}F}$ = 22 Hz, *meta*-C$_6$*F*$_5$). **^{31}P NMR** (CD_2Cl_2): δ 56.50 (dm, $^1J_{P\text{-}H}$ = 444 Hz, $^3J_{P\text{-}H}$ = 17 Hz)

Reaction between HSPh and B(C$_6$F$_5$)$_3$ (1:1): A NMR tube was charged with B(C$_6$F$_5$)$_3$ (0.025 g, 0.049 mmol), PhSH (5 μL, 0.05 mmol), and CD_2Cl_2 (0.75 mL). The sample was shaken and analyzed by NMR spectroscopy. **^{19}F NMR** (CD_2Cl_2): δ -126.0 (s, 6F, *ortho*-C$_6$*F*$_5$), -142.3 (s, 3F, *para*-C$_6$*F*$_5$), -158.8 (s, 6F, *meta*-C$_6$*F*$_5$). **^{19}F NMR** (CD_2Cl_2, 213 K): δ -128.5 (s, 6F, *ortho*-C$_6$*F*$_5$), -150.6 (s, 3F, *para*-C$_6$*F*$_5$), -160.2 (s, 6F, *meta*-C$_6$*F*$_5$).

Reaction between HSPh and $B(C_6F_5)_3$ (12:1): A NMR tube was charged with $B(C_6F_5)_3$ (0.025 g, 0.049 mmol), PhSH (60 μL, 0.60 mmol), and CD_2Cl_2 (0.75 mL). The sample was shaken and analyzed by NMR. **^{19}F NMR** (CD_2Cl_2): δ -129.7 (s, 6F, *ortho*-C_6F_5), -149.9 (s, 3F, *para*-C_6F_5), -162.4 (s, 6F, *meta*-C_6F_5). **^{19}F NMR** (CD_2Cl_2, 213 K): δ -131.2 (s, 6F, *ortho*-C_6F_5), -155.4 (s, 3F, *para*-C_6F_5), -163.4 (s, 6F, *meta*-C_6F_5).

Table 5.1 Selected NMR data for phosphonium borates, and phosphino-borane adducts of MesCN.

Compound	δ ^{31}P (J_{P-H})	δ ^{11}B(J_{B-H})	^{19}F Δ_{p-m}*	δ ^{19}F (o-F, p-F, m-F)
Reference (R = MesCN)				
$B(C_6F_5)_3$[98]		59	18.2	-128.5, -143.1, -161.3
$(R)B(C_6F_5)_3$[a]		-10.6	7.1	-134.4, -157.7, -164.8
Phosphonium Borates $R_2PH(C_6F_4)BH(C_6F_5)_2$ and (^{t}Bu)R'$PH(C_6F_4)BH(C_6F_5)_2$				
3-5 R = ^{t}Bu[b]	34.0(462)	-25.2(82)	3.6	-134.1, -164.0, -167.6
3-6 R = Mes[b]	-37.9(502)	-25.2(85)	3.5	-134.1, -163.9, -167.4
5-1 R' = Mes[c]	-2.9 (467)	-24.7(85)	3.1	-133.5, -165.4, -168.5
5-2 R' = Ph[b]	20.2(480)	-24.9(94)	3.6	-134.0, -163.8, -167.4
5-9 R = Cy[c]	9.9(495)	-24.6(88)	4.7	-133.8, -163.3, -168.0
Phosphino-boranes $R_2P(C_6F_4)B(C_6F_5)_2$ and (^{t}Bu)R'$P(C_6F_4)B(C_6F_5)_2$				
3-13 R = ^{t}Bu[a]	25.1	50	18.1	-128.9, -142.6, -160.7
3-14 R = Mes[a]	-41.7	55	17.6	-129.3, -143.0, -160.6
5-3 R' = Mes[b]	-2.0	59	16.1	-132.5, -149.1, 165.2
5-4 R' = Ph[b]	4.2	58	16.8	-131.9, -148.1, -164.9
Phosphino-boranes $R_2P(C_6F_4)B(MesCN)(C_6F_5)_2$ and (^{t}Bu)R'$P(C_6F_4)B(MesCN)(C_6F_5)_2$				
5-10 R = ^{t}Bu[d]	22.1	-9.7	11.9	-134.0, -155.5, -167.4
5-8 R = Mes[d]	-47.5	-9.3	7.2	-133.6, -156.1, -163.3
5-11 R' = Mes[d]	-7.2	-8.3	7.1	-133.7, -156.2, -163.3
5-12 R' = Ph[d]	0.3	-9.5	11.4	-133.5, -156.0, -167.4
5-13 R = Cy[d]	-5.1	-10.1	11.8	-133.6, -156.2, -168.0
Phosphonium Borates $[R_3PH][HB(C_6F_5)_3]$				
5-5 R = ^{t}Bu[c]	56.6(454)	-25.8(100)	2.9	-131.7, -162.9, -165.8
5-6 R = Mes[c]	-27.5(480)	-25.5(112)	2.9	-132.8, -164.1, -167.0

[a]C_6D_6, [b]CD_2Cl_2, [c]THF-d_8, [d]C_6D_5Br, *Chemical shift difference between *para* and *meta* resonances in ^{19}F NMR spectrum

5.2.11 General Kinetic Methods and T_1 data

Table 5.2 Spin-lattice relaxation times (T_1) determined using a standard inversion recovery experiment for **3-6**, **3-14**, and **5-8** at 25 and 150 °C in C_6H_5Br.

	T_1 values (seconds)					
Compound	^{31}P	*m*-C_6F_4B	*o*-C_6F_4B	*o*-C_6F_5B	*m*-C_6F_5B	*p*-C_6F_5B
3-6	0.46	0.78	0.78	0.94	1.29	1.00
3-14	3.57					
3-14*	4.11					
5-8		0.40	0.45	0.49	0.58	0.45
5-8*		1.57	1.54	1.81	2.85	2.23

* At 150 °C. Octafluoronaphthalene T_1 times = 1.73 and 1.93 @ 25 °C, 3.28 and 3.72 @ 150 °C

General NMR kinetic experiment for the conversion of 3-6 to 3-14 in the presence of MesCN. All kinetic runs were performed in a similar fashion, thus only one example is detailed. A stock solution (A) of MesCN (107 mg, 0.074 mmol) and octafluoronaphthalene (internal standard) (107 mg, 0.038 mmol) in C_6H_5Br (7.0 mL) was prepared. To a 20 mL vial was added **3-6** (64 mg, 0.028 mmol) and 2.1 mL of stock solution A, generating stock solution B. The vial was capped and vigorously shaken for 5 minutes. With constant mixing 0.7 mL of stock solution B was drawn from the vial and added to an NMR tube. The NMR tube was capped, wrapped with Para-film, and inserted into an NMR spectrometer pre-heated to 140 °C. The sample was allowed to reach thermal equilibrium over 2 minutes before the start of data acquisition. The disappearance of **3-6** and appearance of **3-14** was followed by ^{19}F NMR spectroscopy over 3 half-lives (~ 30-60 minutes). A ^{19}F NMR spectrum (8 scans) was recorded at 68 second intervals,

using a relaxation delay of 5 seconds. Concentrations of **3-6** were determined by integrating the *meta*-fluorine (δ -166 to -167) of the C_6F_5 aryl rings and comparing the value to the octafluoronaphthalene internal standard. Concentrations of **3-14** were determined by integrating the *ortho*-fluorine (δ -124 to -126) of the C_6F_4B ring and comparing the value to the octafluoronaphthalene internal standard. Stock solution B was prepared to allow for three kinetic runs with the same sample.

General NMR kinetic experiment for the conversion of 3-6 to 3-14. All kinetic runs were performed in a similar fashion, thus only one example is detailed. A re-sealable J-Young NMR tube was charged with **3-6** (35 mg, 0.046 mmol) and C_6H_5Br (1.142 g) and sealed, which formed a 0.060 M solution. The sample was inserted into an NMR spectrometer pre-heated to 140 °C and allowed to reach thermal equilibrium over 2 minutes before the start of data acquisition. The disappearance of **3-6** and appearance of **3-14** was followed by $^{31}P\{^1H\}$ NMR spectroscopy over 3 half-lives (~ 3 hours). A $^{31}P\{^1H\}$ NMR spectrum was recorded at 330 second intervals, using a relaxation delay of 5 seconds. For concentrations less than 0.060 M and temperatures greater than 140 °C, total experiment times were increased to account for the slower kinetics. At concentrations greater than 0.060 M, prolonged reaction resulted in significant back-conversion of **3-14** to **3-6** via reaction with generated H_2; therefore, all kinetic parameters were determined using initial rate data over the first hour of the reaction. Rate data obtained at concentrations 0.02 M, 0.04 M, 0.06 M, 0.08 M, 0.10 M and 0.12 M at both 120 °C and 140 °C. Rate data obtained at temperatures 100 °C, 110 °C, 120 °C, 130 °C, 140 °C, 150 °C at the concentration 0.06 M. Concentrations determined from integration of ^{31}P NMR signals for **3-6** (δ -36 to -38) and **3-14** (δ -41 to -43) relative to each other and $P(C_6F_5)_3$,

used as internal standard. The method of initial rates was used to determine the order of the reaction.

5.2.12 Computational Details

Theoretical calculations were carried out on the full structure at the B3LYP/LACVP** level of theory using the PB-PCM method and the GAUSSIAN 03 program package.[298] Calculations were run taking into account solvent (toluene) effects.

5.2.13 X-ray Data Collection, Reduction, Solution and Refinement

Single crystals were mounted in thin-walled capillaries either under an atmosphere of dry N_2 in a glove box and flame sealed or coated in Paratone-N oil. The data were collected using the SMART software package[104] on a Siemens SMART System CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71069 Å) at 25 °C. A hemisphere of data was collected in 1448 frames with 10 second exposure times unless otherwise noted. Data reductions were performed using the SAINT software package[105] and absorption corrections were applied using SADABS.[106] The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[107] All non-H atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Phosphorus and nitrogen-bound hydrogen atoms were located in the electron difference

map and their positions refined isotropically. For compound **5-1** disordered CH_2Cl_2 solvent molecules were removed using the 'squeeze' command in PLATON.[108, 109]

Table 5.3 Selected crystallographic data for compounds **5-1**, **5-5**, **5-6**.

Crystal	**5-1**	**5-5**	**5-6**
Formula	$C_{31}H_{22}BF_{14}P$	$C_{30}H_{29}BF_{15}P$	$C_{44}H_{35}BF_{15}P$
Formula weight	702.27	716.31	843.23
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/n$	$P2_1/n$
a(Å)	11.799(4)	12.1252(18)	12.8795(33)
b(Å)	12.014(4)	18.510(3)	21.6851(55)
c(Å)	14.644(4)	14.973(2)	16.2734(42)
$\alpha(^o)$	66.840(4)	90	90
$\beta(^o)$	69.755(4)	107.956(3)	110.425(4)
$\gamma(^o)$	74.829(4)	90	90
V ($Å^3$)	1771.6(9)	3196.8(8)	
Z	2	4	
d(calc) g cm^{-1}	1.317	1.488	
Abs coeff, μ, cm^{-1}	0.170	0.194	
Data collected	16933	30348	
Data $F_o^2>3\sigma(F_o^2)$	6209	5623	
Variables	432	424	
R^a	0.0520	0.1254	
$R_w{}^b$	0.1364	0.3352	
Goodness of Fit	0.958	1.069	

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{½}$.

Table 5.4 Selected crystallographic data for compounds **5-15**, **5-24**.

Crystal	**5-15**	**5-24**
Formula	$C_{63}H_{35}BF_{30}PO$	$C_{36}H_{33}BF_{15}PS$
Formula weight	1430.5	824.46
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a(Å)	11.678(4)	13.739(3)
b(Å)	17.010(6)	16.066(4)
c(Å)	17.068(6)	17.959(4)
α(°)	88.204(5)	89.986(3)
β(°)	81.021(5)	89.972(3)
γ(°)	76.337(5)	68.314(3)
V (Å^3)	3254(2)	3684(2)
Z	3	4
d(calc) g cm^{-1}	1.460	1.487
Abs coeff, μ, cm^{-1}	1.169	0.234
Data collected	31093	36931
Data $F_o^2>3\sigma(F_o^2)$	7138	16161
Variables	882	981
R^a	0.0694	0.0676
$R_w{}^b$	0.1512	0.1274
Goodness of Fit	0.826	1.1012

This data was collected at 25 °C with Mo Kα radiation (λ = 0.71069 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$.

5.3 Results and Discussion

5.3.1 Liberation and Activation of Dihydrogen by Phosphines and Boranes

5.3.1.1 Reactivity of $R_2PH(C_6F_4)BH(C_6F_5)_2$ and $R_2P(C_6F_4)B(C_6F_5)_2$

Existence of both cationic phosphonium PH and anionic hydridoborate BH fragments in the compounds $R_2PH(C_6F_4)BH(C_6F_5)_2$ (R = alkyl or aryl) prompted us to investigate the potential for the loss of H_2 from these species. To probe this, a sample of $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-6**) in bromobenzene solution was sealed in a J-Young NMR tube and subjected to a controlled heating experiment. The thermal decomposition of **3-6** was monitored by ^{31}P NMR spectroscopy. The sample remained stable below 100 °C, but heating above this temperature caused a new ^{31}P NMR resonance to appeare upfield at -45 ppm attributed to the phosphino-borane $Mes_2P(C_6F_4)B(C_6F_5)_2$ (**3-14**). Prolonged heating at 150 °C for several hours showed complete disappearance of the ^{31}P NMR resonance of **3-6** and quantitative formation of **3-14**. The ^{19}F NMR spectrum showed a shift in the resonance for the *para*-fluorine of the C_6F_5 rings from -164 to -143 ppm consistent with a change from four- to three-coordinate boron. Loss of the PH and BH resonances in the ^1H NMR spectrum confirmed formation of **3-14** and concurrent appearance of H_2 (4.5 ppm) was also observed. Upon removal from the NMR spectrometer, it was noted that the sample had changed from colorless to deep orange, characteristic of the phosphino-borane **3-14**. Upon cooling to room temperature and shaking several times the color of the sample lost intensity.

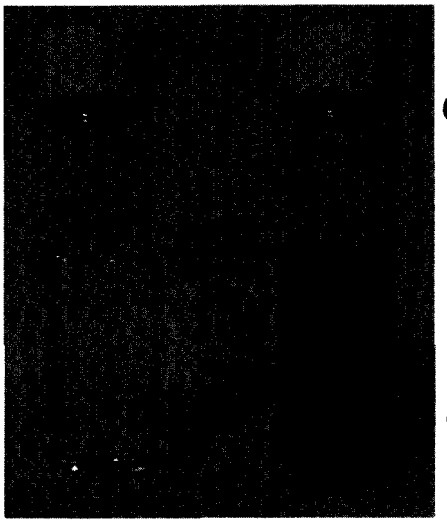
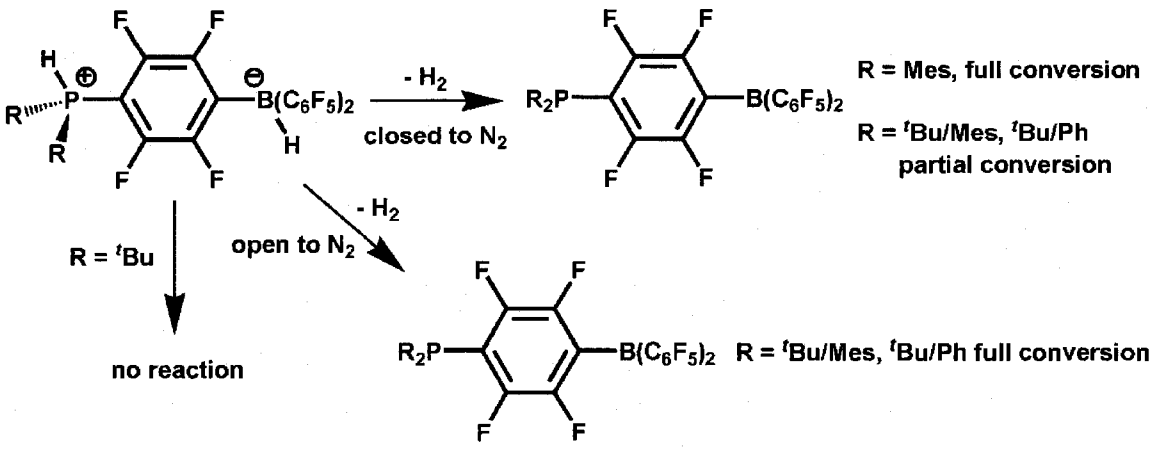


Figure 5.1 Inter-conversion between **3-6** and **3-14**.

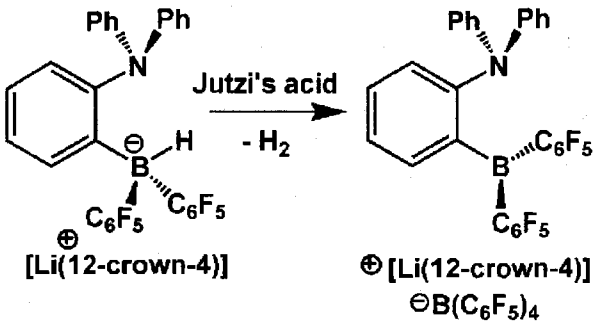
Re-acquiring the ^{1}H, ^{11}B, ^{19}F and ^{31}P NMR spectra revealed the partial regeneration of the parent phosphonium borate **3-6**, indicating that hydrogen loss was reversible. At high temperatures, H_2 loss is thermodynamically favorable and H_2 gas is presumably driven out of solution and upon cooling and mixing the sample; H_2 re-dissolves in solution and is activated by the phosphino-borane, a process which is now thermodynamically favorable. This notion was confirmed by heating a bromobenzene solution of **3-14** to 125 °C for several hours in a J-Young NMR tube open to N_2. This resulted in complete H_2 loss and no regeneration of **3-6** upon cooling, as all H_2 had escaped from the system. To further probe the surprising reactivity of **3-14** with H_2, an orange solution of phosphino-borane **3-14** in bromobenzene was degassed and sealed under 1 atm of H_2 at -196 °C. Warming the sample to 25 °C generated a system with a H_2 pressure of ~ 3.5 atm, which after rigorous mixing for 10 minutes went colorless.



Scheme 5.1 Liberation of H_2 from a series of phosphonium borates at 150 °C in C_6H_5Br or C_6D_5Br. Increased basicity of the phosphorus center inhibits H_2 loss.

Immediate analysis by multi-nuclear NMR spectoscopy revealed quantitative formation of the **3-6**, which indicated heterolytic cleavage of H_2 with a proton ending up on phosphorus and a hydride at boron. A variable-temperature NMR spectroscopy study showed the heterolytic cleavage of H_2 occurs at temperatures as low as -25 °C. To confirm that the source of the proton and hydride of **3-6** was indeed H_2, an independent deuterium experiment was performed. A solution of **3-14** in proteo bromobenzene was pressurized with ~3.5 atm D_2 and mixed for 10 minutes. The ^2H NMR spectrum gave rise to a doublet and singlet resonances at 7.8 ($J_{D\text{-}P}$ = 77 Hz,) and 3.5 ppm for the PD and BD fragments, respectively, while the $^{31}P\{^1H\}$ NMR spectrum showed a 1:1:1 triplet resonance at -37.5 with a PD coupling constant of 77 Hz. The ^{11}B NMR spectrum exhibited a broad peak at -25 ppm with no observable BH coupling, which indicated BD formation. Thus, it has be demonstrated that the phosphonium hydridoborate **3-6** thermally liberates H_2 above 100 °C yielding the phosphino-borane **3-14**, which in turn reacts with H_2 at 25 °C regenerating the parent phosphonium hydridoborate **3-6** (Figure 5.1). While protonation of inorganic hydrides is known,[299] the resulting Lewis acids and

bases often form strongly bound complexes with one another preventing the reversible uptake of H_2. In the present case the steric bulk about the Lewis acidic and basic sites thwarts quenching of the reactive sites allowing for the reactivation of H_2. This unprecedented reactivity represents the first known metal-free system to reversibly activate H_2.



Scheme 5.2 Elimination of H_2 from an amino-hydrioborate reported by Piers *et al.*

Piers and co-workers have reported on a related amino-borane (1-(NPh_2)-2-($B(C_6F_5)_2$)C_6H_4) where the nitrogen and boron sites are *ortho* to each another.[300] This compound does not activate H_2 or form a stable ammonium hydridoborate as H_2 is rapidly generated upon attempting to protonate the amino moiety in the presence of a hydridoborate (Scheme 5.2). This emphasizes the importance of having the phosphine and borane *para* to one another in the present case, as this orientation prevents a close intramolecular proton and hydride approach. Additionally, while the present phosphonium-borates can be compared to related phosphine-boranes of the type R_2HP-BH_3 in that they both release H_2, the greater sterics at P and B in the present case prevent classical phosphine-borane adduct formation after H_2 release, allowing for the re-uptake of H_2 not capable with R_2HP-BH_3 systems.

To test the generality of reversible H_2 activation, thermal reactivity of the compound $^tBu_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-5**) was investigated (Scheme 5.1). Surprisingly, heating a bromobenzene solution of **3-5** from 100-150°C for several hours in an open or closed vessel resulted in no observed liberation of H_2. Clearly the replacement of the Mes groups on phosphorus with the more electron-donating ^{t}Bu groups diminishes the compounds ability to liberate H_2.

To determine if basicity of the phosphorus center was indeed affecting H_2 loss, the phosphonium borates (^{t}Bu)(Mes)$PH(C_6F_4)BH(C_6F_5)_2$ (**5-1**), and (^{t}Bu)(Ph)$PH(C_6F_4)BH(C_6F_5)_2$ (**5-2**) were synthesized, where a ^{t}Bu group is replaced with a less electron-donating Mes or Ph substituent. Both compounds were fully characterized by multi-nuclear NMR, EA, and for **5-1** X-ray crystallography (Table 5.3, Figure 5.2). The metrical parameters of **5-1** are similar to those of **3-5** and **3-6** and are unexceptional. A close intermolecular PH...HB approach of 2.41 Å (2.01 Å corrected, *vide infra*) was determined from the solid-state strucutre. Upon heating bromobenzene solutions of **5-1** and **5-2** to 150 °C in J-Young NMR tubes, the solutions changed color from colorless to orange and yellow-orange, respectively. The ^{31}P NMR spectra of each solution showed new phosphine resonances at -2.0 and 4.2 ppm, respectively, while the ^{19}F NMR spectra of each showed fluorine signals attributed to C_6F_5 groups bound to a 3-coordinate boron. Additionally H_2 was seen in the ^{1}H NMR spectra of both. This data confirms that the compounds **5-1** and **5-2** thermally liberate H_2 in a similar fashion to **3-6**. However, complete liberation of H_2 from **5-1** and **5-2** was not observed in sealed J-Young NMR tubes, even after prolonged heating at 150 °C. Only after heating to 150 °C in a vessel open to dynamic N_2 were the compounds **5-1** and **5-2** quantitatively converted into the phosphino-boranes (^{t}Bu)(Mes)$P(C_6F_4)B(C_6F_5)_2$ (**5-3**) and (^{t}Bu)(Ph)$P(C_6F_4)B(C_6F_5)_2$ (**5-4**).

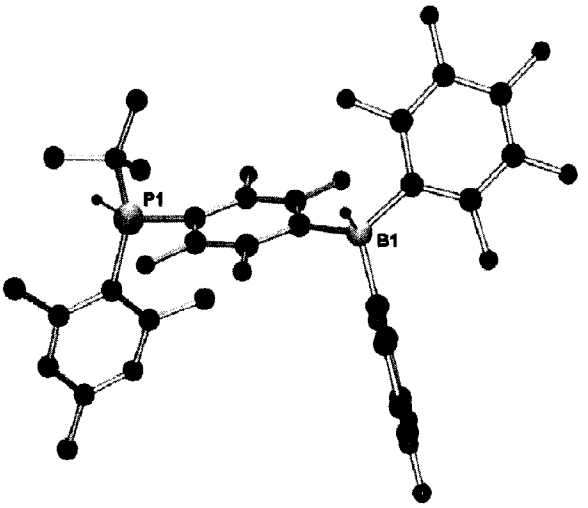
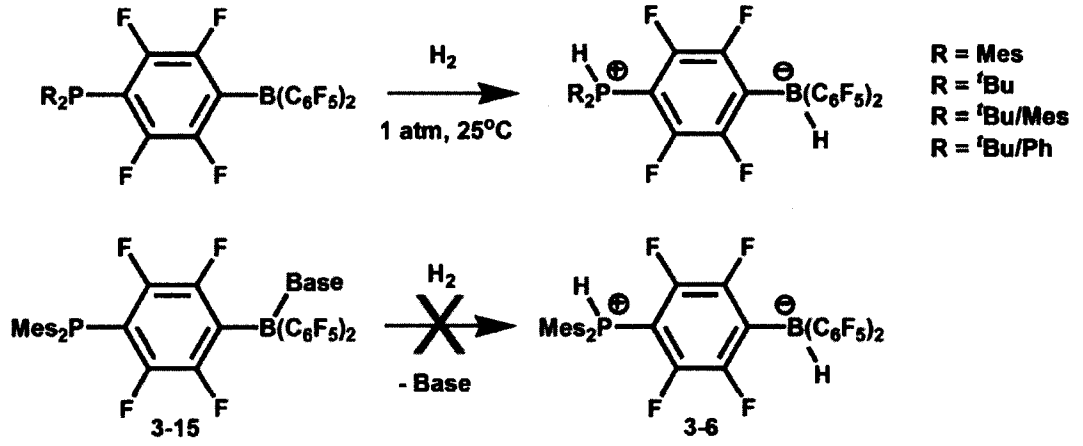


Figure 5.2 POV-ray depiction of **5-1**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green. Carbon hydrogen atoms omitted for clarity.

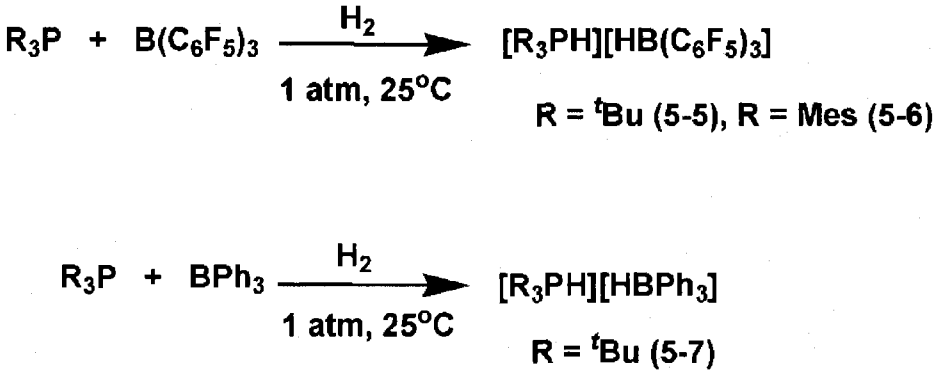
(For further confirmation of the product, both **5-3** and **5-4** were independently generated upon treatment of **2-6** and **2-24**, respectively, with MeMgBr). These results demonstrate how the basicity at phosphorus can affect the thermal liberation of H_2. The strong inductive effect of the alkyl groups renders the PH moiety less protic, which inhibits the protonation of BH and generation of H_2. A similar inductive effect was observed for the rhodium catalyzed dehydrocoupling of phosphine-BH_3 adducts.[122, 301] While not all phosphonium hydridoborates readily liberate H_2, each of the phosphino-boranes **3-13**, **5-3**, and **5-4** uptake H_2 in a facile manner at 25 °C to yield the corresponding phosphonium hydridoborates (Scheme 5.3). The addition of H_2 to the series of phosphino-boranes is solvent dependent, as H_2 activation is not observed in coordinating solvents such as THF, pyridine, or acetonitrile even at reflux. Here, the solvent coordinates to the Lewis acidic boron center quenching a site of reactivity.



Scheme 5.3 Activation of H_2 by phosphino-boranes $R_2P(C_6F_4)B(C_6F_5)_2$. Base coordinated phosphino-borane **3-15** does not activate H_2. Base = THF, pyridine, or acetonitrile.

5.3.1.2 Reactivity of R_3P and BR_3

Given these findings, we sought simpler systems capable of the heterolytic cleavage of H_2. In Chapter two it was discussed that the sterically demanding phosphines $^tBu_3P$ and Mes_3P to do not react with $B(C_6F_5)_3$ in solution to form classical Lewis acid-base adducts or phosphonium borate zwitterions. These unique non-reacting phosphine/borane combinations were described as 'frustrated' Lewis pairs and were designated FLP 1 and 4. Interestingly, exposure of toluene solutions of FLP 1 and 4 to an atmosphere of H_2 at 1 atm pressure and 25 °C resulted in the quantitative formation of white precipitates **5-5** and **5-6**. NMR data for these products were consistent with the formulation as $[R_3PH][HB(C_6F_5)_3]$ (R = ^{t}Bu **5-5**, Mes **5-6**) (Scheme 5.4). The cations of these species exhibit ^{31}P NMR resonances at 56.6 and -27.5 ppm for **5-5** and **5-6**, respectively, and P-H couplings of 454 and 480 Hz, respectively. The anion gives rise to an ^{11}B NMR resonance at -25.5 ppm with a B-H coupling of 100 Hz.



Scheme 5.4 Heterolytic cleavage of H_2 by sterically demanding phosphines and boranes.

Moreover, the ^{19}F NMR chemical shift difference (Δ m,p) between the *ortho*- and *meta*-F atoms of the C_6F_5 fragments is consistent with the presence of a four-coordinate anionic boron center.[302] Of note, the related compound $[Et_3NH][HB(C_6F_5)_3]$ has been reported, but was formed as a decomposition product from the reaction of Et_3N with $B(C_6F_5)_3$.[303] A crystallographic study of **5-5** showed disorder of the ^{t}Bu groups of the cation. The most chemically reasonable model required the constraint of the C-C distances with the ^{t}Bu groups. Nonetheless, the crystallographic data confirmed the formulation based on NMR spectroscopy (Table 5.3, Figure 5.3). In the case of **5-6**, a preliminary solution confirmed atom connectivity, but poor crystal quality precluded a fully acceptable refinement (Table 5.3). The metrical parameters determined for **5-5** are unexceptional. The cations and anions pack such that the PH and BH units are oriented toward each other with the BH...HP approach being 2.75 Å, which is much larger than typical intermolecular dihydrogen bonding distances, which tend to range from 1.8-2.2 Å.[221] The P...B distance was found to be 4.67 Å. Interestingly, the calculated PH...HB distance of 1.87 Å was found to be almost a full angstrom shorter that the distance determined by X-ray diffraction, while the calculated P...B distance of 4.50 Å was similar to the distance found

in the solid-state structure.[17] These results indicated that the H positions located on the electron density map are not accurate. Using idealized PH and BH distances determined by microwave spectroscopy[304] and neutron diffraction,[305] respecitivly, a PH...HB distance of 2.04 Å is obtained from the solid-state strucutue.[122] Thus, the proton and hydride can be considered to be engaged in dihydrogen bonding.

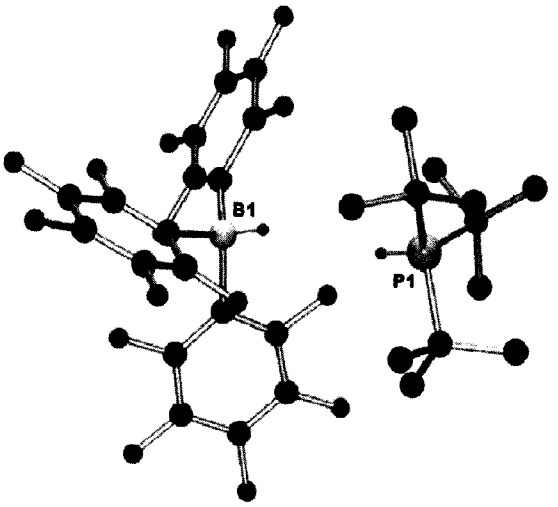
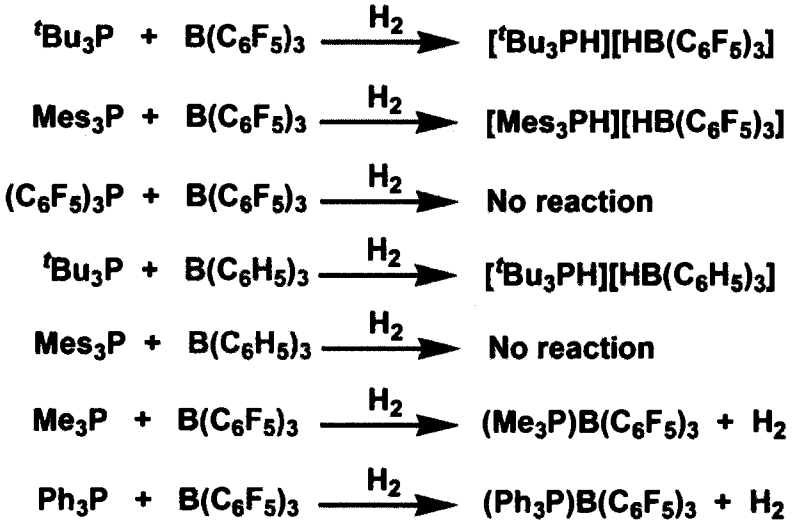


Figure 5.3 POV-ray depiction of **5-5**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green. Carbon hydrogen atoms omitted for clarity.

Despite this orientation in the solid state, the heating of **5-5** or **5-6** in bromobenzene solutions to 150 °C did not result in the loss of H_2, reminiscent of the compound $^tBu_2PH(C_6F_4)BH(C_6F_5)_2$, thus again demonstrating the effect the basicity of phosphorus has on H_2 liberation. In a similar experiment described previously, a solution of Mes_3P and $B(C_6F_5)_3$ in proteo bromobenzene under ~ 3.5 atm of D_2 in a sealable J-Young NMR tube, was shaken and allowed to sit for several hours. The ^{31}P NMR spectrum showed a 1:1:1 triplet at -28.1 ppm ($^1J_{PD}$ = 74 Hz), while the ^2H NMR spectrum gave rise to a doublet at 7.5 ppm and a broad singlet at 3.8 ppm, attributed to the PD and BD fragments,

respectively. This again affirms that the source of PH and BH is indeed H_2 and not solvent. While FLP's 2 and 3 $[R_3PH][HB(C_6F_5)_3]$ (R = *o*-$C_6H_3Me_2$ or *o*-C_6H_4Me) were not investigated, it is presumed that they would uptake H_2 in a similar fashion to FLP 1 and 4. Of note, compounds **5-5** and **5-6** are sensitive to H_2O, affording the phosphonium salt of the known anion $[R_3PH][(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]$.[303] In order to gain insight into the generality of the reaction, several phosphine/borane combinations were investigated. Attempts to effect analogous H_2 cleavage reactions employing $^tBu_3P$ and BPh_3 resulted in the formation of **5-7** in 33 % yield, although longer reaction times are required for H_2 activation, presumably due to the reduced Lewis acidity at boron. The spectroscopy for **5-7** showed features similar to those of **5-5** for the cation, while the anion gave rise to a signal at -6.9 with a B-H coupling of 75 Hz in the ^{11}B NMR spectrum, supporting the formation of **5-7** as $[^tBu_3PH][HBPh_3]$. In contrast, reactions of Mes_3P and BPh_3, $(C_6F_5)_3P$ and $B(C_6F_5)_3$, or $^tBu_3P$ and $BMes_3$ resulted in no reaction at 25 °C under an atmosphere of H_2. As well, addition of Ph_3P or Me_3P to toluene solutions of $B(C_6F_5)_3$ saturated with H_2 at 25°C gave rise to only the classical Lewis acid-base adducts $(R_3P)B(C_6F_5)_3$ (R = Ph, Me) (Scheme 5.5). These results support the view that reaction with H_2 occurs only under favourable electronic and steric conditions. Not only must the Lewis acidity and basicity be correctly matched in terms of cumulative strength to effect heterolytic cleavage of H_2, but steric constraints must be sufficient to preclude the quenching of the respective basicity and acidity via adduct formation.



Scheme 5.5 General reactivity of phosphines and boranes with H_2 at 25 °C in solution.

5.3.1.3 Liberation of H_2 in the Solid-State

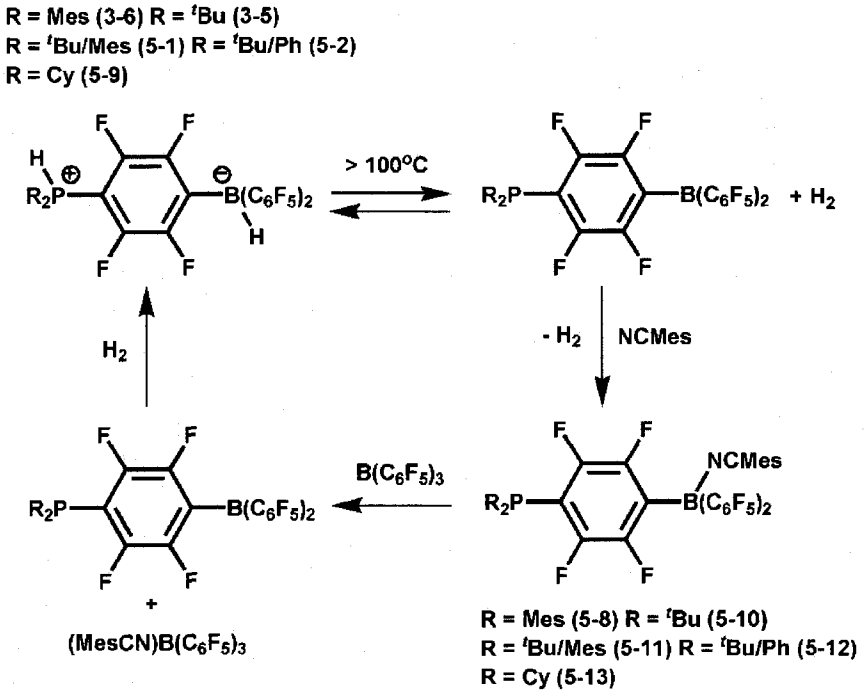
Loss of H_2 is not limited to solutions of the compound $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-5**), as H_2 liberation was observed in the solid state. Heating a solid sample of **3-6** at 150 °C under dynamic vacuum for 48 hours showed a slight color change of the solid from white to orange. Solvating the sample in CD_2Cl_2 and acquiring the $^{31}P\{^1H\}$ NMR spectrum revealed ~ 50 % conversion of **3-6** to **3-14**. Near quantitative conversion of **3-6** to **3-14** by loss of H_2 in the solid state was observed after ~ 7 days at 150 °C under dynamic vacuum. The reaction was not clean as several resonances were observed in the NMR spectra, which were attributed to unidentifiable by-products. Nonetheless, these results demonstrate the ability of the present species to liberate H_2 in both solution and the solid state. While the solid state structure of $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-6**) shows that the molecule packs in an off-set head-to-tail fashion, no close PH...HB approaches were

observed. The solid-state structures of $R_2PH(C_6F_4)BH(C_6F_5)_2$ (R = ^{t}Bu, (**3-5**), R = ^{t}BuMes (**5-1**)) do exhibit head-to-tail packing with close PH...HB interactions, therefore, it is not unreasonable to assume that in the bulk sample of **3-6**, a close PH...HB approach exists, allowing for the thermal generation of H_2. Heating a solid sample of $[Mes_3PH][HB(C_6F_5)_3]$ (**5-2**) to a 150 °C under dynamic vacuum resulted in no appreciable loss of H_2. This result is not surprising as **5-2** does not liberate H_2 in solution under similar conditions.

Attempts were made to add H_2 to the phosphino-borane **3-14**, by pressurizing a vessel containing solid **3-14** with ~ 3.5 atm H_2. While the orange solid lost some of its color after several days at room temperature, ^1H, ^{11}B, and ^{31}P NMR spectroscopy did not clearly indicate that the solid sample was taking up H_2. Resonances in the NMR spectra attributable to the water adduct of **3-14** were detected which is consistent with the ability of Lewis acidic boranes to scavenge trace amounts of water in the absence of other donors. Additionally, the addition of H_2 to a mixture of the solids of Mes_3P and $B(C_6F_5)_3$ was investigated. A purple solution of Mes_3P and $B(C_6F_5)_3$ was reduced under vacuum to give a white solid which was pressurized with ~ 3.5 atm H_2 and left to stand 24 hours. The NMR spectrum of the resulting solid showed primarily un-reacted starting material and minor amounts of the water activated species $[Mes_3PH][(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]$. The inability of 'frustrated' Lewis pairs to activate H_2 in the solid state indicates that in solution, pre-organization of the P and B sites precedes H_2 activation (*vide infra*).

5.3.1.4 Liberation of H_2 in the Presence of Mesitylnitrile (MesCN) in Solution

The observation that H_2 does not react with Lewis base coordinated boranes prompted us to investigate the liberation of hydrogen for the series of phosphonium hydridoborates in the presence of a donor molecule. It was believed that as H_2 loss occurred, the donor molecule would coordinate to the Lewis acidic boron center, which prevents the reversible H_2 activation and allows for complete H_2 liberation in closed systems. In the selection of an appropriate Lewis base, it was noted that nitriles readily coordinate to $B(C_6F_5)_3$[100, 121] and are not known to deprotonate phosphonium cations. These properties are advantageous, because the nitrile will not interact with the phosphonium PH moiety and will quench the boron center upon H_2 liberation. Mesitylnitrile (MesCN) was selected as it coordinates to the boron center of $R_2P(C_6F_4)B(C_6F_5)_2$, is a solid and will not become gaseous at high temperatures; as well the methyl CH and aromatic CH protons are conveniently observed by NMR spectroscopy. Addition of MesCN to $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-5**) in bromobenzene resulted in no reaction. Upon heating the sample to 150 °C in a sealed J-Young NMR tube, immediate evolution of H_2 was observed. ^1H NMR spectra confirmed complete liberation of H_2 within 15 minutes at 150 °C and formation of the Lewis base-coordinated phosphino-borane $Mes_2P(C_6F_4)B(MesCN)(C_6F_5)_2$ (**5-8**) (Scheme 5.6). Compound **5-8** was independently generated upon addition of MesCN to **3-14**, confirming its formation. The spectroscopic data are similar to the THF coordinated species **3-15** aside from the expected differences in the ^1H and ^{13}C NMR spectra due to the presence of different bases.



Scheme 5.6 Liberation of H_2 from $R_2PH(C_6F_4)BH(C_6F_5)_2$ in the presence of MesCN. The active phosphino-borane is re-generated upon addition of $B(C_6F_5)_3$.

This result implies that upon liberation of H_2, MesCN coordinates to the newly generated Lewis-acidic borane, preventing reactivation of H_2, thus decreasing the reaction time for the conversion of phosphonium borate to phosphino-borane. A variable-temperature NMR study showed that liberation of H_2 from a mixture of **3-6** and MesCN, began to occur above 100 °C, similar to the reaction without MesCN, which indicates MesCN was not affecting the activation barrier to H_2 liberation. In a similar fashion, MesCN was added to the compounds $R'RPH(C_6F_4)BH(C_6F_5)_2$ (R' = R = ^{t}Bu **3-5**, R' = ^{t}Bu, R = Mes **5-1**, R' = ^{t}Bu, R = Ph **5-2**) in bromobenzene and heated to 150 °C in a sealed J-Young NMR tube. Evolution of H_2 gas was observed and complete conversion to the corresponding base coordinated phosphino-boranes $R'R_2P(C_6F_4)B(MesCN)(C_6F_5)_2$ (R' = R = ^{t}Bu **5-10**, R' = ^{t}Bu, R = Mes **5-11**, R' = ^{t}Bu, R = Ph **5-12**) (Scheme 5.6).

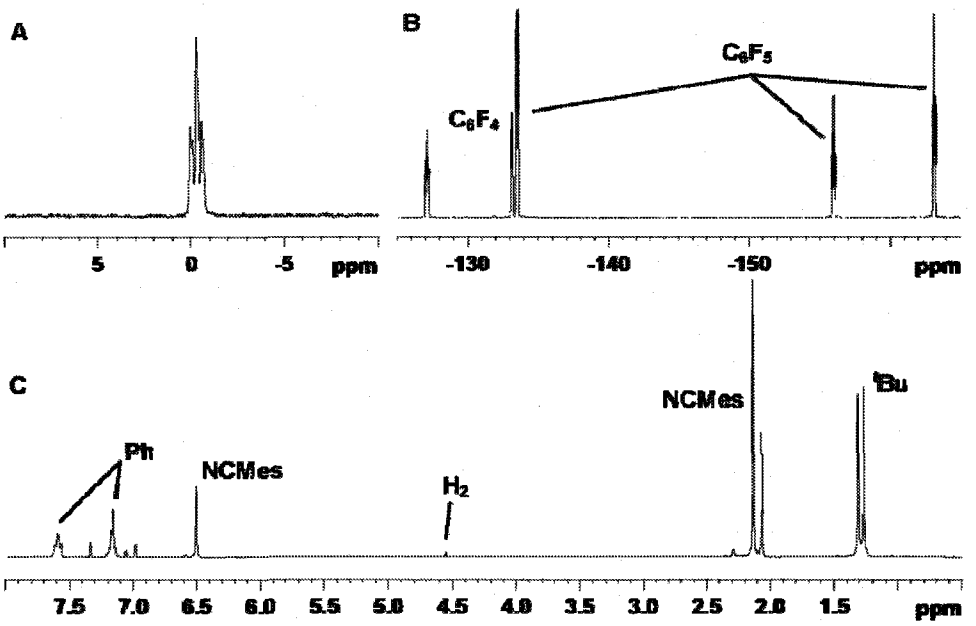


Figure 5.4. NMR spectra of (^{t}Bu)(Ph)P(C_6F_4)B(MesCN)(C_6F_4)$_2$ in C_6D_5Br at 25°C. (**A**) ^{31}P NMR spectrum. (**B**) ^{19}F NMR spectrum. (**C**) ^{1}H NMR spectrum.

The spectroscopic data of each is summarized in Table 5.1, and that of **5-12** is shown in Figure 5.4. In each case the ^{31}P NMR resonances are shifted upfield from the corresponding phosphino-boranes while the ^{11}B and ^{19}F NMR spectra are consistent with quarternization at boron. For **3-4**, the liberation of H_2 and conversion to **5-10** was complete within 270 minutes, while the conversion of **5-1** to **5-11** and **5-2** to **5-12** was complete within 65 and 30 minutes, respectively (Table 5.5). The phosphonium borate $Cy_2PH(C_6F_4)BH(C_6F_5)_2$ (**5-9**) was readily converted to $Cy_2P(C_6F_4)B(MesCN)(C_6F_5)_2$ (**5-13**) in 135 minutes under similar conditions (Table 5.5). This confirms that an increased basicity at phosphorus inhibits the liberation of H_2, due to the inductive effect of the alkyl groups, by rendering the PH moiety less polar. Ion pairs of the form $[R_3PH][HB(C_6F_5)_3]$ also liberate H_2 in the presence of MesCN. A bromobenzene solution of **5-6** with one equivalent of MesCN was heated to 150 °C. Within 15 hours, complete liberation of H_2 was observed with formation of phosphine (Mes_3P) and the base coordinated borane,

(MesCN)B(C_6F_5)$_3$ (**5-14**). Formation of **5-14** was confirmed by independent generation. The ion pair **5-5** was also shown to liberate H_2 at 150 °C in the presence of MesCN, but multiple decomposition products were observed by NMR spectroscopy preventing determination of the approximate reaction time. Presumably, after H_2 liberation, the free phosphine ^{t}Bu$_3$P reacts with B(C_6F_5)$_3$ as described in Chapter 2. The ability of the ion pairs **5-5** and **5-6** to liberate H_2 suggests that H_2 loss from these species must follow an intermolecular process. In a similar fashion to **5-6**, the combination of Mes$_2$PH(C_6F_4)BF(C_6F_5)$_2$ (**2-5**) and Cy$_3$P(C_6F_4)BH(C_6F_5)$_2$ (**3-7**) in bromobenzene readily gave off H_2 at 150 °C in the presence of MesCN, which implies that H_2 liberation may follow an intermolecular process. The intermediate ion pair [Cy$_3$P(C_6F_4)B(MesCN)(C_6F_5)$_2$]$^+$[Mes$_2$P(C_6F_4)BF(C_6F_5)$_2$]$^-$ was never observed by NMR spectroscopy as rapid fluoride transfer occurred to give **5-8** and **2-1** (Cy$_3$P(C_6F_4)BF(C_6F_5)$_2$).

Table 5.5 Liberation of H_2 from phosphonium hydrido borates in the presence of one equivalent of MesCN at 150 °C.

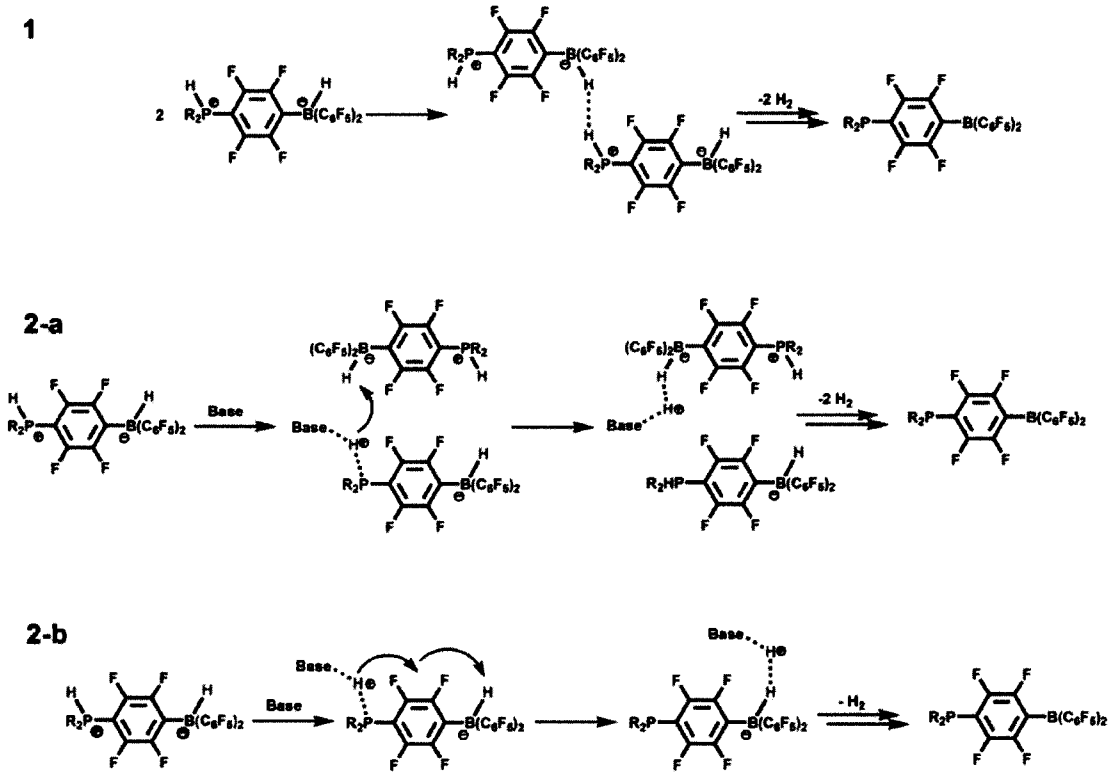
Compound[a]	Reaction time for complete H_2 loss (minutes)
Mes$_2$PH(C_6F_4)BH(C_6F_5)$_2$ (**3-6**)[b]	60
Mes$_2$PH(C_6F_4)BH(C_6F_5)$_2$ (**3-6**)	15
(^{t}Bu)(Ph)PH(C_6F_4)BH(C_6F_5)$_2$ (**5-2**)	30
(^{t}Bu)(Mes)PH(C_6F_4)BH(C_6F_5)$_2$ (**5-1**)	65
Cy$_2$PH(C_6F_4)BH(C_6F_5)$_2$ (**5-9**)	135
^{t}Bu$_2$PH(C_6F_4)BH(C_6F_5)$_2$ (**3-5**)	270
[Mes$_3$PH][HB(C_6F_5)$_3$] (**5-6**)	900

[a] 0.05 M solutions in C_6D_5Br. Reaction in sealed J-Young NMR tube. [b] no MesCN added

The liberation of H_2 from the range of phosphonium borates in the presence of MesCN is summarized in Table 5.5. In the case of **3-6** the reaction time is decreased as MesCN coordinates to generated free borane preventing the reverse activation of H_2. For **3-5**, **5-5**, and **5-6** liberation of H_2 can only be accomplished in the presence of MesCN, which indicates, that without base, the reverse activation of H_2 is faster than H_2 removal from the system. It is possible that at high temperatures, equilibria exist between free and activated H_2. Overall, from the approximate reaction times, it is clear that the basicity of the phosphorus center has a pronounced affect on the liberation of hydrogen. Increasing the basicity at phosphorus by incorporating electron-donating substituents inhibits the liberation of H_2, which indicates that P-H bond breakage may be involved in the rate determining step. While the addition of MesCN allows for the liberation of H_2 from the full range of phosphonium borates, the reaction is effectively made irreversible. Only upon addition of the stronger Lewis acid $B(C_6F_5)_3$ to solutions of **5-8** and **5-10** to **5-13** were the active phosphino-boranes regenerated. Here, $B(C_6F_5)_3$ abstracts the coordinated MesCN resulting in a color change of the solution from colorless to yellow-orange depending on the substituents at phosphorus (Scheme 5.5). It should be noted that borane activated nitriles are readily reduced by H_2 at high temperatures using **3-5**, **3-6** or **5-6** as catalysts.[7, 9]

5.3.2 Mechanism for Reversible H_2 Activation

5.3.2.1 Mechanistic Insights into the Liberation of H_2 in Solution



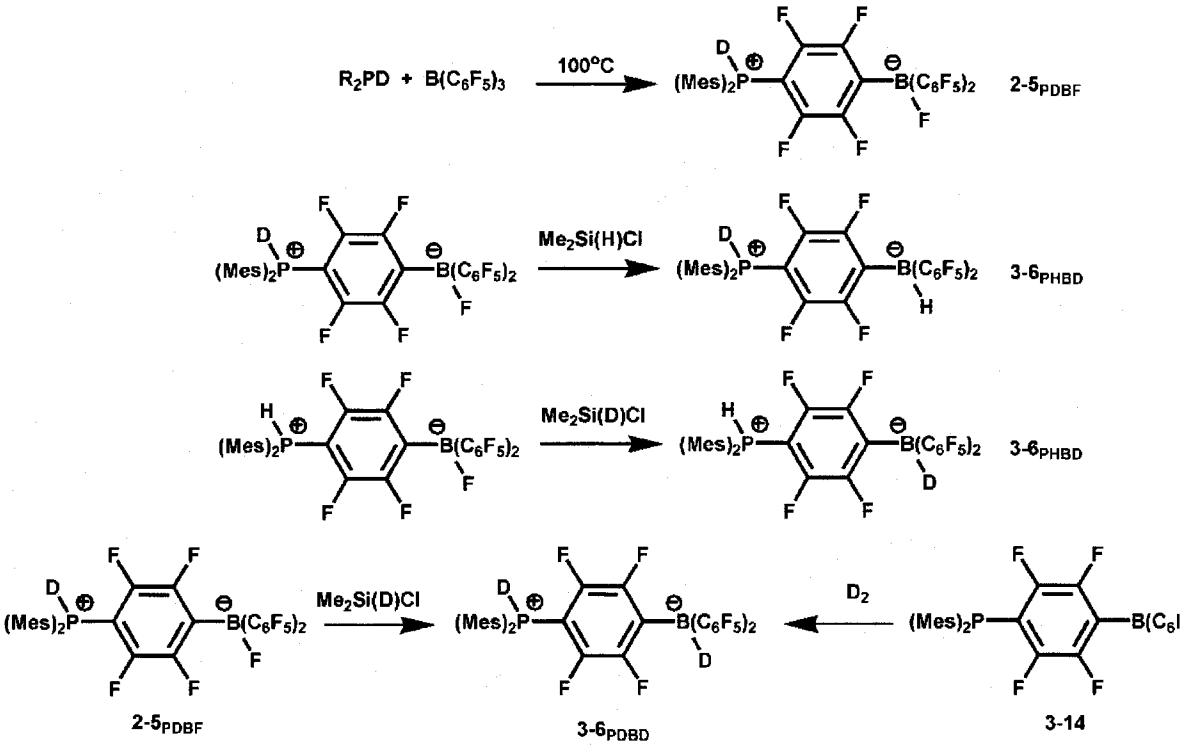
Scheme 5.7 Three possible mechanisms for the loss of H_2 from the series of phosphino-boranes. (**1**) The most straight forward mechanism would involve the intermolecular close approach of a PH and BH fragment followed by H_2 loss. (**2**) An alternate mechanism would involve PH bond breakage followed by; (**2-a**) Base or solvent assisted proton transfer to the vicinity of BH of a second molecule or (**2-b**) Base or solvent assisted proton transfer to the vicinity of BH of the same molecule, followed by H_2 loss.

The protonation of hydride ligands to give hydrogen is well known in the literature,[306] while the generation of H_2 from amino-borane (H_3NBH_3)[65, 66] and related phosphino-boranes[122, 124] has been the focus of many recent experimental and theoretical studies.[307-314] The hydride affinity of the boron center in $Mes_2PH(C_6F_4)B(C_6F_5)_2$ was calculated to be much higher than the proton affinity of the phosphorus center in $Mes_2P(C_6F_4)BH(C_6F_5)_2$ (ca. 478 vs. 289 kcal mol^{-1}). Therefore the liberation of H_2 from the series of phosphonium borohydrides most likely proceeds via protonation of the BH moiety. This could occur via a close intermolecular approach of PH and BH fragments

and or via P-H bond breakage followed by solvent or base assisted migration of a proton to the borohydride (Scheme 5.7).

5.3.2.2 Deuterium Experiments

In order to gain a better understating of how this series of phosphonium hydridoborates liberate H_2, deuterium labelling studies were performed. The site specific species **3-6$_{PDBH}$** and **3-6$_{PHBD}$** were readily synthesized by treatment of the corresponding phosphonium fluoroborates **2-5$_{PDBF}$** and **2-5** with $Me_2Si(H)Cl$ or $Me_2Si(D)Cl$, respectively (Scheme 5.8). The doubly deuteriated species **3-6$_{PDBD}$** was generated by treatment of the phosphino-borane **3-14** with D_2 gas or upon reaction of $Me_2Si(D)Cl$ with **2-5$_{PDBF}$** (Scheme 5.8). The monodeuterated species **3-6$_{PDBH}$** and **3-6$_{PHBD}$** showed no significant H/D exchange in bromobenzene solution below 100 °C, while heating each individually to 150 °C to liberate HD, and cooling to 25 °C to reactivate HD, showed statistical formation of PH, BH, PD, and BD as determined by ^1H, ^2H, ^{11}B, and ^{31}P NMR spectroscopy. The scrambling of sites could occur via a bimolecular exchange process with subsequent loss of H_2, D_2, or and HD, or this exchange could occur simply via HD liberation, followed by rapid HD activation, scrambling the deuterium label (Scheme 5.9). To probe this result, **3-6$_{PHBD}$** was heated to 150 °C in the presence of MesCN and converted to **5-8**, which eliminated the possibility for the reactivation of HD (Scheme 5.8). The ^1H NMR spectrum (Figure 5.5) showed the existence of both HD and H_2 in an approximate 12:1 ratio, although the integration depends on the solubility of each gas in solution. The appearance of primarily HD supports the notion that when the free boron site is not trapped, rapid reactivation of HD is occurring, which scrambles the labels.



Scheme 5.8 Synthesis of deuterium isotopomers of **3-6**.

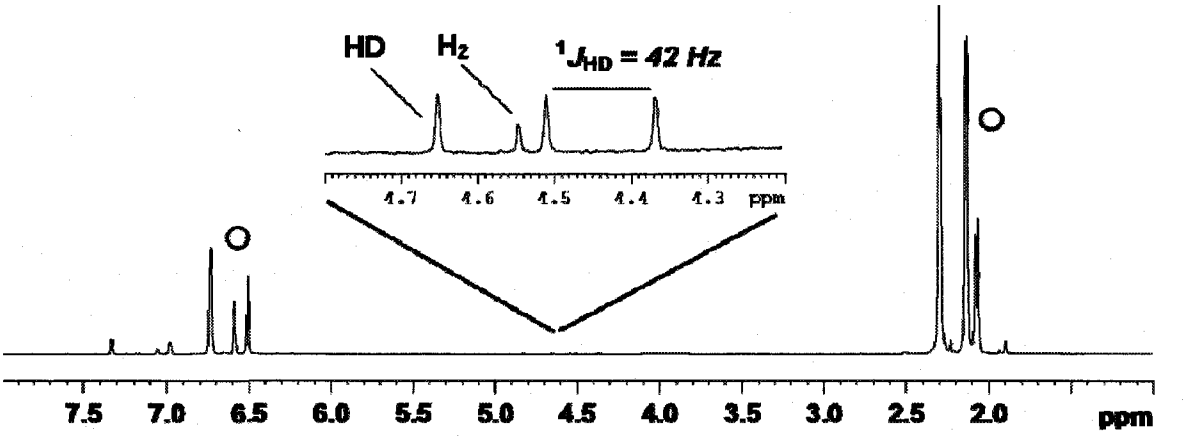
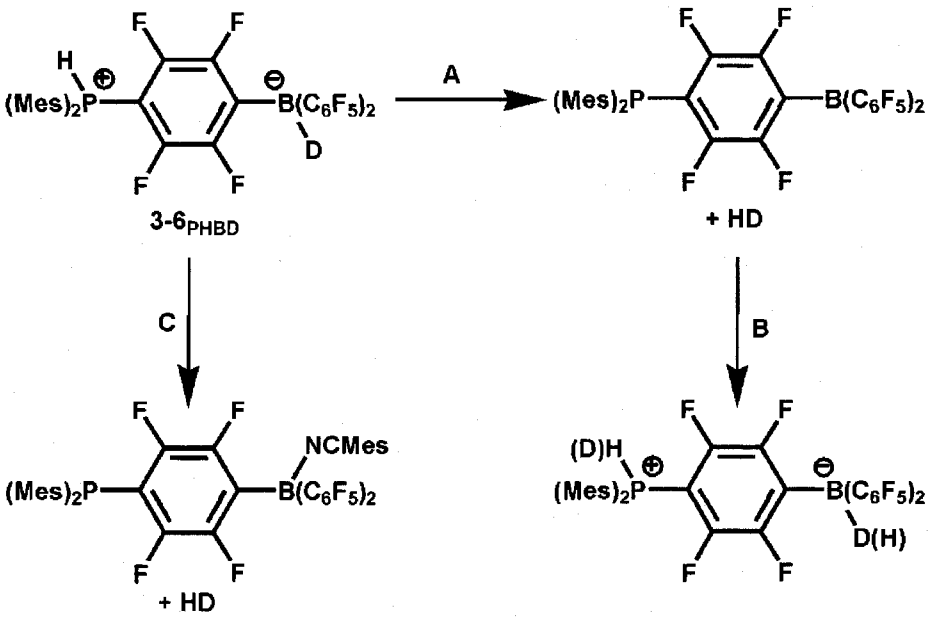


Figure 5.5 ^{1}H NMR spectrum at 25 °C after heating $Mes_2PH(C_6F_4)BD(C_6F_5)_2$ **3-6$_{PHBD}$** and MesCN to 150 °C in a sealed J-Young NMR tube in C_6D_5Br. O = Signals for mesityl substituents.



Scheme 5.9 Observed H/D scrambling. (**A**) Heating **3-6$_{PHBD}$** to 150 °C results in loss of HD (**B**) cooling to 25 °C results in reactivation of HD and statistical formation of PH, BH, PD, and BD. (**C**) Heating **3-6$_{PHBD}$** to 150 °C in the presence of MesCN and cooling to 25°C results in liberation of primarily HD.

The appearance of H_2 in the ^1H NMR spectrum of **3-6$_{PHBD}$** (Figure 5.5) does indicate that minor scrambling of the labels did occur. Using a large excess of MesCN may prevent any reactivation of gas, preventing the scrambling of labels. In any case the liberation of H_2, D_2, and HD likely occurs via a close intermolecular PH(D)...D(H)B approach and upon cooling subsequent reactivation of each gas gives the observed products. The heating of 1:1 combinations of **3-6** and **3-6$_{PDBD}$** to 150°C in the presence of MesCN in C_6D_5Br or C_6H_5Br produced statistical mixtures of H_2, D_2 and HD as determined by NMR spectroscopy. The observation of HD implies that the reaction proceeds through a close intermolecular approach of PH(D)...H(D)B fragments.

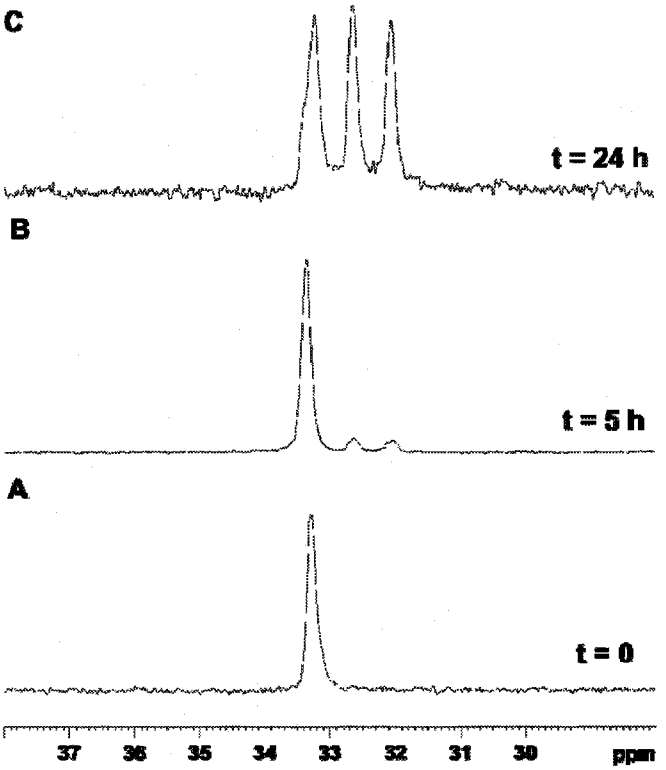
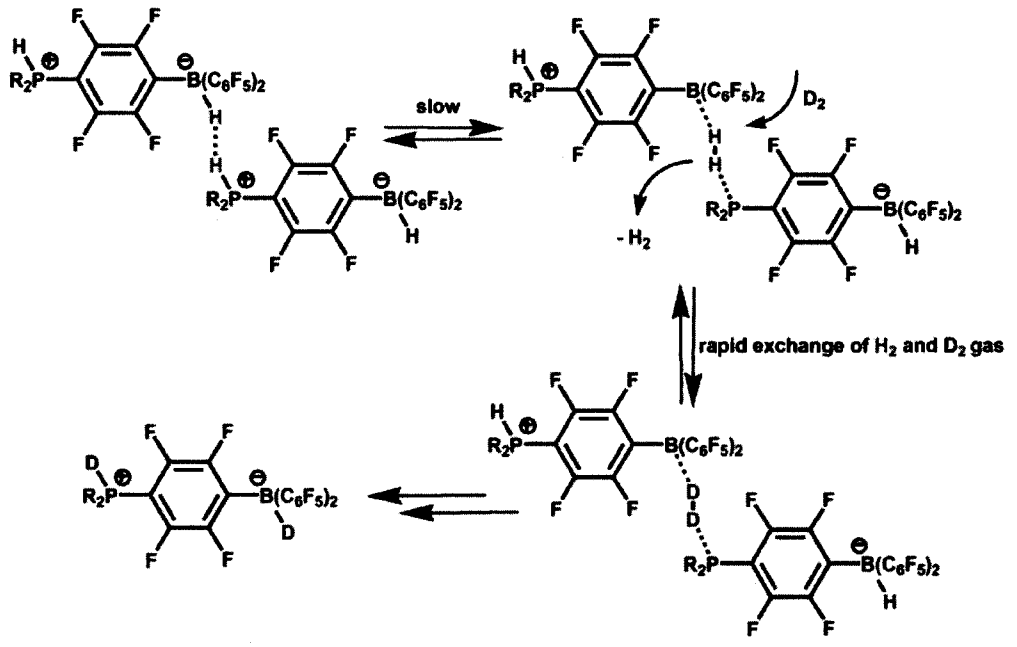


Figure 5.6 $^{31}P\{^{1}H\}$ NMR spectra at 25 °C of $^{t}Bu_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-5**) under 3.5 atm D_2 (g). (**A**) Initial spectrum at 25 °C. (**B**) After 5 hours at 150 °C. (**C**) After 24 hours at 150 °C.

Additional deuterium labelling experiments were performed using **3-5** and its isotopomer **3-5**$_{PHBD}$ which was synthesized in a similar fashion to **3-6**$_{PHBD}$. These compounds were selected as **3-5** was shown not to liberate H_2 up to 150°C in the absence of a boron trap. Heating **3-5**$_{PHBD}$ to 150 °C showed exchange of the H/D sites without loss of hydrogen from the system as determined by ^{31}P NMR spectroscopy. Heating **3-5** under ~ 3.5 atm D_2 to 150 °C for 24 hours and monitoring by ^{31}P NMR spectroscopy showed almost complete disaperance of the PH resonance from **3-5** (Figure 5.6, Scheme 5.10). An approximate calculation showed D_2 to be in a 10-fold excess over H_2, consistent with the observed result.



Scheme 5.10 Possible mechanism for the observed H_2 for D_2 exchange in **3-5** under ~ 3.5 atm of D_2 at 150 °C. R= ^{t}Bu.

These results again confirm the ability of the phosphonium borohydrides to readily exchange PH(D) and BH(D) sites without H_2 removal from the system. Heating the ion pair **5-6** ([Mes_3PH][$HB(C_6F_5)_3$]) under ~ 3.5 atm of D_2 showed only minor incorporation of D_2 (< 15 %) after 24 hours at 150 °C consistent with slower liberation of H_2 observed for **5-6** (15 hours) vs. **3-5** (4 hours) in the presence of MesCN. All three results imply that H/D exchange is coouring and most likely occurs via hydrogen loss and rapid reactivation. A possible mechanism for H/D exchange is shown in Scheme 5.8. Heating to 150 °C presumably results in the slow formation of H_2 which exchanges with the excess D_2, activation of D_2 results in formation the deuterated phosphonium borate. In the case of heating a C_6D_5Br solution of ^{t}$Bu_2PH(C_6F_4)BD(C_6F_5)_2$ on its own to 150 °C (**3-5**$_{PHBD}$), HD is released and rapidly reactived scrambling the labels. In summary the deuterium labelling experiments have demonstrated that in the absence of a borane trap,

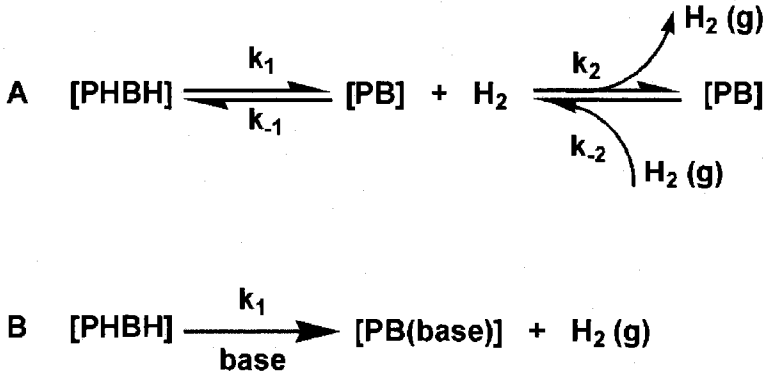
the proton and hydride sites can undergo exchange via slow gas loss and rapid reactivation. It should be noted that a similar isotope labelling experiment was used to established an intermolecular H_2 elimination process for the amine-borane $(Me_2NH)BH_3$.[315, 316]

5.3.2.3 Preliminary Kinetic Experiments and 2-D NMR experiments

To gain further insight into the mechanism of H_2 liberation and activation, preliminary kinetic experiments were conducted using the species **3-6** and **3-14**. While obtaining reliable kinetic data can be readily accomplished using one of many spectroscopic techniques (NMR, UV, IR), the present case offered many challenges. For both the liberation and activation of H_2, NMR spectroscopy was employed. For the liberation of H_2 the major problem encountered was the selection of solvent. A solvent with a boiling point in excess of 150 °C and the ability to dissolve phosphonium borate **3-6** was required. While several solvents were tried including tetrachloroethane, and trichlorobenzene, bromobenzene was selected due to its high boiling point and ability to partially dissolve **3-6**. ^{1}H NMR spectroscopy proved unreliable due to significant overlap of reactant and product signals, while high temperature ^{19}F NMR was initially unavailable, therefore preliminary kinetic data was obtained using $^{31}P\{^1H\}$ NMR spectroscopy.

Over a concentration range of **3-6** from 0.02 M to 0.8 M, the consumption of **3-6** and the generation of **3-14** were monitored over the first hour of reaction (Table 5.6). These preliminary rate data showed the decay of the concentration of **3-6** followed first-order decay kinetics with a rate constant of $6.4 \pm 0.57 \times 10^{-4}$ s^{-1} at 150°C, which indicates

a unimolecular mechanism. The temperature dependence of H_2 liberation was monitored between 100 °C and 150 °C with the concentration of **3-6** held at 0.06 M. An Eyring plot gave the activation parameters: $\Delta H^{\ddagger}$ = 21(3) kcal mol^{-1} and $\Delta S^{\ddagger}$ = -23(6) eu. Additionally the rate constants for the isotopomers of **3-6** were determined at 150 °C. All rate data is summarized in Table 5.6. The observation that all three isotopomers of **3-6** have a similar kinetic isotope effect (KIE) (Table 5.8, $k_{H/D} \sim 6{:}1$), is consistent with the high-temperature scrambling of the deuterium sites due to rapid reactivation of liberated HD. This observation possibly indicates that rapid equilibrium exists between **3-6** and **3-16** before H_2 removal from the system, indicating that the true rate constant for H_2 liberation might not be being measured but rather the loss of H_2 from solution (Equation 5.1). Therefore all the kinetic experiments were repeated in the presence of the base MesCN to trap generated free borane. The observation of a KIE does indicate that PH and/or BH bond breakage may be a part of the rate determining step, but this data is unreliable and was not considered.



Equation 5.1 (**A**) Liberation of H_2 from **3-6** at 150 °C in a sealed NMR tube. Based on the rate data it is likely that k_{-1} is faster than k_2. k_1 is the rate of H_2 loss from PHBH and k_{-2} is the rate of hydrogen diffusion into solution. (**B**) Liberation of H_2 from **3-6** at 150 °C in a sealed NMR tube in the presence of base. Trapping of borane prevents reactivation of H_2. PHBH = $Mes_2PH(C_6F_4)BH(C_6F_5)_2$, PB = $Mes_2P(C_6F_4)B(C_6F_5)_2$.

Table 5.6 Rate of H_2 liberation from **3-6**, HD liberation from **3-6$_{PDBH}$** or **3-6$_{PHBD}$**, and D_2 liberation from **3-6$_{PDBD}$** in dry C_6H_5Br (without MesCN).

Compound*	Temperature (°C)	Rate Constant (s^{-1})
3-6	150	$6.35 \pm 0.57 \times 10^{-4}$
3-6	140	$3.51 \pm 0.59 \times 10^{-4}$
3-6	130	$2.02 \pm 0.60 \times 10^{-4}$
3-6	120	$1.09 \pm 0.33 \times 10^{-4}$
3-6	110	$4.12 \pm 1.75 \times 10^{-5}$
3-6	100	$1.84 \pm 0.69 \times 10^{-5}$
3-6$_{PDBH}$	150	$1.06 \pm 0.56 \times 10^{-4}$
3-6$_{PHBD}$	150	$1.10 \pm 0.37 \times 10^{-4}$
3-6$_{PDBD}$	150	$1.08 \pm 0.30 \times 10^{-4}$

* Concentration of solutions with respect to phosphonium borate = 0.06 M

During the course of the investigation, high temperature ^{19}F NMR spectroscopy became available and was used to obtain the second set of preliminary kinetic data. The ^{19}F NMR spectra of **3-6** gave a better signal to noise ratio compared to the ^{31}P NMR spectra which allowed for more accurate concentration determination from integration. The liberation of H_2 from **3-6** to in the presence of approximately 3 equivalents of MesCN in bromobenzene to give **5-8** was again found to follow first-order decay kinetics with a rate constant of $4.29 \pm 0.23 \times 10^{-3}$ s^{-1} at 150 °C (Table 5.7). The liberation of H_2 was independent of MesCN concentration (1-3 equivalents of MesCN compared to **3-6**) and is described by the rate law; Rate = $k[PHBH]^1[MesCN]^0$. The rate constant is significantly larger than that for the reaction without added MesCN, which is consistent with the trapping of generated free borane, preventing the back reaction from taking place (Equation 5.1). The activation parameters were determined to be $\Delta H^{\ddagger} = 23.8(3)$ kcal mol^{-}

[1] and $\Delta S^{\ddagger}$ = -13.8(8) eu. The large enthalpy value suggests substantial bond breakage in the transition state and is consistent with the high reaction temperature, while the large negative entropy value indicates a highly ordered transition state. The calculated free energy ($\Delta G^{\ddagger}_{25\,°C}$ = 27.9(1) kcal mol^{-1}) is consistent with the high stability of **3-6** at 25 °C. A KIE was observed for the monodeuterated species **3-6$_{PDBH}$** (k_{PHBH} / k_{PDBH} = 3.85 ± 0.33) while a similar KIE was observed for the doubly deuterated species **3-6$_{PDBD}$** (k_{PHBH} / k_{PDBD} = 3.96 ± 0.36) (Table 5.8). No KIE was observed for species **3-6$_{PHBD}$**. These large KIE and first order kinetics suggest that the rate determining step involves PH bond breakage in a single transition state. These data support mechanistic pathways 2-a and 2-b shown in scheme 5.x. The rate of H_2 liberation from **3-5** is considerably slower than that for **3-6**, consistent with previous observations and again suggests that P-H bond breakage is involved in the rate determining step. An interesting observation is the similar reaction rates observed for H_2 liberation from **3-6** in $C_2H_2Cl_4$ vs. C_6H_5Br. These results indicate that slightly chaning the solvent polarity has minial impact on the reaction. It is noteworthy to mention, that attempts to monitor the loss of H_2 from **3-6** in decane were unsuccessful due to the complete lack of solubility of **3-6** in decane, even at 150 °C. While the present kinetic data was thoroughly performed, the first order kinetics was surprising, and therefore there may have been errors in the method for data aquisition and/or analysis of data not realized by the auother.

Table 5.7 Rate of H_2 liberation from $R_2PH(C_6F_4)BH(C_6F_5)_2$, HD liberation from **3-6$_{PDBH}$** or **3-6$_{PHBD}$**, and D_2 liberation from **3-6$_{PDBD}$** in the presence of MesCN.

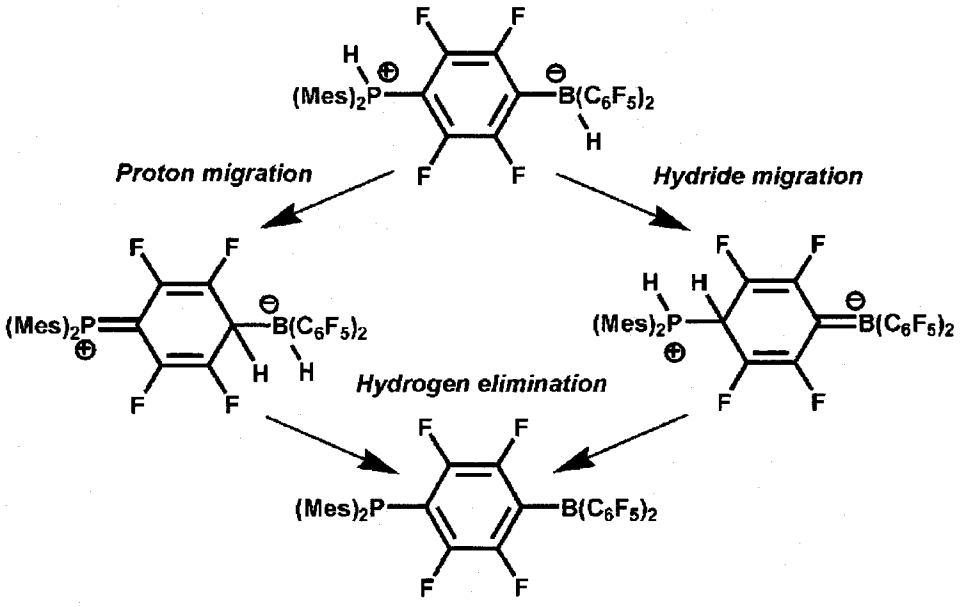
Compound*	Temperature (°C)	Solvent	Rate Constant (s^{-1})
R = Mes **3-6**	150	C_6H_5Br	$4.29 \pm 0.23 \times 10^{-3}$
R = Mes **3-6**	140	C_6H_5Br	$2.37 \pm 0.20 \times 10^{-3}$
R = Mes **3-6**	130	C_6H_5Br	$8.81 \pm 0.05 \times 10^{-4}$
R = Mes **3-6**	120	C_6H_5Br	$4.49 \pm 0.30 \times 10^{-4}$
R = Mes **3-6**	110	C_6H_5Br	$2.16 \pm 0.08 \times 10^{-4}$
R = Mes **3-6**	140	$C_2H_2Cl_4$	$1.67 \pm 0.11 \times 10^{-3}$
R = ^{t}Bu **3-5**	140	C_6H_5Br	$2.93 \pm 0.61 \times 10^{-4}$
3-6$_{PDBH}$	140	C_6H_5Br	$6.15 \pm 0.11 \times 10^{-4}$
3-6$_{PHBD}$	140	C_6H_5Br	$2.37 \pm 0.05 \times 10^{-3}$
3-6$_{PDBD}$	140	C_6H_5Br	$5.99 \pm 0.21 \times 10^{-4}$

* Concentration of solutions with respect to phosphonium borate = 0.03-0.04 M

Table 5.8 Kinetic isotope effects for the liberation H_2, D_2, and HD from **3-6**, **3-6$_{PDBD}$**, **3-6$_{PDBH}$**, and **3-6$_{PHBD}$**, in the presence and absence of excess MesCN in C_6H_5Br.

	with MesCN	without MesCN
k_{PHBH} / k_{PDBH}	3.85 ± 0.33	5.04 ± 0.96
k_{PHBH} / k_{PHBD}	1.00 ± 0.09	6.34 ± 1.36
k_{PHBH} / k_{PDBD}	3.96 ± 0.36	5.88 ± 1.74
k_{PDBH} / k_{PDBD}	1.03 ± 0.04	1.17 ± 0.38
k_{PHBD} / k_{PDBD}	3.96 ± 0.17	0.93 ± 0.34

The first-order kinetic data was surprising, as intuitively a bimolecular process (**1**) outline in Scheme 5.7, which would follow second-order kinetics, would be the most obvious mechanistic pathway. Although pathways **2-a** and **2-b** outlined in scheme 5.7 have rate determining steps that are first order with respect to phosphonium borate. Nonetheless, we initially assumed that the liberation of H_2 followed a unimolecular process where the proton or hydride undergoes intramolecular migration to the site adjacent boron or phosphorus, respectively, with rapid H_2 elimination (Scheme 5.11).



Scheme 5.11 First mechanism proposed for the liberation of H_2 assuming a unimolecular process. Either a proton or hydride thermally migrates across the C_6F_4 ring to the position adjacent boron or phosphorus, respectively. No experimental evidence for the intermediates was obtained and recent theoretical calculations have since disproved this mechanism.

Although the observation of intermolecular H/D exchange, the large negative entropy, and the fact that the bimolecular ion pairs $[R_3PH][HB(C_6F_5)_3]$ liberate H_2, implies that the generation of H_2 is accomplished through a bimolecular process involving atleast two molecules of phosphonium borate. The-first order rate law could be

rationalized in terms of the phosphonium borates existing as dimers in solution. Ion pairs are known to interact in solution,[317] the present phosphonium borates $R_2PH(C_6F_4)BH(C_6F_5)_2$ are charge neutral overall, although the positive and negative fragments are well separated and could easily pair with a corresponding ion from a another molecule forming dimers, or even high order aggregates. To shed light on the aggregation of the phosphonium borates in solution, NOESY and DOSY NMR experiments were performed.

Nuclear Overhauser effect spectroscopy (NOESY) experiments were carried out to determine if an intermolecular dipolar coupling interaction exists between the PH and BH sites of the phosphonium borates of the form $R_2PH(C_6F_4)BH(C_6F_5)_2$. Such an interaction would suggest that the species come in close contact in solution. 2D ^1H-^1H NOESY experiments with mixing times (τ, time allowed for magnetization transfer) ranging from 0.1-0.5s and 1s, were run on solutions of **3-5** and **3-6** in CD_2Cl_2 and C_6D_5Br. Cross peaks were only observed between the PH moiety and the CH_3 groups of the ^{t}Bu or Mes substituents on phosphorus. It was noted that a strong cross peak was observed in a $^1H\{^{11}B\}$-^1H NOESY (τ = 0.26) experiment between the NH and BH moieties of the related ion pair $[Et_3NH][HB(C_6F_5)_3]$,[303] Therefore, additional boron decoupled $^1H\{^{11}B\}$-^1H NOESY (τ = 0.1-0.3s) experiments were carried out on **3-6** in CD_2Cl_2 and C_6D_5Br. Again, no cross peaks were observed between the PH and BH moieties. In each case, the NOESY experiments were run for several hours to increase signal intensity. While no through-space intermolecular interaction between a PH and BH of **3-5** or **3-6** was observed by NOESY experiments, such an interaction cannot be ruled out, as nOe interactions are sensitive to many factors including temperature, solvent viscosity, and spin-lattice relaxation. Therefore, further investigation may be required.

Table 5.9 Diffusion coefficients (D, 10^{-10} m^2s^{-1}),[a] hydrodynamic radii (r_H, Å),[b] hydrodynamic volume (V_H, $Å^3$),[c] volume determined from crystallographic data for one molecule (V_{XRAY}),[d] aggregation number ($N = V_H/V_{XRAY}$)[e].

Compound	D	r_H	V_H	V_{XRAY}	N	N*
$Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (**3-6**)	9.15	5.51	698	830	0.84	1.10
$Mes_2PH(C_6F_4)BF(C_6F_5)_2$ (**2-5**)	8.70	5.79	811	950[f]	0.85	1.10
$Cy3P(C_6F_4)BH(C_6F_5)_2$ (**3-7**)	8.65	5.82	825	968	0.85	1.11
$Cy_3PH(C_6F_4)BF(C_6F_5)_2$ (**2-1**)	8.54	5.99	859	970	0.89	1.15
$Mes_2P(C_6F_4)B(C_6F_5)_2$ (**3-13**)	8.93	5.64	750	926[g]	0.81	1.05
BPh_3	10.54	3.30	146			

[a] Determined by ^1H DOSY experiments at 25°C in CD_2Cl_2 (viscosity, $\eta = 4.13x10^{-4}$ kg $m^{-1}s^{-1}$) with sample concentrations = 0.05M. [b] Determined using the Stokes-Einstein equation assuming a c factor = 6. [c] Calculated assuming spherical shape in solution. [d] Determined from unit cell volume. [e] $N = V_H / V_{XRAY}$. [f,g] Volume for the closely related compounds $Mes_2PH(C_6F_4)BCl(C_6F_5)_2$ (**3-3**) and $Mes_2P(C_6F_4)B(THF)(C_6F_5)_2$ (**3-14**). *Assuming a low limit c factor of 5.5.

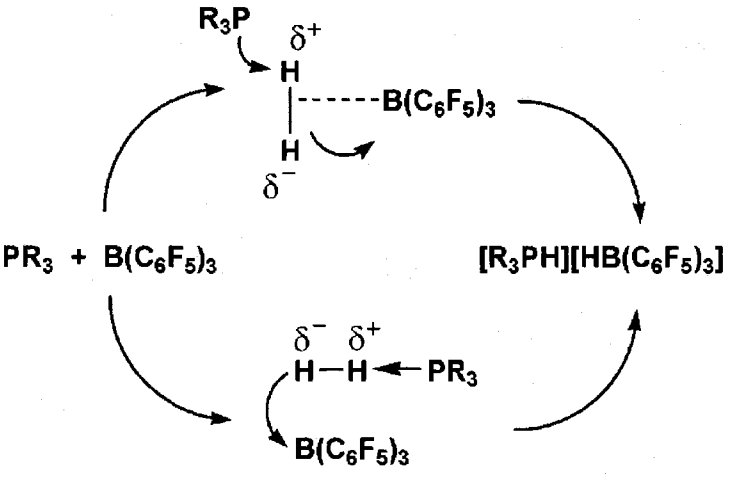
Additional ^1H-^{19}F HOESY experiments may prove invaluable for the detection of intermolecular interactions between these 'frustrated' Lewis pairs. Such techniques have been widely employed to detect ion par interactions between fluoroarylborate anions and their respective cations.[188, 303, 317-320] Unfortunately, the equipment for such experiments was not available at the University of Windsor to conduct these experiments.

Diffusion ordered spectroscopy (DOSY) experiments were carried out to estimate the rates of diffusion for the series of phosphonium borates. It has been well established that molecules of different sizes diffuse in solution at different rates.[317, 321] The rate at which a molecule diffuses in solution can be easily determined using pulse gradient NMR spectroscopy, and from this diffusion constant, the molecules' approximate hydrodynamic radii can be determined using the Stokes-Einstein equation.[318, 322] This

value, or the readily obtained hydrodynamic volume, can be compared to standards or calculated values to determine the aggregation of the molecule in solution, i.e. monomer vs. dimer. Results are summarized in Table 5.9. The experimental hydrodynamic volumes compare well those obtained from crystallographic data. From the aggregation number it is apparent that the present phosphonium borates exist as monomers in solution. These results imply that any intermolecular pairing of two molecules of compounds $R_2PH(C_6F_4)BH(C_6F_5)_2$ is transient. Attempts to run these experiments at 100 °C were unsuccessful, although any weak aggregation is likely to be unfavourable at high temperatures. No experiments at low temperatures (less than 25 °C) were conducted as these temperatures are far outside the temperature regime for H_2 liberation. To gain more accurate data, PGSE experiments over a broad concentration range are suggested along with a precise determination of the correct `c` factor (these factors have been shown to vary from 5-6 for molecules of similar size to the present species).[318, 319] Additionally, calculated volumes for monomers and dimers for direct comparison to experimental values would be beneficial. Results obtained from these experiments, coupled with extensive variable-temperature ^{1}H-^{19}F HOESY experiments will be crucial for the accurate determination of aggregation in solution. Overall there is no experimental evidence that phosphonium borates $R_2PH(C_6F_4)BH(C_6F_5)_2$ exist as dimers, therefore coupled with the first order kinetics, it is unlikey that H_2 loss follows pathway **1** outlined in scheme 5.7.

5.3.2.4 Mechanistic Insights into the Activation of H_2 in Solution

Transition metal centers are known to bind molecular hydrogen reversibly and can split H_2 via homolytic or heterolytic cleavage pathways. Homolytic cleavage involves oxidative addition at the metal center, while heterolytic cleavage involves electrophilic activation of H_2 at the metal center followed by proton transfer to a metal bound ligand.[25, 35, 323, 324] In the present case the phosphino-borane combinations heterolytically cleave H_2 as a proton and a hydride end up on different atoms.



Scheme 5.12 Initial proposed mechanisms for the heterolytic cleavage of H_2 by phosphines and boranes based on examples in the literature. Note: While not shown, it can be assumed that the phosphino-boranes $R_2P(C_6F_4)B(C_6F_5)_2$ could react with H_2 in a similar intermolecular fashion.

By analogy to transition metal chemistry, one might intuitively anticipate that a side-on interaction of H_2 with the Lewis acidic boron center results in polarization of H_2, thus facilitating protonation of an approaching phosphine resulting in the formation of phosphonium hydridoborate (Scheme 5.12). Attempts to observe such a Lewis acid-H_2 interaction were undertaken by treatment of $B(C_6F_5)_3$ with higher pressures of H_2 (4 atm).

Monitoring these mixtures by ^{1}H and ^{19}F NMR spectroscopy at temperatures as low as 190 K, showed major resonances attributable to free $B(C_6F_5)_3$ and minor resonances attributed to $(H_2O)B(C_6F_5)_3$ (*vide infra*). No other species were observed and thus this experimental evidence suggests that a borane-H_2 adduct is not stable. While computational studies have examined the existence of BH_5 and described this species as a weak $(\eta^2\text{-}H_2)BH_3$ adduct,[325-328] recent calculations have shown that H_2 does not form an adduct with $B(C_6F_5)_3$,[17] supporting the experimental observation. An alternative mechanism that warrants consideration involves the interaction of Lewis bases with H_2 (Scheme 5.12). In this regard, Sweany and co-workers have demonstrated the formation of van der Waal complexes for a variety of Lewis bases including phosphines with H_2 in an argon matrix.[329] Such interactions are thought to lead to polarization of H_2 via an end-on base-H_2 interaction involving lone pair donation to the σ^* orbital of H_2. Attempts to observe such interactions by low-temperature NMR spectroscopy proved unsuccessful. A third possible mechanism involves the synergistic activation of H_2 where both the phosphine and borane sites simultaneously interact with H_2. Very recent calculations by Papai and coworkers have suggested that in solution the 'frustrated' Lewis pair combinations $^{t}Bu_3P/B(C_6F_5)_3$, $Mes_3P/B(C_6F_5)_3$ and $[^{t}Bu_2P(C_6F_4)B(C_6F_5)_2]_2$ exist as encounter complexes held together by dispersion forces and weak intermolecular CH...FC interactions with phosphorus/boron distances of approximately 4.2, 4.3 and 4.7 Å, respectively (Figure 5.7).[17] These 'encounter complexes' provide a cavity where H_2 is activated along the P...B axis via a synergistic push-pull process, resulting in the formation of PH and BH covalent bonds. The overall process was found to be exothermic consistent with the rapid room temperature activation of H_2.

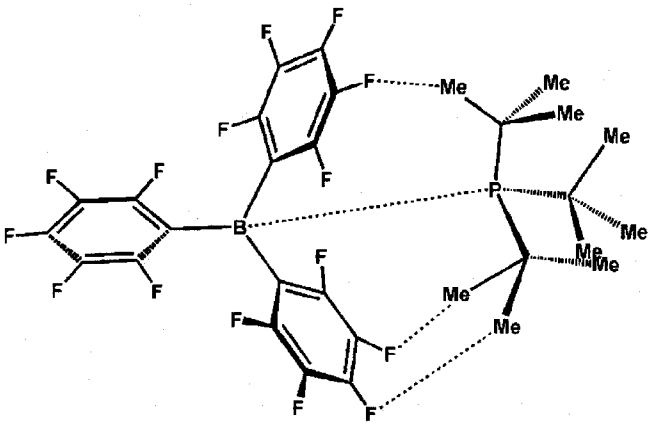


Figure 5.7 Phosphine/borane 'encounter complex' held together by weak CF...HC and dispersion interactions suggested by Papai and co-workers based on theoretical calculations (P-B distance > 4 Å). It is thought that H_2 is activated in a synergistic fashion by the P and B atoms of the 'encounter complex'.

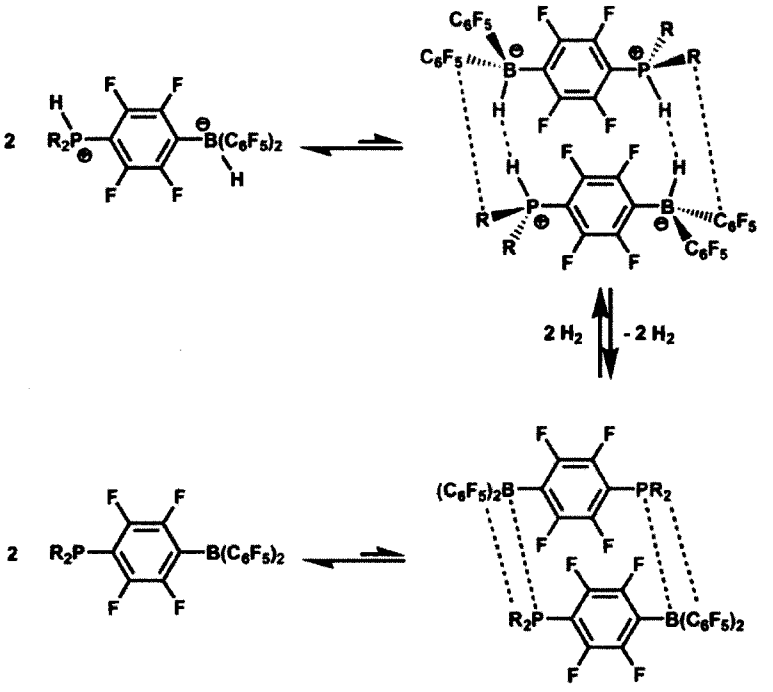
Additionally, the authors predicted that the 'frustrated' Lewis pair $^t Bu_3P/BPh_3$ has a lower 'association energy' than that of $^t Bu_3P/B(C_6F_5)_3$, which is consistent with the observed slower rate of reaction observed for the former. A related theoretical study also suggested a similar bimolecular mechanism for the activation of H_2 and found the overall process to be exothermic, again consistent with the experimental results, although the authors indicate that a phosphino-borane dimer is likely transient and not thermodynamically stable.[21]

In order to gain further insight into the mechanism of H_2 activation, an effort was put forth to obtain kinetic data. For the conversion of **3-14** to **3-6** under an atmosphere of H_2, two major problems were encountered. First was the fast rate at which the reaction proceeds and second was the low solubility of H_2 in solution. Numerous attempts were made to monitor the activation of H_2 by **3-14** using $^{31}P\{^1H\}$ NMR spectroscopy over a temperature range from -30 °C to 25 °C . Reaction conditions consisted of using CH_2Cl_2

or toluene solutions with H_2 pressures of 1 or 3.5 atm. In each case, inconsistent results were obtained as the diffusion of H_2 into solution was slower than the activation of H_2. Therefore no useful mechanistic information was obtained for this reaction. While no accurate data was gathered in the current study, other methods for obtaining kinetic data do exist and may prove useful in the future. Monitoring the disappearance of an orange solution of **3-14** by UV-vis spectroscopy or the appearance of the B-H stretch by IR spectroscopy (if observable) under H_2 at low temperatures may be an option. Additionally, experimental NMR apparatuses exist where a NMR tube can be put under a positive flow of H_2 which may solve the issue of mixing hydrogen in solution.[330, 331] Another option may be to run the experiments under pseudo first order conditions by using extremely high pressures of H_2. This could be accomplished by employing sapphire NMR tubes which can with stand gas pressures up to 50 atm.[332]

5.3.2.5 Final Proposed Mechanism for Activation and Liberation of H_2

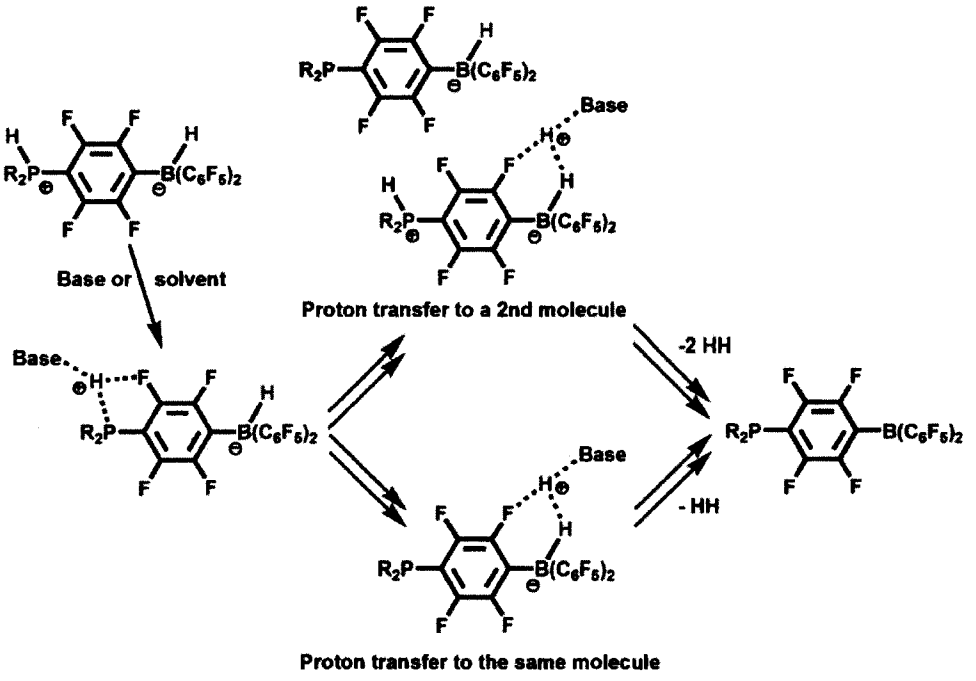
Based on the principle of microscopic reversibility, the activation of H_2 should follow the reverse mechanistic pathway as the liberation of H_2. From the experimental results and recent theoretical calculations[17, 21] an overall mechanism can be proposed. While it is tempting to agree with the theoretical calculations and propose that the reversible loss of H_2 proceeds through an 'encounter complex' or phosphonium borate/phosphino borane dimers, and that H_2 bond formation and breaking is concerted (Scheme 5.13), no experimental evidence was obtained supporting such a mechanism. Therefore, this mechanism can be ruled out based on the current data.



Scheme 5.13 Suggested reversible H_2 activation based on computational analysis. While not disproved, no experimental evidence exists for the formation of dimers in solution and the concerted breaking and forming of H-H bonds.

The first order kinetics and the PH/PD KIE implied that the rate determining step for loss of H_2 is a unimolecular process involving PH bond breakage. The intermolecular H/D exhcange implied that at least two molecules of phosphonium borate are involved in generating hydrogen. These results can be rationalized by following a mechanism outlined in Scheme 5.7. Here, breaking of the PH bond is the inital step, which is followed by transfer of the proton to a borohydride moiety of the same or different molecule with subsequent H_2 elimination (Scheme 5.14). There should be no significant preference for which borohydride moiety is protonated. While 'naked' proton transfer is unlikey, it is probable that the proton transfer is assited by the solvent or an as yet unidentified base, such as glass. For this mechanism to hold true, addition of stoicometric

amounts of base should accelerate the loss of H_2, which is the foucs of section 5.3.3. It should be noted that this mechanism is only probale and more detailed work will be required to conclusively corfirm the mechanism for the unprecedented reversible H_2 activation for the present phosphonium borate/phosphino borane systems.



Scheme 5.14 Proposed mechanism for liberation of H_2 based on current experimental results. Liberation of H_2 is first order with respect to one molecule of phosphonium-borate. PH bond break is the rate determining step, followed by rapid proton transfer to the vicinity of a borohydride moiety, with subsequent rapid H_2 elimination. Proton transfer is probably facilitated by solvent or an unidentified base.

5.3.2.6 Independent H_2O Experiments

A major problem with the addition of H_2 to these unique combinations of phosphines and boranes is the interference of trace H_2O. It is well known that $B(C_6F_5)_3$

and H_2O form a weak adduct and the dynamics between these two species has been thoroughly investigated.[121, 292, 333] Such $(H_2O)B(C_6F_5)_3$ adducts are readily deprotonated by solvent or bases, and depending on stoichiometry, can yield several different hydroxy borate anions.[197, 303, 334] Additionally $B(C_6F_5)_3$ can undergo hydrolysis in the presence of H_2O giving the known boronic acid $HOB(C_6F_5)_2$[335-337] and C_6F_5H. [120, 338] Initial experiments involving the addition of H_2 to a mixture of Mes_3P and $B(C_6F_5)_3$ resulted in one major and one minor product.

$$Mes_3P + B(C_6F_5)_3 \xrightarrow{H_2O} [Mes_3PH][HOB(C_6F_5)_3]$$

$$[Mes_3PH][HOB(C_6F_5)_3] \xrightarrow{B(C_6F_5)_3} [Mes_3PH][HO\{B(C_6F_5)_3\}_2]$$

Scheme 5.15 Reaction of FLP's with H_2O.

The major product was the phosphonium hydridoborate **5-2** while the latter minor product was identified as the H_2O activated species $[Mes_3PH]][(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]$ (**5-16**). The formation of this ion pair likely occurs via scavenging of H_2O by $B(C_6F_5)_3$, which is then deprotonated by phosphine; excess $B(C_6F_5)_3$ then coordinates to the hydroxyl borate anion forming **5-16**. To confirm the formation of **5-16**, an independent experiment was carried out. Addition of one equivalent of H_2O to a toluene solution of Mes_3P and $B(C_6F_5)_3$ gave the ion pair $[Mes_3PH][HOB(C_6F_5)_3]$ (**5-15**) in quantitative yield. Addition of a second equivalent of $B(C_6F_5)_3$ to **5-15** gave the species **5-16** (Scheme 5.15). Both products were fully characterized by multi-nuclear NMR spectroscopy and X-ray crystallography for **5-16** (Table 5.4, Fiugre 5.8). While both anions are known,[292, 303, 339-341] they have not been paired with a phosphonium cation.

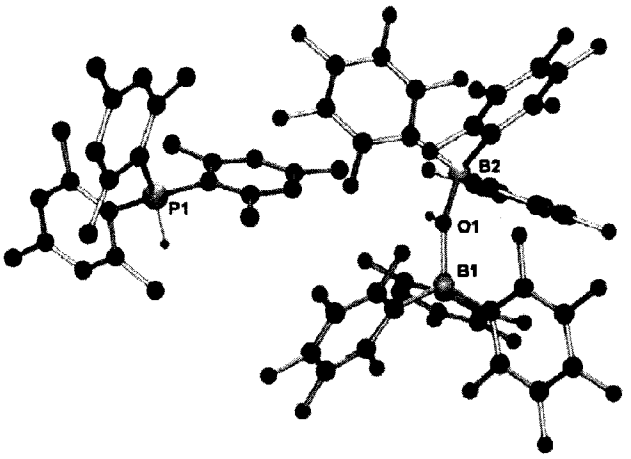


Figure 5.8 POV-ray depictions of **5-16**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: yellow-green, Oxygen: red. Carbon hydrogen atoms omitted for clarity.

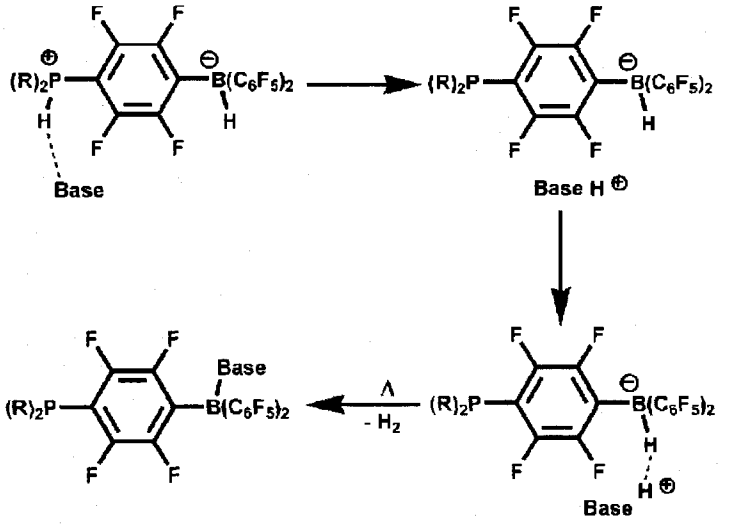
The ^{31}P NMR spectra of both compounds display a resonance at -27.0 ppm ($^{1}J_{PH}$ = 480 Hz), consistent with the presence of the Mes_3PH cation. In addition to expected resonances for the cation, the room-temperature ^{1}H NMR spectra exhibit broad signals at 5.0 and 6.3 ppm for the BOH group of **5-15** and **5-16**, respectively. The former is shifted downfield from that found for the related ion pair with a triethylammonium cation $[Et_3NH][HOB(C_6F_5)_3]$. This is presumably due to the absence of strong hydrogen bonding in **5-15**, which is observed in the NH...O(H)B moiety of $[Et_3NH][HOB(C_6F_5)_3]$.[341] The increased steric bulk of the cation prevents close approach of the PH and BOH moieties, forming a more separated ion pair. This thought is supported by the similar downfield shift of the BOH moiety in the anion $[(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]$ which is not susceptible to hydrogen bonding due to steric constraints.[303] A ^{1}H-^{1}H 2-D nOe experiment on compund **5-15** showed no nOe, only an in-phase cross peak, which indicates that the PH

and OH protons were undergoing exchange,[342] thus the cation and anion are interacting. The ^{11}B NMR resonances appear at -3.7 and -0.5 ppm for **5-15** and **5-16**, respectively, comparing well to those reported by Saverio *et al.*[303] The ^{19}F NMR spectra of **5-15** and **5-16** are typical for 4-coordinate boron centers and again are similar to that reported in the literature.[303] A POV-ray depiction of **5-16** is shown in Figure 5.8. The phosphorus center is pseudo-tetrahedral with an average C-P-C angle of 115.1°. The borate anion appears as would be expected and the metrical parameters are unexceptional. As all solvent and organic reagents were determined to be moisture free, the likely source of H_2O is from the H_2 cylinder. To investigate this issue, a toluene solution of $B(C_6F_5)_3$ was pressurized with 3.5 atm H_2. Variable-temperature ^{19}F NMR spectroscopy showed broadening of the $B(C_6F_5)_3$ resonances at 25 °C and upon cooling to -70 °C, three new minor resonances grew in, which were attributed to the adduct $(H_2O)B(C_6F_5)_3$. This confirms water contamination was from the H_2 cylinder. While trace water could not be completely removed, employing a Drierite molecular sieve column and using two *in-situ* liquid N_2 cold traps greatly reduced the amount H_2O contamination.

5.3.3 Base Assisted Hydrogen Loss for Phosphonium Borates

The base-catalyzed or proton-assisted generation of hydrogen from hydrides is well known. Casey and co-workers demonstrated that phosphines can acts as catalysts for the evolution of hydrogen from a hydroxycyclopentadienyl ruthenium(II) hydride,[321] while a recent review has detailed the protonation of metal hydrides.[306] Based on the current mechanism, it was believed that the liberation of H_2 could be assisted by a Lewis base. As discussed previously, MesCN does not interact with the proton of **3-6** and only

facilitates the liberation of H_2 by trapping free borane, preventing the reactivation of H_2. Addition of the relatively more basic phosphine Mes_3P to a solution of **3-6** resulted in complete deprotonation of **3-6** and generation of the ion pair $[Mes_3PH][Mes_2P(C_6F_4)BH(C_6F_5)_2]$ as determined by ^{31}P NMR spectroscopy. Reminiscent of the ion pair **5-6**, heating this species to 150 °C in bromobenzene resulted in no observable H_2 loss, while upon the addition of one equivalent of MesCN, complete H_2 liberation was observed within 15 hours at 150 °C. This result indicates that Mes_3P is too basic and sterically bulky to assist in the liberation of H_2, making H_2 loss thermodynamically unfavorable. The large size of the phosphine prevents a close approach of the PH and BH fragments, while the increased basicity makes for a stronger X-H bond. Phosphine oxides are known to be good proton acceptors due to their ability to form hydrogen bonds.[343] Addition of one equivalent the phosphine oxide Et_3PO to **3-6** in bromobenzene resulted in a broadening of the ^{31}P NMR resonance for **3-6** indicating possible rapid proton exchange between the phosphine and phosphine oxide. Monitoring by ^{31}P NMR spectroscopy, the reaction mixture was subjected to a controlled heating experiment (Figure 5.9). At 60 °C, H_2 liberation began to occur along with concurrent formation of the adduct $Mes_2P(C_6F_4)B(C_6F_5)_2(Et_3PO)$ (**5-17**). Upon heating to 100 °C complete H_2 liberation was observed. This is in stark contrast to the liberation of H_2 in the absence of phosphine oxide where H_2 loss was only observable above 100 °C, thus demonstrating the ability of phosphine oxide to accelerate the liberation of H_2 from **3-6**. A similar result was observed for a 1:1 mixture of Et_3PO and **3-5** in bromobenzene. H_2 liberation and formation of $^tBu_2P(C_6F_4)B(C_6F_5)_2(Et_3PO)$ (**5-18**) began to occur at 100 °C (Figure 5.9). The higher temperature regime is consistent with the increased basicity at phosphorus for **3-5** compared to **3-6**.



Scheme 5.16 Phosphine oxide assisted liberation of H_2. Base = R_3PO.

To determine the effect of the basicity of the phosphine oxide on H_2 liberation, the reaction of the phosphine oxides R_3PO (R = Et, Ph, and *p*-FC_6H_4) with **3-6** were examined. The results are summarized in Table 5.9. The fastest reaction time occurred when Ph_3PO was employed. It is likely that the more basic phosphine oxide Et_3PO forms stronger hydrogen bonds with the proton making it more difficult to protonate the borohydride, while the less basic phosphine oxide $(p\text{-}FC_6H_4)_3PO$ forms weaker hydrogen bonds with the proton of **3-6**, making it a poor proton shuttle. To gain further insight into the base assisted H_2 liberation, the reaction of **3-6** with varying equivalents of Ph_3PO in bromobenzene at 100 °C was explored (Table 5.10). Increasing the amount of Ph_3PO in the reaction mixture resulted in a decreased reaction time for the liberation of H_2. The fastest reaction occurred when two equivalents of Ph_3PO were added. Even though the reactions were carried out in the presence of one equivalent of MesCN, it has been independently determined that Ph_3PO displaces MesCN and coordinates to the Lewis acidic boron forming $Mes_2P(C_6F_4)B(Ph_3PO)(C_6F_5)_2$ (**5-19**).

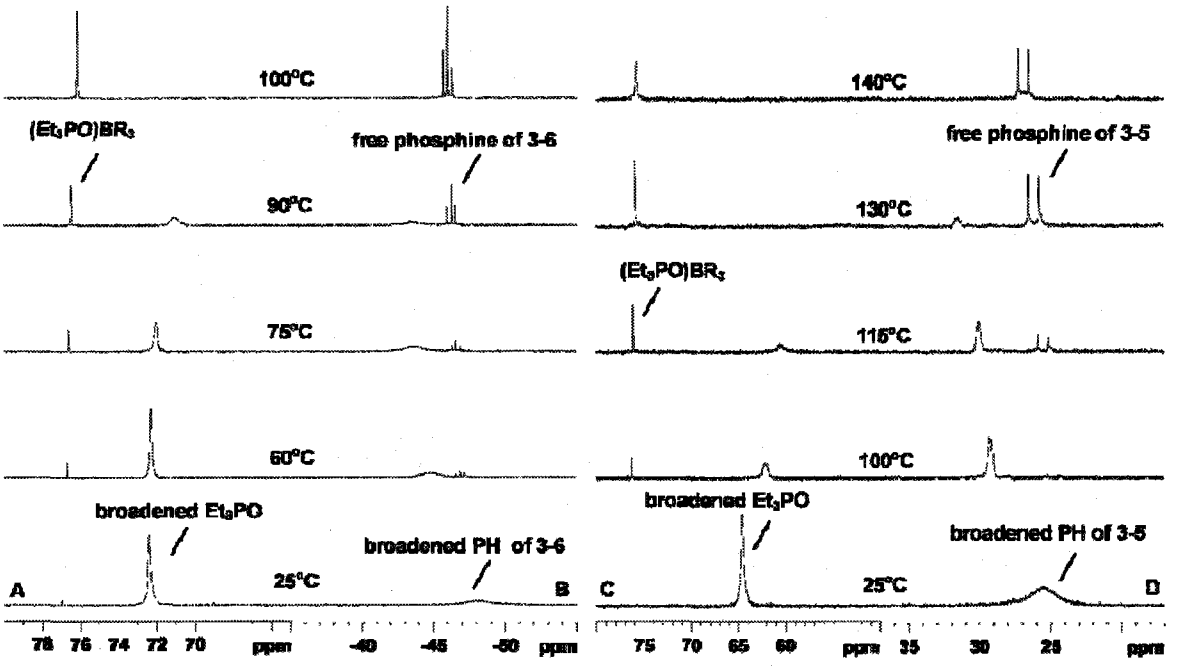


Figure 5.9 Stacked plots showing the base assisted liberation of H_2 from **3-5** and **3-6**. (**Left**) ^{31}P NMR of **3-6** + Et_3PO in C_6H_5Br. Observe broadening of PH (δ -47 ppm) resonance at 25 °C and that H_2 liberation begins to occur above 60 °C. (**Right**) ^{31}P NMR of **3-5** + Et_3PO in C_6H_5Br. Observed broadening of PH (δ 25 ppm) resonance at 25 °C and that H_2 liberation begins to occur above 100 °C. In both cases free borane is trapped by Et_3PO.

Therefore, below one equivalent, Ph_3PO must dissociate from B in order for the reaction to proceed, while above one equivalent, there is always free Ph_3PO present to assist in the liberation of H_2. These results demonstrate the ability of Lewis bases to catalyze the liberation of H_2 from the phosphonium hydridoborate $Mes_2PH(C_6F_4)BH(C_6F_5)_2$. Of note is the large ^{31}P NMR chemical shift difference of 20.7 ppm between free Ph_3PO and coordinated Ph_3PO in **5-19**. This value is considerably larger than that found between free Ph_3PO and coordinated Ph_3PO ($\Delta\delta$ = 4.2) in $(Ph_3PO)B(C_6F_5)_3$ and can be attributed to the absence of phenyl/fluorophenyl π-stacking interactions in **5-19**, which exists in $(Ph_3PO)B(C_6F_5)_3$.[344] Presumably, the large phosphorus substituent on one of the fluoroaryl rings of **5-19** prevents the formation of an

eclipsed conformation. In summary it has been demonstrated that phosphine oxides have the ability to catalyze the liberation of H_2 from phosphonium hydridoborates. These results are important as the relatively lower temperature regime for H_2 liberation allows for the use of a wider variety of solvents and may prove useful in application of these systems for hydrogen delivery. Preliminary results have shown that H_2O can act as a proton transfer reagent, although at high concentrations of H_2O, hydrolysis of the BH bond was observed, and solubility in organic solvents was problematic. While this reactivity was not explored in detail, the search for efficient catalysts, including ethers and siloethers may be an area of future work.

Table 5.10 Liberation of H_2 from **3-6** in the presence of various phosphine oxides and in the presence of varying equivalents Ph_3PO[a].

R_3PO	Equivalents of R_3PO	Temperature (°C)	Reaction time for complete H_2 loss (minutes)[c]
R = Et[b]	1	75	170
R = Ph[b]	1	75	105
R = *p*-FC_6H_4[b]	1	75	390
R = Ph[b]	0	100	1010
R = Ph[b]	0.1	100	306
R = Ph[b]	0.5	100	45
R = Ph[b]	1	100	15
R = Ph[b]	2	100	12

[a] All experiments carried out in the presence of 1 equivalent MesCN. [b] Concentration = 0.06 M in C_6D_5Br. [c] Reaction monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

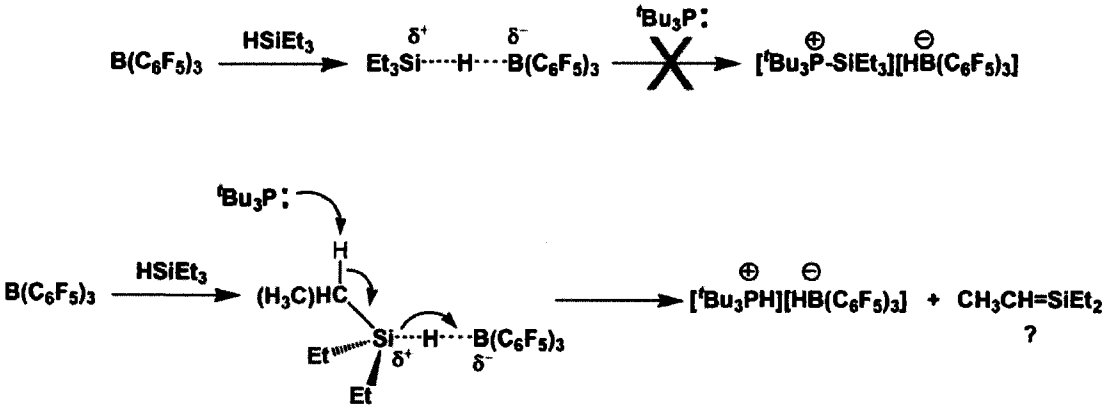
5.3.4 Activation of Small Molecules other than Hydrogen

The discovery of the unprecedented metal-free activation of H_2 by sterically `frustrated` Lewis pairs prompted us to investigate the activation of other small molecules in the absence of metals. Fellow graduate student Jenny McCahill has demonstrated that FLP`s readily activate α-olefins to give alkyl linked phosphonium borates.[6] This result is interesting as α-olefins are not known to react with phosphines or boranes independently. As most catalytic processes are predicated on the activation of small molecules, expanding the scope of reactive functional groups with FLP scaffold is of interest. Herein is described the reactivity of FLP's with silanes, thiols, and disulfides.

5.3.4.1 Reaction of FLP's with Silanes

The hydrosilation of alcohols, ketones, aldehydes, esters and imines is a well known process and is a common method for the reduction C= O and C= N functionalities. Recently, Piers and co-workers have demonstrated that the Lewis acid $B(C_6F_5)_3$ is an effective hydrosilation catalyst.[302, 345-348] The reaction is governed by a nucleophilic-electrophilic mechanism where $B(C_6F_5)_3$ polarizes the Si-H bond through a Si-H...B interaction rendering the silicon center susceptible to nucleophilic attack. Additionally, the Si-H bond of organosilanes are known to be activated by transition metal centers in an analogous fashion to H_2.[324] To test the scope of FLP type reactivity we investigated the reaction of FLP`s with R_3SiH in an effort to activate the Si-H bond and generate silylphosphonium hydridoborates of the form $[R_3PSiR_3][HB(C_6F_5)_3]$.

Addition of Et_3SiH to a toluene solution of $^tBu_3P$ and $B(C_6F_5)_3$ resulted in formation of a yellow solution which upon removal of solvent gave an off-white solid. Analysis by multi-nuclear NMR spectroscopy revealed an ^{11}B NMR resonance at -25 ppm and a ^{19}F NMR spectrum consistent with the presence of the anion $HB(C_6F_5)_3$. Interestingly, the ^{31}P and ^1H NMR spectra revealed resonances consistent with the formation of the protonated phosphonium cation $^tBu_3PH$. No resonances attributable to an Et_3Si^+ fragment were observed. The product was formulated as the ion pair $[^tBu_3PH][HB(C_6F_5)_3]$ (**5-5**) (Scheme 5.17).



Scheme 5.17 Possible reaction between FLP's and Et_3SiH.

The reaction was repeated with the silanes Bu_3SiH and Ph_2MeSiH only to produce similar results. No reaction was observed between the FLP and Ph_3SiH. Similarly, employing the less basic phosphine Mes_3P in the reaction with $B(C_6F_5)_3$ and Et_3SiH resulted in no reaction. Mechanistically it is likely that $B(C_6F_5)_3$ first interacts with the silane polarizing the Si-H bond resulting in the silicon center adopting a partial positive charge, analogous to the observation of Piers. While relatively small nucleophiles such as ketones or

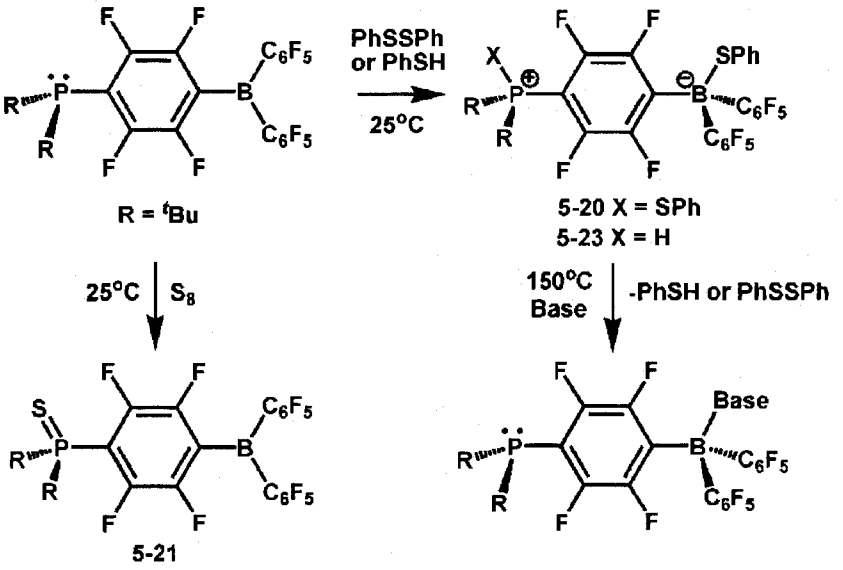
aldehydes readily interact with the silicon center through oxygen atom, $^{t}Bu_3P$, is too bulky to undergo nucleophilic attack and instead acts as a base by abstracting a α- or β-hydrogen off a silicon alkyl chain. The resulting silicon containing by-product was not detected by NMR spectroscopy. Future studies may attempt to confirm the source of H atoms by using deuteriated silanes. This mechanistic view is supported by the fact that no reaction is observed with the silane Ph_3SiH which has no alkyl hydrogen atoms and that the less basic phosphine Mes_3P is also unreactive as it does not abstract a hydrogen atom from the incipient silylium cation. Additionally, it has been reported that while the small phosphine Me_3P and Me_3Si^+ form the silylphosphonium cation $[Me_3SiPMe_3]^+$, no reaction is observed between the much larger phosphine $(Me_3Si)_3P$ and Me_3Si^+.[349] Ultimately the inability of FLP`s to form stable silylphosphonium hydridoborate ion pairs led us to investigate other reactivity.

5.3.4.2 Reaction of FLP's with Thiols and Disulfides

The activation of E-E and E-H bonds (E = B, Si, S, Sn) and their transfer to unsaturated carbon molecules are import processes in organic synthesis.[350-353] Specifically carbon-sulphur bond forming reactions are important for drug development and many organosulphur compounds are biologically active.[354] The cleavage of S-H and S-S bonds is well known and can be accomplished using transition metals[350, 355] and/or main group nucleophiles and electrophiles.[356] Recently, several papers have described the Lewis acid catalyzed disulphidation of alkenes and alkynes employing BF_3,[357] $AlCl_3$,[358] $GaCl_3$,[359, 360] $FeCl_3$,[358] and $ZnCl_2$[361] as catalysts. In each case it is proposed that the Lewis acid initially

interacts with a disulphide generating a partial sulphenium cation which reacts with olefin. Nucleophilic attack of the intermediate by the thiolate anion gives the desired dithiolated product. On the other hand phosphines have been shown to promote the desulphurization of *di-* and *tri*-sulphides,[362] while the conversion of disulphides to thiols by phosphines in the presence of H_2O is widely known.[363-367] Additionally, a recent computational study has suggested that phosphines react with disulfides via an S_N2 mechanism generating phosphonium cation-thiolate anion salts of the form $[R_3PSR][SR]$, which should exist experimentally upon stabilization of the anion.[368] In both the disulphidation of unsaturated substrates and the desulphurization of sulphides, the intermediates have not been fully observed. While thiolate anions $[RS]^-$ can be readily generated through deprotonation of the corresponding thiol with an appropriate base, reports of sulphenium cations $[RS]^+$ are rare with the elusive species only being observed in the gas phase[369] or via stabilization with one[370] or two[371] nitrogen donors. The related thioalkoxyphosphonium cations $[R_3PSR]^+$ are relatively stable species.[372-374] Therefore, we envisioned employing sterically 'frustrated' Lewis pairs for the activation of disulfides to generate phosphorus thioalkoxyphosphonium cations and alkoxythioborate anions.

Addition of diphenyldisulphide (PhSSPh) to an orange toluene solution of the phosphino-borane $^t Bu_2P(C_6F_4)B(C_6F_5)_2$ (**3-13**) at room temperature resulted in immediate loss of color. After stirring for one hour at 25 °C and removal of the solvent an off-yellow solid was recovered in 76 % yield. The ^{31}P NMR spectrum revealed a singlet resonance at 76.2 ppm, shifted ~ 51 ppm downfield from the parent phosphino-borane. The ^1H NMR spectrum showed resonances from 7.9-7.2 ppm and at 1.3 ppm attributable to Ph and $^t Bu$ groups, respectively.

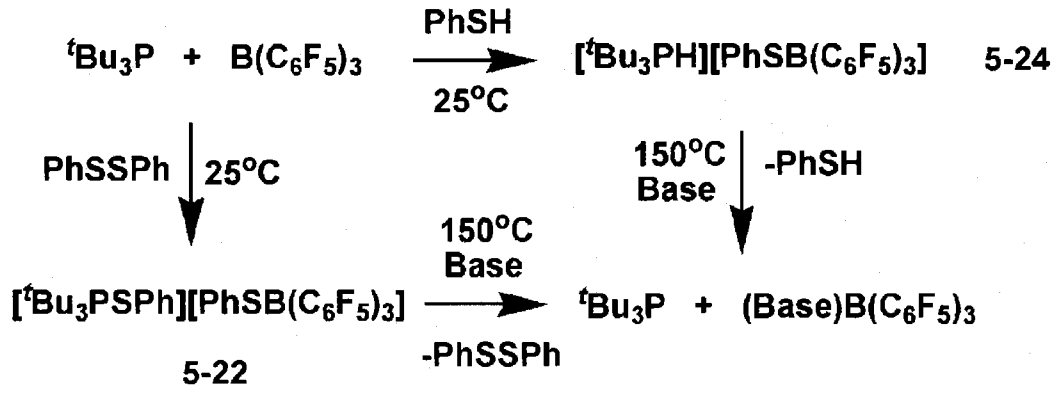


Scheme 5.18 Activation of PhSSPh and PhSH with **3-5**.

The ^{11}B NMR chemical shift of -9.8 and the small gap in the *meta* and *para* ^{19}F NMR resonances ($\Delta_{m,p}$) of 4.4 ppm are consistent with the formation of a 4-coordinate anionic borate center.[130-133] The latter value is comparable to a related alkoxythioborate anion.[375] Based on the above spectroscopic data, the product of the reaction of **3-13** with PhSSPh was formulated as the phosphonium borate $^tBu_2P(SPh)(C_6F_4)B(SPh)(C_6F_5)_2$ (**5-20**) (Scheme 5.18). To confirm that the phosphine had not been oxidized, the corresponding phosphine sulphide was independently generated. Addition of elemental sulphur to **5-20** in toluene solution at room temperature gave the phosphine sulphide $^tBu_2P(S)(C_6F_4)B(C_6F_5)_2$ (**5-21**) as an off-yellow solid after appropriate work-up (Scheme 5.18). The ^{31}P NMR chemical shift at 85.9 ppm is ~ 10 ppm downfield shifted from **5-20**, confirming the presence of a PSR^+ fragment in the latter. The ^{19}F NMR exhibits chemical shifts consistent with the presence of a C_6F_4 unit and slightly broadened *ortho*-, *meta*-, and *para*- fluorine resonances for two equivalent C_6F_5 rings, consistent with the presence

of a 3-coordinate boron center. Additionally, the chemical shift difference between the *meta-* and *para-* fluorine resonances of 16 ppm is similar to that found for **3-13** ($\Delta_{m,p}$ = 18) and $B(C_6F_5)_3$ ($\Delta_{m,p}$ = 18).[121] The NMR data confirms that **5-21** does not aggregate in solution via phosphine sulphide coordination to boron at 25 °C. This is not surprising, as phosphine sulphides are soft bases and do not form strong adducts with Lewis acidic boranes.[141] Additionally, the steric bulk about phosphorus likely prevents a close approach of the sulphide towards boron. Upon cooling to -50 °C the *meta-*, *para-* fluorine chemical shift difference changes from 16 to 8 ppm, which indicates the presence of weak aggregation at low temperature. Heating **5-20** in the presence of MesCN or coordinating solvent to temperatures in excess of 100 °C resulted in regeneration of the disulfide and the base coordinated phosphino-borane $^tBu_2P(C_6F_4)B(Base)(C_6F_5)_2$ implying that the activation of the disulfide PhSSPh with sterically demanding phosphines and boranes is reversible, similar to H_2. This result is not surprising because thiolate nucleophiles are known to react with alkoxythiophosphonium cations to give the corresponding disulphides.[374]

In an analogous fashion to **3-13**, the FLP $^tBu_3P$ / $B(C_6F_5)_3$ readily activates PhSSPh at 25 °C in toluene solution to give $[^tBu_3PSPh][PhSB(C_6F_5)_3]$ (**5-22**) as a white solid in 84 % yield (Scheme 5.19). The NMR spectroscopic data are similar to that for **5-20**. The alkoxythioborate anion gives rises to a characteristic ^{11}B NMR chemical shift at -10.0 ppm while the ^{31}P NMR resonance for the cation appears at 85.7 ppm. This latter signal is shifted downfield from the parent phosphine, $^tBu_3P$ (^{31}P δ = 57.8 ppm), and upfield from the known phosphine sulphide $^tBu_3PS$ (^{31}P δ = 90 ppm).[376] A independent variable-temperature NMR spectroscopy experiment showed activation of the PhSSPh by the present 'frustrated' Lewis pair to be facile at -30 °C.



Scheme 5.19 Activation of PhSSPh and PhSH with 'frustrated' Lewis pairs. Base = MesCN.

As with compound **5-20**, the activation of PhSSPh is reversible. Heating a bromobenzene solution of **4** to 150 °C in the presence of a donor molecule showed formation of free phosphine, the disulfide, and the base coordinated borane, (base)$B(C_6F_5)_3$, although other decomposition products were observed. No reaction was observed between $^tBu_3P$ and PhSSPh from -80 °C to 25 °C, while only a weak interaction between $B(C_6F_5)_3$ and PhSSPh was observed below -30 °C. Thus, the activation of the disulphide is dependent on the presence of both phosphine and borane. Of note, related thioalkoxyphosphonium salts have been prepared by electrochemical reduction of disulphides in the presence of phosphines[373] and by the reduction of phosphine sulphides,[374] although the cations were not paired with a thiolate anion.

In addition to disulphides, thiols can be reversibly activated by FLP's. Addition of one equivalent of thiophenol (PhSH) to toluene solutions of **3-13** and $^tBu_3P/B(C_6F_5)_3$ generated the corresponding zwitterion $^tBu_2PH(C_6F_4)B(SPh)(C_6F_5)_2$ (**5-23**) and ion pair $[^tBu_3PH][PhSB(C_6F_5)_3]$ (**5-24**) in 82 % and 84 % yield, respectively (Scheme 5.18 and 5.19). The ^{31}P NMR spectra of **5-23** and **5-24** showed doublet resonances at 32.4 ($^1J_{PH}$ =

486 Hz) and 56.5 ($^1J_{PH}$ = 444 Hz) ppm, respectively, while the ^{1}H NMR spectra of each exhibited ^{t}Bu, Ph and PH resonances. The ^{11}B and ^{19}F NMR spectra of both species were consistent with the formation of an alkoxythiolborate anion. In both cases, the activation of HSPh was observed at -30 °C in bromobenzene. In the case of **5-24** the formulation as [^{t}Bu$_3$PH][PhSB(C$_6$F$_5$)$_3$] was confirmed by a single crystal X-ray diffraction study (Table 5.4). A POV-ray depiction is shown in Figure 5.10. The geometry about phosphorus and boron is pseudo-tetrahedral, while the B-S bond distance was found to be 1.997(4) Å, which is slightly shorter than the B-S bond distances found for the adducts (C$_4$H$_8$S)B(C$_6$F$_5$)$_3$ (2.084(4) Å)[377] and (Me$_2$S)B(C$_6$F$_5$)$_3$ (2.09(1) Å).[124] Interestingly PhSH does not form a strong adduct with B(C$_6$F$_5$)$_3$. The room temperature ^{19}F NMR spectra of a 1:1 mixture of PhSH and B(C$_6$F$_5$)$_3$ in CD$_2$Cl$_2$ revealed resonances only attributable to free B(C$_6$F$_5$)$_3$ ($\Delta_{m,p}$= 16 ppm). Upon cooling to -60 °C a new set of *ortho-*, *meta-*, and *para-* fluorine resonances appeared at -128.5, -150.6, and -160.2, respectively, attributable to the adduct (PhSH)B(C$_6$F$_5$)$_3$. Adding excess PhSH to B(C$_6$F$_5$)$_3$ in CD$_2$Cl$_2$ (12:1 ratio of S to B) resulted in a broadening of the *ortho-*, *meta-*, and *para-* fluorine resonances at 25 °C in the ^{19}F NMR spectrum and upon cooling to -60 °C the (PhSH)B(C$_6$F$_5$)$_3$ adduct was observed. These results indicate that slow equilibrium exits between free and coordinated B(C$_6$F$_5$)$_3$. Adding excess PhSH shifts the equilibrium towards coordinated B(C$_6$F$_5$)$_3$, while cooling favours adduct formation. The inability of PhSH to form an observable adduct with B(C$_6$F$_5$)$_3$ at room temperature indicates that there is a possibility that the activation of PhSH by FLP's follows a synergistic mechanistic pathway similar to that reported for the activation of H$_2$,[17] although it is likely that reversible adduct formation between PhSH and B(C$_6$F$_5$)$_3$ is followed by irreversible deprotonation by phosphine at 25 °C.

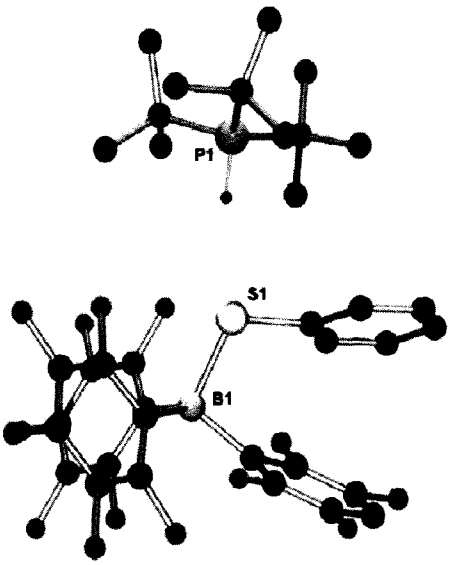


Figure 5.10 Pov-ray depiction of **5-24**. Carbon: black, Phosphorus: orange, Fluorine: pink, Boron: Yellow-green. Carbon hydrogen atoms omitted for clarity.

Heating bromobenzene solutions of **5-22** and **5-24** to 150 °C in the presence of a donor molecule resulted in reformation of PhSH. Quenching of the Lewis acid boron center by base coordination prevents reactivation of PhSH. It should be noted that alcohol- and thiol-$B(C_6F_5)_3$ adducts can act as initators for the polymerization of olefins[378, 379] while the deprotonation of such adducts by Lewis bases to generate ion pairs has been reported in the literature.[341, 375, 380]

In summary, it has been demonstrated that FLP's react with disulphides and thiols in a facile manner. Such reactivity has shown to be reversible at high temperatures. This chemistry may have synthetic value in the hydrothiolation of unsaturated organic molecules.

5.4 Summary and Conclusions

In summary it has been demonstrated that 'frustrated' Lewis pairs consisting of phosphines and boranes can heterolytically cleave molecular H_2 in facile manner at 25°C. The resulting phosphonium borates of the form $R_2PH(C_6F_4)BH(C_6F_5)_2$ or $[R_3PH][HB(C_6F_5)_3]$ (R= alkyl or aryl) are stable at 25°C and undergo thermal liberation of H_2 above 100°C in the presence of a borane trap. These findings represent the first metal-free systems capable of the reversible activation of H_2. The liberation of H_2 was found to be dependent on the basicity of the phosphorus center with the rate decreasing with increased basicity. Mechanistically, the liberation of H_2 possibly proceeds through slow PH bond breakge at high temperatures, followed by assisted transfer of the proton to the vicinity of a borohydride moiety, and subsequent protonation of borohydride to give H_2. Phosphine oxides proved to act as catalysts for the liberation of H_2 through interaction with the phosphonium cation. While much mechanistic work still needs to be carried out, these inital findings of reversible H_2 activation are exciting. Expanding the scope of reactivity, FLP's were shown to readily activate thiols and disulphides to give phosphonium alkoxythioborates and alkoxythiophosphonium alkoxythioborates.

Since our first report of the reactivity of FLP's, numerous reports have been published by our own group and independent research groups exploiting the simple, unique, and unprecedented reactivity of these and related systems towards H_2. Bertrand and co-workers have elegantly shown that certain amino(alkyl)carbenes readily activate H_2,[13] while recent findings in our group have described the ability of *N*-heterocyclic carbenes to active H_2 heterolytically with $B(C_6F_5)_3$.[8] Erker and co-workers have reported that alkyl linked phosphine-boranes can activate H_2[18] and most recently a new finding in

our group has shown that directly P-B bonded phosphino-boranes can heterolytically cleave H_2.[11] Finally, and most importantly, the series of phosphonium borates described in this chapter act as efficient catalysts for the hydrogenation of imines, nitriles, and the ring opening of aziridines using H_2 as the hydrogen source. This remarkable finding has opened new doors in metal-free catalysis by offering the ability to easily carry out hydrogenations without the use of expensive precious metals or environmentally unfriendly stoichiometric reducing reagents.[7, 9]

Final Conclusions

In summary the work in this thesis has demonstrated the unique reactivity between sterically demanding phosphines and boranes. Steric demand prevents formation of traditional Lewis adducts between bulky tertiary and secondary phosphines and $B(C_6F_5)_3$, resulting in the formation of zwitterionic phosphonium borates and 'frustrated' Lewis pairs. The former compounds are readily modified to give anionic phosphines, cationic boranes, or ambiphilic phosphino-boranes. 'Frustrated' Lewis pairs effect the reversible activation of H_2, representing the first metal-free system capable of such a fundamental process. These new findings open new vistas in metal-free catalytic hydrogenation and hydrogen storage. In 2007 William J. Evans authored a paper prompting chemists to challenge scientific assumptions, in an effort to overturn 'rules' that have long been followed.[381] By challenging the assumption that the Lewis acid $B(C_6F_5)_3$ will typically form traditional adducts with Lewis bases, we have discovered a new area of chemistry with the utmost potential to affect both academic and industrial chemistry.

References

1. G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124-1126.
2. G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880-1881.
3. G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. R. Wei and D. W. Stephan, *Dalton T.*, 2007, 3407-3414.
4. G. C. Welch, T. Holtrichter-Roessmann and D. W. Stephan, *Inorg. Chem.*, 2008, **47**, 1904-1906.
5. G. C. Welch, J. D. Masuda and D. W. Stephan, *Inorg. Chem.*, 2006, **45**, 478-480.
6. J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2007, **46**, 4968-4971.
7. P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2007, **46**, 8050-8053.
8. P. A. Chase and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2008, **Early View**.
9. P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701-1703.
10. M. A. Dureen, A. Lough, T. M. Gilbert and D. W. Stephan, *Chem. Commun.*, 2008, **Advanced Article**.
11. S. J. Geier, T. M. Gilbert and D. W. Stephan, *J. Am. Chem. Soc.*, 2008, **ASAP**.
12. L. Cabrera, G. C. Welch, J. D. Masuda, P. Wei and D. W. Stephan, *Inorg. Chim. Acta.*, 2006, **359** 3066-3071.
13. G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Science*, 2007, **316**, 439-441.
14. P. Spies, S. Schwendemann, L. Stefanie, G. Kehr, R. Frihlich and G. Erker, *Angew. Chem. Int. Ed.*, 2008, **Early View**.
15. V. Sumerin, F. Schulz, M. Nieger, M. Leskell, T. Repo and B. Rieger, *Angew. Chem. Int. Ed.*, 2008, **Early View**.
16. D. Holschumacher, T. Bannenberg, G. H. Cristian, G. J. Peter and M. Tamm, *Angew. Chem. Int. Ed.*, 2008, **Early View**.
17. T. A. Rokob, A. Hamza, A. Stirling, T. Soos and I. Papai, *Angew. Chem. Int. Ed.*, 2008, **47**, 2435-2438.
18. P. Spies, G. Erker, G. Kehr, K. Bergander, R. Froehlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072-5074.
19. D. Chen and J. Klankermayer, *Chem. Commun.*, 2008, **Advanced Article**.
20. A. Stirling, A. Hamza, A. R. Tibor and I. Papai, *Chem. Commun.*, 2008, **Advanced Article**.
21. Y. Guo, Li, S, *Inorg. Chem.*, 2008, **ASAP**.
22. Y. Guo and S. Li, *Eur. J. Inorg. Chem.*, 2008, 2501-2505.
23. D. W. Stephan, *Org. Biomol. Chem*, 2008, **6**, 1535-1539.
24. A. L. Kenward and W. E. Piers, *Angew. Chem. Int. Ed.*, 2008, **47**, 38-41.
25. G. J. Kubas, *Science*, 2006, **314**, 1096-1097.
26. G. J. Kubas, *Metal Dihydrogen and Sigma-bonded Complexes: Structure, Theory and Reactivity*, Kluwer Academic/Plenum Publishers, London, 2001.
27. D. M. Heinekey, A. Lledos and J. M. Lluch, *Chem. Soc. Rev.*, 2004, **33**, 175-182.
28. G. S. McGrady and G. Guilera, *Chem. Soc. Rev.*, 2003, **32**, 383-392.

29. P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155-284.
30. J. K. Burdett, O. Eisenstein and S. A. Jackson, *Transition Met. Hydrides*, 1992, 149-843.
31. R. H. Crabtree, *Accts Chem. Res.*, 1990, **23**, 95-101.
32. G. J. Kubas, *Accts Chem. Res.*, 1988, **21**, 120-128.
33. P. E. M. Siegbahn, *Adv. Inorg. Chem.*, 2004, **56**, 101-105.
34. H. A. Wittcoff, Reuben, B. G., *Industrial Organic Chemicals*, John Wiley & Sons, INC., 1996.
35. G. J. Kubas, *Chem. Rev.*, 2007, **107**, 4152-4205.
36. R. Noyori, *Angew. Chem. Int. Ed.*, 2002, **41**, 2008-2022.
37. R. Noyori and T. Ohkuma, *Angew. Chem. Int. Ed.*, 2001, **40**, 40-73.
38. Y. Shvo, D. Czarkie, Y. Rahamim and D. F. Chodosh, *J. Am. Chem. Soc.*, 1986, **108**, 7400-7402.
39. S. Shima, E. J. Lyon, R. K. Thauer, B. Mienert and E. Bill, *J. Am. Chem. Soc.*, 2005, **127**, 10430-10435.
40. E. J. Lyon, S. Shima, G. Buurman, S. Chowdhuri, A. Batschauer, K. Steinbach and R. K. Thauer, *Eur. J. Biochem.*, 2004, **271**, 195-204.
41. O. Pilak, B. Mamat, S. Vogt, C. H. Hagemeier, R. K. Thauer, S. Shima, C. Vonrhein, E. Warkentin and U. Ermler, *J. Mol. Biol.*, 2006, **358**, 798-809.
42. A. P. Scott, B. T. Golding and L. Radom, *New. J. Chem.*, 1998, **22**, 1171-1173.
43. J. H. Teles, S. Brode and A. Berkessel, *J. Am. Chem. Soc.*, 1998, **120**, 1345-1346.
44. M. R. Dubois, *Chem. Rev.*, 1989, **89**, 1-9.
45. S. Aldridge and A. J. Downs, *Chem. Rev.*, 2001, **101**, 3305-3365.
46. Z. L. Xiao, R. H. Hauge and J. L. Margrave, *Inorg. Chem.*, 1993, **32**, 642-646.
47. H. J. Himmel, *Dalton T*, 2003, 3639-3649.
48. H. Himmel and J. Vollet, *Organometallics*, 2002, **21**, 5972-5977.
49. S. A. Kulkarni and A. K. Srivastava, *J. Phys. Chem. A*, 1999, **103**, 2836-2842.
50. S. A. Kulkarni, *J. Phys. Chem. A*, 1998, **102**, 7704-7711.
51. M. W. Haenel, J. Narangerel, U. B. Richter and A. Rufinska, *Angew. Chem. Int. Ed.*, 2006, **45**, 1061-1066.
52. E. Osthaus, Haenel, M. W., *Coal Science and Technology*, Elsevier, 1987.
53. F. L. Ramp, E. J. DeWitt and L. E. Trapasso, *J. Org. Chem.*, 1962, **27**, 4368.
54. E. J. DeWitt, F. L. Ramp and L. E. Trapasso, *J. Am. Chem. Soc.*, 1961, **83**, 4672.
55. M. Yalpani, R. Koster and M. W. Haenel, *Erdol Kohle Erdgas P*, 1990, **43**, 344-347.
56. M. Yalpani and R. Koster, *Chem. Ber.*, 1990, **123**, 719-724.
57. M. Yalpani, T. Lunow and R. Koster, *Chem. Ber.*, 1989, **122**, 687-693.
58. G. H. Spikes, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232-12233.
59. J. Wang, A. D. Ebner and J. A. Ritter, *Adsorption-J. Int. Adsorption Soc.*, 2005, **11**, 811-816.
60. J. A. Ritter, A. D. Ebner, J. Wang and R. Zidan, *Materials Today*, 2003, **9**, 18.
61. S. A. Gadre, A. D. Ebner, S. A. Al-Muhtaseb and J. A. Ritter, *Ind. Eng. Chem. Res*, 2003, **42**, 1713-1722.
62. J. J. Vajo, S. L. Skeith and F. Mertens, *J. Phys. Chem. B.*, 2005, **109**, 3719-3722.
63. J. J. Vajo, S. L. Skeith, F. Mertens and S. W. Jorgensen, *J. Alloy Compd.*, 2005, **390**, 55-61.

64. D. E. Schwarz, T. M. Cameron, P. J. Hay, B. L. Scott, W. Tumas and D. L. Thorn, *Chem. Commun.*, 2005, 5919-5921.
65. T. B. Marder, *Angew. Chem. Int. Ed.*, 2007, **46**, 8116-8118.
66. F. H. Stephens, V. Pons and R. T. Baker, *Dalton T.*, 2007, 2613-2626.
67. R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, John Wiley & Sons, New York, 1994.
68. M. Bochmann, S. J. Lancaster, M. D. Hannant, A. Rodriguez, M. Schormann, D. A. Walker and T. J. Woodman, *Pure & Appl. Chem.*, 2003, **75**, 1183-1195.
69. E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391-1434.
70. G. Erker, *Dalton T.*, 2005, 1883-1890.
71. K. Ishihara and H. Yamamoto, *Eur. J. Org. Chem.*, 1999, 527-538.
72. T. Chivers, *J. Fluorine Chem.*, 2002, **115**, 1-8.
73. M. B. Smith and J. March, *March's Advanced Organic Chemistry; Reactions, Mechanisms and Structure*, John Wiley and Sons, Inc., New York, 2001.
74. H. Yamamoto and ed., *Lewis Acid Reagents* Oxford University Press, Oxford, 1999.
75. M. Santelli and J.-M. Pons, *Lewis Acids and Selectivity in Organic Synthesis*, CRC Press, New York, 1996.
76. W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345-354.
77. E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391-1434.
78. J. C. W. Chien, W. M. Tsai and M. D. Rausch, *J. Am. Chem. Soc.*, 1991, **113**, 8570-8571.
79. G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalogue Company, Inc., New York, 1923.
80. W. E. Piers, *Advances in Organometallic Chemistry*, 2005, **52**, 1-76.
81. H. C. Brown, H. I. Schlesinger and S. Z. Cardon, *J. Am. Chem. Soc.*, 1942, **64**, 325.
82. F. Focante, P. Mercandelli, A. Sironi and L. Resconi, *Coordin. Chem. Rev.*, 2006, **250**, 170-188.
83. X. G. Fang, B. L. Scott, K. D. John, G. J. Kubas and J. G. Watkin, *New. J. Chem.*, 2000, **24**, 831-833.
84. J. B. Lambert and J. H. So, *J. Org. Chem.*, 1991, **56**, 5960-5962.
85. G. Bidan and M. Genies, *Tet. Lett.*, 1978, 2499-2502.
86. R. A. Jones, G. Wilkinson, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc. Perk. T. 2*, 1980, 117-120.
87. J. R. Sanders, *J. Chem. Soc. Dalton T.*, 1973, 743-747.
88. Y. Okamoto and Shimakaw.Y, *J. Org. Chem.*, 1970, **35**, 3752-&.
89. H. Hoffmann and Schellen.P, *Chem. Ber-Recl*, 1966, **99**, 1134-&.
90. R. Damico and C. D. Broaddus, *J. Org. Chem.*, 1966, **31**, 1607-&.
91. W. R. G. Briegleb, W. Jung, *Angew. Chem. Int. Ed.*, 1963, **2**, 545-546.
92. L. I. Cabrera, Masters Thesis, University of Windsor, Windsor, 2004.
93. S. Doring, G. Erker, R. Frohlich, O. Meyer and K. Bergander, *Organometallics*, 1998, **17**, 2183-2187.
94. G. Rodriguez, Exxon-Mobil Chemical Patents Inc., US, 2002, pp. 1-75.
95. M. W. Holtcamp, Pham, T. H., Univation Technologies LLC, US, 2002, pp. 1-44.
96. R. A. Bartlett, M. M. Olmstead, P. P. Power and G. A. Sigel, *Inorg. Chem.*, 1987, **26**, 1941-1946.

97. W. McFarlane and C. T. Regius, *Polyhedron*, 1997, **16**, 1855-1861.
98. N. Millot, C. C. Santini, B. Fenet and J. M. Basset, *Eur. J. Inorg. Chem.*, 2002, 3328-3335.
99. J. C. Tebby, *Handbook of Phosphorus-31 Nuclear Magentic Resonace Data*, CRC Press Inc., United States, 1991.
100. H. Jacobsen, H. Berke, S. Doring, G. Kehr, G. Erker, R. Frohlich and O. Meyer, *Organometallics*, 1999, **18**, 1724-1735.
101. P. A. Chase, M. Parvez and W. E. Piers, *Acta Crystallogr. E.*, 2006, **62**, O5181-O5183.
102. H. Goldwhite and A. S. Hirschon, *Transit. Metal Chem.*, 1977, **2**, 144-149.
103. S. J. Lancaster, A. J. Mountford, D. L. Hughes, M. Schormann and M. Bochmann, *J. Organomet. Chem.*, 2003, **680**, 193-205.
104. Bruker AXS Inc, Madison, WI, 2001.
105. Bruker AXS Inc., Madison, WI, 2003.
106. Bruker AXS Inc., Madison, WI, 2003.
107. G. M. Sheldrick, Bruker AXS Inc., Madison, WI, 2000.
108. A. L. Spek, Utrecht University, Utrecht, The Netherlands, 2008.
109. A. L. Spek, *J. Applied Crystallography*, 2003, **36**, 7-13.
110. D. C. Bradley, G. E. Hawkes, P. R. Haycock, K. D. Sales and D. H. Zheng, *Philos. T. Roy. Soc. A*, 1994, **348**, 315-322.
111. M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima and F. P. Gabbai, *Chem. Commun.*, 2007, 1133-1135.
112. R. Taube, S. Wache and J. Sieler, *J. Organomet. Chem.*, 1993, **459**, 335-347.
113. M. H. Hannant, J. A. Wright, S. J. Lancaster, D. L. Hughes, P. N. Horton and M. Bochmann, *Dalton T.*, 2006, 2415-2426.
114. S. M. Cornet, K. B. Dillon, C. D. Entwistle, M. A. Fox, A. E. Goeta, H. P. Goodwin, T. B. Marder and A. L. Thompson, *Dalton T.*, 2003, 4395-4405.
115. C. A. Tolman, *Chem. Re.v*, 1977, **77**, 313-348.
116. M. M. Rahman, H. Y. Liu, K. Eriks, A. Prock and W. P. Giering, *Organometallics*, 1989, **8**, 1-7.
117. S. W. Watt, C. Dai, A. J. Scott, J. M. Burke, R. L. Thomas, J. C. Collings, C. Viney, W. Clegg and T. B. Marder, *Angew. Chem. Int. Ed.*, 2004, **43**, 3061-3063.
118. J. C. Collings, K. P. Roscoe, R. L. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard and T. B. Marder, *New. J. Chem.*, 2001, **25**, 1410-1417.
119. L. Cabrera, E. Hollink, J. C. Stewart, P. R. Wei and D. W. Stephan, *Organometallics*, 2005, **24**, 1091-1098.
120. D. C. Bradley, I. S. Harding, A. D. Keefe, M. Motevalli and D. H. Zheng, *J. Chem. Soc., Dalton T.: Inorg. Chem.*, 1996, 3931-3936.
121. C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner and G. Parkin, *J. Am. Chem. Soc.*, 2000, **122**, 10581-10590.
122. T. L. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda and I. Manners, *Chem-Eur. J.*, 2005, **11**, 4526-4534.
123. D. C. Bradley, M. B. Hursthouse, M. Motevalli and D. H. Zheng, *J. Chem. Soc. Chem. Commun.*, 1991, 7-8.
124. J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec and A.-C. Gaumont, *Chem. Commun.*, 2003, 54-55.
125. A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245-250.

126. L. H. Doerrer, A. J. Graham and M. L. H. Green, *J. Chem. Soc., Dalton T.: Inorg. Chem.*, 1998, 3941-3946.
127. G. S. Hair, R. A. Jones, A. H. Cowley and V. Lynch, *Organometallics*, 2001, **20**, 177-181.
128. P. A. Chase, L. D. Henderson, W. E. Piers, M. Parvez, W. Clegg and M. R. J. Elsegood, *Organometallics*, 2006, **25**, 349-357.
129. P. A. Chase, P. E. Romero, W. E. Piers, M. Parvez and B. O. Patrick, *Can. J. Chem.*, 2005, **83**, 2098-2105.
130. J. M. Blackwell, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 1295-1306.
131. J. M. Blackwell, W. E. Piers and M. Parvez, *Org. Lett.*, 2000, **2**, 695-698.
132. A. D. Horton and J. deWith, *Organometallics*, 1997, **16**, 5424-5436.
133. A. D. Horton, J. de With, A. J. van der Linden and H. van de Weg, *Organometallics*, 1996, **15**, 2672-2674.
134. J. Cano, M. Sudupe, P. Royo and M. E. G. Mosquera, *Angew. Chem. Int. Ed.*, 2006, **45**, 7572-7574.
135. S. J. Lancaster, A. J. Mountford, D. L. Hughes, M. Schormann and M. Bochmann, *J. Organomet. Chem.*, 2003, **680**, 193-205.
136. F. Focante, I. Camurati, L. Resconi, S. Guidotti, T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, *Inorg. Chem.*, 2006, **45**, 1683-1692.
137. A. Sundararaman and F. Jakle, *J. Organomet. Chem.*, 2003, **681**, 134-142.
138. D. J. Morrison and W. E. Piers, *Org. Lett.*, 2003, **5**, 2857-2860.
139. R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 801-808.
140. S. A. Cummings, M. Iimura, C. J. Harlan, R. J. Kwaan, I. V. Trieu, J. R. Norton, B. M. Bridgewater, F. Jakle, A. Sundararaman and M. Tilset, *Organometallics*, 2006, **25**, 1565-1568.
141. G. J. P. Britovsek, J. Ugolotti and A. J. P. White, *Organometallics*, 2005, **24**, 1685-1691.
142. L. Li, C. L. Stern and T. J. Marks, *Organometallics*, 2000, **19**, 3332-3337.
143. S. Toyota, M. Asakura, M. Oki and F. Toda, *B. Chem. Soc. Jpn*, 2000, **73**, 2357-2362.
144. W. V. Konze, B. L. Scott and G. J. Kubas, *Chem. Commun.*, 1999, 1807-1808.
145. F. Zettler, H. D. Hausen and H. Hess, *J. Organomet. Chem.*, 1974, **72**, 157-162.
146. Hutching.Mg, Maryanof.Ca and K. Mislow, *J. Am. Chem. Soc.*, 1973, **95**, 7158-7159.
147. S. Ege, *Organic Chemistry Strucutre and Reactivity*, Houghton Mifflin Company United States, 1999.
148. L. D. Quin, *A Guide to Organophosphorus Chemistry*, Wiley & Sons, New York, 2000
149. F. R. Hartley, *Chemisty of Organophosphorus Compounds*, Wiley & Sons, New York, 1990.
150. J. H. Kirchhoff, C. Y. Dai and G. C. Fu, *Angew. Chem. Int. Ed.*, 2002, **41**, 1945-+.
151. A. F. Littke and G. C. Fu, *Angew. Chem. Int. Ed.*, 2002, **41**, 4176-4211.
152. J. J. Yin, M. P. Rainka, X. X. Zhang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 1162-1163.
153. M. Stradiotto, J. Cipot and R. McDonald, *J. Am. Chem. Soc.*, 2003, **125**, 5618.

154. C. M. Thomas and J. C. Peters, *Inorg. Chem.*, 2004, **43**, 8-10.
155. C. C. Lu and J. C. Peters, *J. Am. Chem. Soc.*, 2004, **126**, 15818-15832.
156. J. C. Thomas and J. C. Peters, *Inorg. Chem.*, 2003, **42**, 5055-5073.
157. J. C. Thomas and J. C. Peters, *J. Am. Chem. Soc.*, 2003, **125**, 8870-8888.
158. J. C. Thomas and J. C. Peters, *J. Am. Chem. Soc.*, 2001, **123**, 5100-5101.
159. Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 6287-6305.
160. Y.-X. Chen, C. L. Stern, S. Yang and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 12451-12452.
161. T. J. Marks and Y.-X. Chen, in *U.S.*, (Northwestern University). USA, 2001, pp. 28 pp., Cont.-in-part of U.S. 26,087,460.
162. T. J. Marks and Y.-X. Chen, in *U.S.*, (Northwestern University). USA, 2001, pp. 20 pp., Cont.-in-part of U.S. Ser. No. 222,326, abandoned.
163. T. J. Marks, L. Li, Y.-X. Chen, M. H. McAdon and P. N. Nickias, in *PCT Int. Appl.*, (The Dow Chemical Company, USA; Northwestern University). Wo, 1999, p. 30 pp.
164. M. V. Metz, D. J. Schwartz, C. L. Stern, T. J. Marks and P. N. Nickias, *Organometallics*, 2002, **21**, 4159-4168.
165. H. Li, L. Li, T. J. Marks, L. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 2003, **125**, 10788-10789.
166. H. Li, L. Li, D. J. Schwartz, M. V. Metz, T. J. Marks, L. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 2005, **127**, 14756-14768.
167. L. Li and T. J. Marks, *Organometallics*, 1998, **17**, 3996-4003.
168. M. V. Metz, D. J. Schwartz, C. L. Stern, P. N. Nickias and T. J. Marks, *Angew. Chem., Int. Ed.*, 2000, **39**, 1312-1316.
169. D. J. H. Emslie, W. E. Piers and M. Parvez, *Angew. Chem. Int. Ed.*, 2003, **42**, 1252-1255.
170. P. E. Romero, W. E. Piers, S. A. Decker, D. Chau, T. K. Woo and M. Parvez, *Organometallics*, 2003, **22**, 1266-1274.
171. I. Ghesner, W. E. Piers, M. Parvez and R. McDonald, *Organometallics*, 2004, **23**, 3085-3087.
172. R. Roesler, W. E. Piers and M. Parvez, *J. Organomet. Chem.*, 2003, **680**, 218-222.
173. P. A. Chase, W. E. Piers and B. O. Patrick, *J. Am. Chem. Soc.*, 2000, **122**, 12911-12912.
174. K. Kohler and W. E. Piers, *Can. J. Chem.*, 1998, **76**, 1249-1255.
175. D. J. Morrison, W. E. Piers and M. Parvez, *Synlett*, 2004, 2429-2433.
176. R. Roesler, B. J. N. Har and W. E. Piers, *Organometallics*, 2002, **21**, 4300-4302.
177. V. C. Williams, C. Dai, Z. Li, S. Collins, W. E. Piers, W. Clegg, M. R. J. Elsegood and T. B. Marder, *Angew. Chem. Int. Ed.*, 1999, **38**, 3695-3698.
178. V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins and T. B. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3244-3245.
179. W. E. Piers, G. J. Irvine and V. C. Williams, *Eur. J. Inorg. Chem.*, 2000, 2131-2142.
180. J. R. Galsworthy, M. L. H. Green, V. C. Williams and A. N. Chernega, *Polyhedron*, 1997, **17**, 119-124.
181. G. Kehr, R. Fröehlich, B. Wibbeling and G. Erker, *Chem.- Eur. J.*, 2000, **6**, 258-266.

182. M.-C. Chen, J. A. S. Roberts and T. J. Marks, *J. Am. Chem. Soc.*, 2004, **126**, 4605-4625.
183. P. A. Deck, C. L. Beswick and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 1772-1784.
184. S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. H. Hughes and M. Bochmann, *Organometallics*, 2002, **21**, 451-453.
185. R. E. LaPointe, G. R. Roof, K. A. Abboud and J. Klosin, *J. Am. Chem. Soc.*, 2000, **122**, 9560-9561.
186. H. Li and T. J. Marks, *Proc. Nat. Acad. Sci., USA*, 2006, **103**, 15295-15302.
187. L. Li, M. V. Metz, H. Li, M.-C. Chen, T. J. Marks, L. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 2002, **124**, 12725-12741.
188. F. Song, S. J. Lancaster, R. D. Cannon, M. Schormann, S. M. Humphrey, C. Zuccaccia, A. Macchioni and M. Bochmann, *Organometallics*, 2005, **24**, 1315-1328.
189. J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, **123**, 223-237.
190. S. P. Lewis, L. D. Henderson, B. D. Chandler, M. Parvez, W. E. Piers and S. Collins, *J. Am. Chem. Soc.*, 2005, **127**, 46-47.
191. S. P. Lewis, N. J. Taylor, W. E. Piers and S. Collins, *J. Am. Chem. Soc.*, 2003, **125**, 14686-14687.
192. D. J. Morrison, J. M. Blackwell and W. E. Piers, *Pure & Appl. Chem.*, 2004, **76**, 615-623.
193. M. A. Beckett, G. C. Strickland, J. R. Holland and K. S. Varma, *Polymer*, 1996, **37**, 4629-4631.
194. R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 809-812.
195. J. Bould, T. Jelinek, S. A. Barrett, S. J. Coles, M. B. Hursthouse, M. Thornton-Pett, B. Stibr and J. D. Kennedy, *Dalton T.*, 2005, 1499-1503.
196. M. A. Fox, A. E. Goeta, A. K. Hughes and A. L. Johnson, *J. Chem. Soc. Dalton T.*, 2002, 2132-2141.
197. M. J. Drewitt, M. Niedermann and M. C. Baird, *Inorg. Chim. Acta.*, 2002, **340**, 207-210.
198. B. Stibr, J. Holub, M. Bakardjiev, D. Hnyk, O. L. Tok, W. Milius and B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 2002, 2320-2326.
199. T. Jelinek, J. D. Kennedy, B. Stibr and M. Thornton-Pett, *Inor.g Chem. Commun.*, 1998, **1**, 179-181.
200. K. N. Robertson, P. K. Bakshi, S. D. Lantos, T. S. Cameron and O. Knop, *Can. J. Chem.*, 1998, **76**, 583-611.
201. K. Wozniak, T. M. Krygowski, B. Kariuki, W. Jones and E. Grech, *J. Mol. Struct.*, 1990, **240**, 111-118.
202. B. Ronig, H. Schulze, I. Pantenburg and L. Wesemann, *Eur. J. Inorg. Chem.*, 2005, 314-320.
203. D. W. Stephan, *Organometallics*, 2005, **24**, 2548-2560.
204. S. Hawkeswood and D. W. Stephan, *Dalton T.*, 2005, 2182-2187.
205. W. Fraenk, T. M. Klapotke, B. Krumm, H. Noth, M. Suter, M. Vogt and M. Warchhold, *Can. J. Chem.*, 2002, **80**, 1444-1450.
206. W. Fraenk, T. M. Klapotke, B. Krumm, P. Mayer, H. Piotrowski and M. Vogt, *Z. Anor.g Allg. Chem.*, 2002, **628**, 745-750.

207. W. Fraenk, T. M. Klapotke, B. Krumm, P. Mayer, H. Noth, H. Piotrowski and M. Suter, *J. of Fluor. Chem.*, 2001, **112**, 73-81.
208. W. Fraenk, T. M. Klapotke, B. Krumm, H. Noth, M. Suter and M. Warchhold, *J. Chem. Soc. Dalton T.*, 2000, 4635-4638.
209. W. Fraenk, T. M. Klapotke, B. Krumm and P. Mayer, *Chem. Commun.*, 2000, 667-668.
210. W. Fraenk, T. Habereder, T. M. Klapotke, H. Noth and K. Polborn, *J. Chem. Soc. Dalton T.*, 1999, 4283-4286.
211. W. Fraenk, H. Noth, T. M. Klapotke and M. Suter, *Z. Naturforsch B.*, 2002, **57**, 621-624.
212. W. Fraenk, T. Habereder, A. Hammerl, T. M. Klapotke, B. Krumm, P. Mayer, H. Noth and M. Warchhold, *Inorg. Chem.*, 2001, **40**, 1334-1340.
213. R. T. Paine, W. Koestle, T. T. Borek, G. L. Wood, E. A. Pruss, E. N. Duesler and M. A. Hiskey, *Inorg. Chem.*, 1999, **38**, 4920-4920.
214. B. Eble, D. Berning, C. L. Barnes, K. V. Katti and S. Jurisson, *J. Chem. Crystallogr.*, 1999, **29**, 39-43.
215. M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, I. S. Neretin and K. Wade, *Chem. Commun.*, 1999, 1649-1650.
216. Kynoch, ed., *International Tables of X-ray Crystallography*, Birmingham, England, 1968.
217. F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 1999.
218. J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, **123**, 223-237.
219. B. E. Bosch, G. Erker, R. Frohlich and O. Meyer, *Organometallics*, 1997, **16**, 5449-5456.
220. D. J. Brauer, H. Burger, Y. Chebude and G. Pawelke, *Inorg. Chem.*, 1999, **38**, 3972-3977.
221. R. Custelcean and J. E. Jackson, *Chem. Rev.*, 2001, **101**, 1963-1980.
222. I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066-2090.
223. M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima and F. Gabbai, *Chem. Commun.*, 2007, 1133.
224. C. W. Chiu and F. P. Gabbai, *Dalton T.*, 2008, 814-817.
225. M. H. Lee and F. P. Gabbai, *Inorg. Chem.*, 2007, **46**, 8132-8138.
226. T. W. Hudnall and F. P. Gabbai, *J. Am. Chem. So.c*, 2007, **129**, 11978-11986.
227. C. W. Chiu and F. P. Gabbai, *J. Am. Chem. Soc.*, 2006, **128**, 14248-14249.
228. H. J. Reich, *J. Chem. Educ. Software*, 1996, Dynamic WinDNMR NMR Spectra for Windows 3D2.
229. A. J. Mountford, S. J. Lancaster, S. J. Coles, P. N. Horton, D. L. Hughes, M. B. Hursthouse and M. E. Light, *Inorg. Chem.*, 2005, **44**, 5921-5933.
230. J. M. Blackwell, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 1295-1306.
231. J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, **2**, 3921-3923.
232. A. D. Horton and J. De With, *Organometallics*, 1997, **16**, 5424-5436.
233. Z. Yuan, N. J. Taylor, Y. Sun, T. B. Marder, I. D. Williams and L. T. Cheng, *J. Organomet. Chem.*, 1993, **449**, 27-37.

234. G. J. Rowlands, *Tetrahedron*, 2001, **57**, 1865-1882.
235. D. L. Grimmett, J. A. Labinger, J. N. Bonfiglio, S. T. Masuo, E. Shearin and J. S. Miller, *Organometallics*, 1983, **2**, 1325-1332.
236. J. A. Labinger, J. N. Bonfiglio, D. L. Grimmett, S. T. Masuo, E. Shearin and J. S. Miller, *Organometallics*, 1983, **2**, 733-740.
237. J. A. Labinger and J. S. Miller, *J. Am. Chem. So.c*, 1982, **104**, 6856-6858.
238. D. L. Grimmett, J. A. Labinger, J. N. Bonfiglio, S. T. Masuo, E. Shearin and J. S. Miller, *J. Am. Chem. Soc.*, 1982, **104**, 6858-6859.
239. J. Vergnaud, M. Grellier, G. Bouhadir, L. Vendier, S. Sabo-Etienne and D. Bourissou, *Organometallics*, 2008, **27**, 1140-1146.
240. A. Fischbach, P. R. Bazinet, R. Waterman and T. D. Tilley, *Organometallics*, 2008, **27**, 1135-1139.
241. M. Sircoglou, G. Bouhadir, N. Saffon, K. Miqueu and D. Bourissou, *Organometallics*, 2008, **27**, 1675-1678.
242. S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu and D. Bourissou, *Chem-Eur. J.*, 2008, **14**, 731-740.
243. M. W. P. Bebbington, G. Bouhadir and D. Bourissou, *Eur. J. Or.g Chem.*, 2007, 4483-4486.
244. J. Vergnaud, T. Ayed, K. Hussein, L. Vendier, M. Grellier, G. Bouhadir, J. C. Barthelat, S. Sabo-Etienne and D. Bourissou, *Dalton T.*, 2007, 2370-2372.
245. S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.* 2006, **128**, 12056-12057.
246. S. B. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu and D. Bourissou, *Angew. Chem. Int. Ed.*, 2006, **45**, 1611-1614.
247. D. J. H. Emslie, J. M. Blackwell, J. F. Britten and L. E. Harrington, *Organometallics*, 2006, **25**, 2412-2414.
248. S. R. Oakley, K. D. Parker, D. J. H. Emslie, I. Vargas-Baca, C. M. Robertson, L. E. Harrington and J. F. Britten, *Organometallics*, 2006, **25**, 5835-5838.
249. M. H. Thibault, J. Boudreau, S. Mathiotte, F. Drouin, O. Sigouin, A. Michaud and F. G. Fontaine, *Organometallics*, 2007, **26**, 3807-3815.
250. F. G. Fontaine and D. Zargarian, *J. Am. Chem. Soc*, 2004, **126**, 8786-8794.
251. P. Laszlo and M. Teston-Henry, *Tet. Lett.*, 1991, **32**, 3837-3838.
252. W. E. Piers, *Adv. Organomet. Chem.*, 2005, **52**, 1-76.
253. J. T. F. Fenwick and J. W. Wilson, *Inorg. Chem.*, 1975, **14**, 1602-1604.
254. L. Luo and T. J. Marks, *Top. Catal.*, 1999, **7**, 97-106.
255. S. Kobayashi, T. Busujima and S. Nagayama, *Chem.- Eur. J.*, 2000, **6**, 3491-3494.
256. G. A. Olah, S. Kobayashi and M. Tashiro, *J. Am. Chem. Soc.*, 1972, **94**, 7448-7461.
257. C. S. Branch, S. G. Bott and A. R. Barron, *J. Organomet. Chem.*, 2003, **666**, 23-34.
258. M. F. Lappert, *J. Am. Chem. Soc.*, 1962, 542-548.
259. U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.* , 1975, **106**, 1235-1257.
260. V. Gutmann, *Coord. Chem. Rev.*, 1976, **18**, 225-255.
261. M. A. Beckett, D. S. Brassington, S. J. Coles and M. B. Hursthouse, *Inorg. Chem. Commun.*, 2000, **3**, 530-533.
262. M. A. Beckett, D. S. Brassington, M. E. Light and M. B. Hursthouse, *Dalton T.*, 2001, 1768-1772.

263. R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 801-808.
264. P. Laszlo and M. Teston, *J. Am. Chem. Soc.*, 1990, **112**, 8750-8754.
265. S. Doering, G. Erker, R. Froehlich, O. Meyer and K. Bergander, *Organometallics*, 1998, **17**, 2183-2187.
266. H. Jacobsen, H. Berke, S. Doering, G. Kehr, G. Erker, R. Froehlich and O. Meyer, *Organometallics*, 1999, **18**, 1724-1735.
267. W. Piers, *Adv. Organomet. Chem.*, 2005, **52**, 1.
268. T. Agou, J. Kobayashi and T. Kawashima, *Inorg. Chem.*, 2006, **45**, 9137-9144.
269. P. A. Chase, W. E. Piers and B. O. Patrick, *J. Am. Chem. Soc.*, 2000, **122**, 12911-12912.
270. L. Luo and T. J. Marks, *Top Catal*, 1999, **7**, 97-106.
271. L. R. Avens, D. M. Barnhart, C. J. Burns and S. D. McKee, *Inorg. Chem.*, 1996, **35**, 537-539.
272. M. P. C. Campello, A. Domingos and I. Santos, *J. Organomet. Chem.*, 1994, **484**, 37-46.
273. W. J. Evans, J. T. Leman, J. W. Ziller and S. I. Khan, *Inorg. Chem.*, 1996, **35**, 4283-4291.
274. W. J. Evans, T. A. Ulibarri, L. R. Chamberlain, J. W. Ziller and D. Alvarez, *Organometallics*, 1990, **9**, 2124-2130.
275. H. Schumann, E. Palamidis and J. Loebel, *J. Organomet. Chem.*, 1990, **384**, C49-C52.
276. H. Schumann, M. Glanz, J. Winterfeld and H. Hemling, *J. Organomet. Chem.*, 1993, **456**, 77-83.
277. S. T. Liddle and P. L. Arnold, *Dalton T.*, 2007, 3305-3313.
278. A. Mommertz, R. Leo, W. Massa, K. Harms and K. Dehnicke, *Zeit. Anorg. Allgem. Chem.*, 1998, **624**, 1647-1652.
279. M. Polamo, I. Mutikainen and M. Leskela, *Acta Crystallogr., Sec. C: Cry. Struct. Commun.*, 1997, **C53**, 1036-1037.
280. T. L. Breen and D. W. Stephan, *Inorg. Chem.*, 1992, **31**, 4019-4022.
281. Z. Y. Guo, P. K. Bradley and R. F. Jordan, *Organometallics*, 1992, **11**, 2690-2693.
282. R. F. Moreira, E. Y. Tshuva and S. J. Lippard, *Inorg. Chem.*, 2004, **43**, 4427-4434.
283. M. Gomez-Saso, D. F. Mullica, E. Sappenfield and F. G. A. Stone, *Polyhedron*, 1996, **15**, 793-801.
284. J. P. Campbell and W. L. Gladfelter, *Inorg. Chem.*, 1997, **36**, 4094-4098.
285. S. M. Kunnari, R. Oilunkaniemi, R. S. Laitinen and M. Ahlgren, *J. Chem. Soc., Dalton T.*, 2001, 3417-3418.
286. S. M. Naerhi, R. Oilunkaniemi, R. S. Laitinen and M. Ahlgren, *Inorg. Chem.*, 2004, **43**, 3742-3750.
287. S. Streiff, N. Ribeiro and L. Desaubry, *Chem. Commun.*, 2004, 346-347.
288. B. Mudryk and T. Cohen, *J. Am. Chem. So.c*, 1991, **113**, 1866-1867.
289. T. Chivers and G. Schatte, *Eur. J. Inorg. Chem.*, 2003, 3314-3317.
290. R. A. Bartlett, M. M. Olmstead, P. P. Power and G. A. Sigel, *Inorg. Chem. Commun.*, 1987, **26**, 1941.
291. F. Johnson, *Friedial-Crafts and Related Reactions*, Interscience, New York, 1965.

292. A. A. Danopoulos, J. R. Galsworthy, M. L. H. Green, S. Cafferkey, L. H. Doerrer and M. B. Hursthouse, *Chem. Commun.*, 1998, 2529-2530.
293. L. H. Doerrer, A. J. Graham, D. Haussinger and M. L. H. Green, *Dalton T.*, 2000, 813-820.
294. K. Isleib and A. Tzschach, *Chem. Ber.*, 1959, **92**, 118.
295. R. E. Goldsberry, D. E. Lewis and K. Cohn, *J. Organometal. Chem.*, 1968, **15**, 491-493.
296. P. Peringer and P. P. Winkler, *Inorg. Chim. Acta.*, 1986, **118**, L1-L2.
297. K. Tamao, Y. Nakagawa and Y. Ito, *Organometallics*, 1993, **12**, 2297-2308.
298. M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. J.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. , Gaussian Inc., Pittsburgh, 2003.
299. S. C. Gatling and J. E. Jackson, *J. Am. Chem. Soc.*, 1999, **121**, 8655-8656.
300. R. Roesler, W. E. Piers and M. Parvez, *J. Organomet. Chem.*, 2003, **680**, 218-222.
301. C. A. Jaska and I. Manners, *J. Am. Chem. Soc.*, 2004, **126**, 1334-1335.
302. J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, **2**, 3921-3923.
303. A. Di Saverio, F. Focante, I. Camurati, L. Resconi, T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, *Inorg. Chem.*, 2005, **44**, 5030-5041.
304. P. S. Bryan and Kuczkows.Rl, *Inorg. Chem.*, 1972, **11**, 553-&.
305. W. T. Klooster, T. F. Koetzle, P. E. M. Siegbahn, T. B. Richardson and R. H. Crabtree, *J. Am. Chem. Soc.*, 1999, **121**, 6337-6343.
306. V. I. Bakhmutov, *Eur. J. Inorg. Chem.*, 2005, 245-255.
307. X. Z. Yang and M. B. Hall, *J. Am. Chem. Soc.*, 2008, **130**, 1798-1799.
308. V. S. Nguyen, M. H. Matus, D. J. Grant, M. T. Nguyen and D. A. Dixon, *J. Phys. Chem. A.*, 2007, **111**, 8844-8856.
309. M. H. Matus, K. D. Anderson, D. M. Camaioni, S. T. Autrey and D. A. Dixon, *J. Phys. Chem. A.*, 2007, **111**, 4411-4421.
310. M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar and D. A. Dixon, *J. Phys. Chem. A.*, 2007, **111**, 679-690.
311. V. S. Nguyen, M. H. Matus, M. T. Nguyen and D. A. Dixon, *J. Phys. Chem. C.*, 2007, **111**, 9603-9613.
312. D. J. Grant and D. A. Dixon, *J. Phys. Chem. A.*, 2006, **110**, 12955-12962.
313. D. J. Grant and D. A. Dixon, *J. Phys. Chem. A.*, 2005, **109**, 10138-10147.

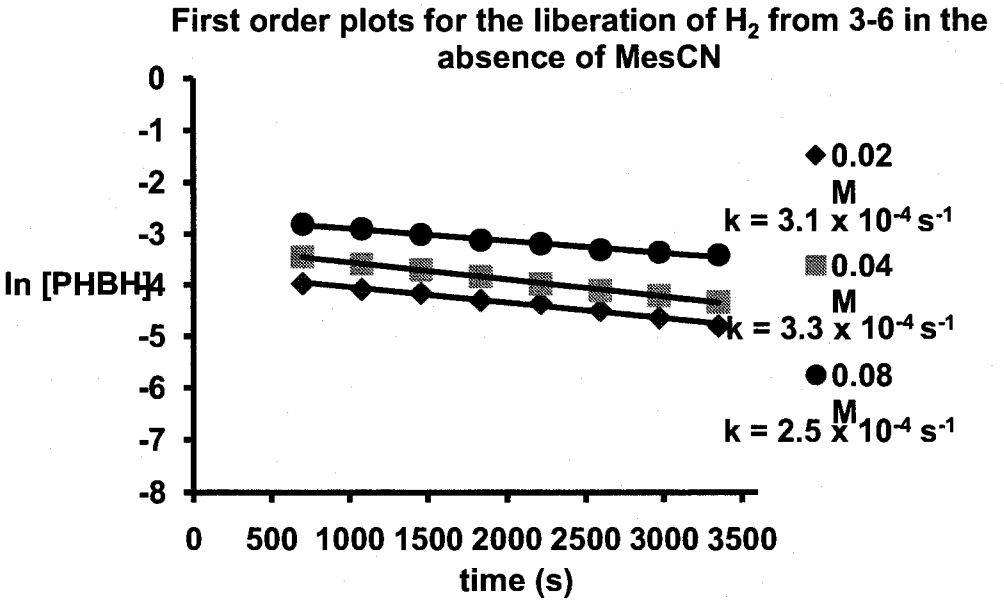
314. D. A. Dixon and M. Gutowski, *J. Phys. Chem. A.*, 2005, **109**, 5129-5135.
315. Ryschkew.Ge and J. W. Wiggins, *Inorg. Chem.*, 1970, **9**, 314-&.
316. R. S. Smith, B. D. Kay, L. Y. Li, B. A. Schmid, N. J. Hess, M. Gutowski and T. Autrey, *Abstr. Pap. Am. Chem. S.*, 2005, **229**, U858-U858.
317. P. S. Pregosin, *Prog. Nucl. Mag. Res. Sp.*, 2006, **49**, 261-288.
318. C. Zuccaccia, N. G. Stahl, A. Macchioni, M. C. Chen, J. A. Roberts and T. J. Marks, *J. Am. Chem. Soc.*, 2004, **126**, 1448-1464.
319. D. Zuccaccia, S. Sabatini, G. Bellachioma, G. Cardaci, E. Clot and A. Macchioni, *Inorg. Chem.*, 2003, **42**, 5465-5467.
320. A. Macchioni, A. Magistrato, I. Orabona, F. Ruffo, U. Rothlisberger and C. Zuccaccia, *New. J. Chem.*, 2003, **27**, 455-458.
321. C. P. Casey, J. B. Johnson, S. W. Singer and Q. Cui, *J. Am. Chem. Soc.*, 2005, **127**, 3100-3109.
322. J. T. Edward, *J. Chem. Educ.*, 1970, **47**, 261-262.
323. G. J. Kubas, *P. Natl. Acad. Sci.*, 2007, **104**, 6901-6907.
324. G. J. Kubas, *Adv. Inorg. Chem.*, 2004, **56**.
325. B. S. Jursic, *J. Mol. Struct.*, 1999, **492**, 97.
326. J. D. Watts and R. J. Bartlett, *J. Am. Chem. Soc.*, 1995, **117**, 825.
327. T. J. J. Tague and L. Andrews, *J. Am. Chem. Soc.*, 1994, **116**, 4970-4976.
328. P. R. Schreiner, H. F. Schaefer and P. v. R. Schleyer, *J. Chem. Phys.*, 1994, **101**, 7625-7632.
329. A. Moroz, R. L. Sweany and S. L. Whittenburg, *J. Phys. Chem.*, 1990, **94**, 1352-1357.
330. L. S. Bouchard, K. V. Kovtunov, S. R. Burt, M. S. Anwar, I. V. Koptyug, R. Z. Sagdeev and A. Pines, *Angew. Chem. Int. Ed.*, 2007, **46**, 4064-4068.
331. I. V. Koptyug, K. V. Kovtunov, S. R. Burt, M. S. Anwar, C. Hilty, S. I. Han, A. Pines and R. Z. Sagdeev, *J. Am. Chem. Soc.*, 2007, **129**, 5580-5586.
332. A. Ienco, M. J. Calhorda, J. Reinhold, F. Reineri, C. Bianchini, M. Peruzzini, F. Vizza and C. Mealli, *J. Am. Chem. Soc.*, 2004, **126**, 11954-11965.
333. T. Beringhelli, D. Maggioni and G. D'Alfonso, *Organometallics*, 2001, **20**, 4927-4938.
334. R. T. Stibrany and P. Brant, *Acta Crystallogr. C*, 2001, **57**, 644-645.
335. T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, *Organometallics*, 2003, **22**, 1588-1590.
336. T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, *Organometallics*, 2004, **23**, 5493-5502.
337. T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, *Organometallics*, 2007, **26**, 2088-2095.
338. K. Ishihara, H. Kurihara and H. Yamamoto, *J. Org. Chem.*, 1997, **62**, 5664-5665.
339. M. Stender, A. D. Phillips and P. P. Power, *Inorg. Chem.*, 2001, **40**, 5314-5315.
340. A. H. Cowley, C. L. B. Macdonald, J. S. Silverman, J. D. Gorden and A. Voigt, *Chem. Commun.*, 2001, 175-176.
341. R. Duchateau, R. A. van Santen and G. P. A. Yap, *Organometallics*, 2000, **19**, 809-816.
342. T. Claridge, *High Resolution NMR Techniques in Organic Chemistry*, Pergamon, 1999.
343. L. M. Epstein and E. S. Shubina, *Coordin. Chem. Rev.*, 2002, **231**, 165-181.

344. M. A. Beckett, D. S. Brassington, M. E. Light and M. B. Hursthouse, *J. Chem. Soc. Dalton T.*, 2001, 1768-1772.
345. D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440-9441.
346. J. M. Blackwell, K. L. Foster, V. H. Beck and W. E. Piers, *J. Org. Chem.*, 1999, **64**, 4887-4892.
347. D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090-3098.
348. J. M. Blackwell, D. J. Morrison and W. E. Piers, *Tetrahedron*, 2002, **58**, 8247-8254.
349. H. Schafer and A. G. Macdiarmid, *Inorg. Chem.*, 1976, **15**, 848-856.
350. I. P. Beletskaya and V. P. Ananikov, *Eur. J. Org. Chem.*, 2007, 3431-3444.
351. I. Beletskaya and C. Moberg, *Chem. Rev.*, 2006, **106**, 2320-2354.
352. F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2004, **104**, 3079-3159.
353. I. Beletskaya and C. Moberg, *Chem. Rev.*, 1999, **99**, 3435-3461.
354. Y. J. Cao, Y. Y. Lai, H. Cao, X. N. Xing, X. Wang and W. J. Xiao, *Can. J. Chem.*, 2006, **84**, 1529-1533.
355. T. Kondo and T. Mitsudo, *Chem. Rev.*, 2000, **100**, 3205-3220.
356. A. J. Parker and N. Kharasch, *Chem. Rev.,* 1959, **59**, 583-628.
357. M. C. Caserio, C. L. Fisher and J. K. Kim, *J. Org. Chem.*, 1985, **50**, 4390-4393.
358. N. Yamagiwa, Y. Suto and Y. Torisawa, *Bioorg. & Med. Chem. Lett.*, 2007, **17**, 6197-6201.
359. M. Yamaguchi and Y. Nishimura, *Chem. Commun.*, 2008, 35-48.
360. S. Usugi, H. Yorimitsu, H. Shinokubo and K. Oshima, *Org. Lett.*, 2004, **6**, 601-603.
361. P. D. Clark, S. T. E. Mesher and M. Parvez, *Cat. Lett.*, 1997, **47**, 73-75.
362. D. N. Harpp and R. A. Smith, *J. Am. Chem. Soc.*, 1982, **104**, 6045-6053.
363. A. Schonberg, *Chem. Ber.*, 1935, **68**, 163.
364. L. E. Overman, Matzinge.D, E. M. Oconnor and J. D. Overman, *J. Am. Chem. Soc.*, 1974, **96**, 6081-6089.
365. L. E. Overman and S. T. Petty, *J. Org. Chem.*, 1975, **40**, 2779-2782.
366. L. E. Overman and E. M. Oconnor, *J. Am. Chem. Soc.*, 1976, **98**, 771-775.
367. J. A. Burns, J. C. Butler, J. Moran and G. M. Whitesides, *J. Org. Chem.*, 1991, **56**, 2648-2650.
368. O. Dmitrenko, C. Thorpe and R. D. Bach, *J. Org. Chem.*, 2007, **72**, 8298-8307.
369. X. B. Zheng, W. A. Tao and R. G. Cooks, *J. Chem. Soc. Perk. T. 2*, 2001, 350-355.
370. H. Takeuchi, J. Tateiwa and S. Moriguchi, *Molecules*, 2003, **8**, 392-400.
371. K. Kobayashi, S. Sato, E. Horn and N. Furukawa, *Tet. Lett.*, 1998, **39**, 2593-2596.
372. C. Peppe, J. A. Nobrega, M. Z. Hernandes, R. L. Longo and D. G. Tuck, *J. Organomet. Chem.*, 2001, **626**, 68-75.
373. H. Ohmori, H. Maeda, K. Konomoto, K. Sakai and M. Masui, *Chem. Pharm. Bull.*, 1987, **35**, 4473-4481.
374. J. Omelanczuk and M. Mikolajczyk, *J. Am. Chem. Soc.*, 1979, **101**, 7292-7295.
375. M. J. Drewitt, M. Niedermann, R. Kumar and M. C. Baird, *Inorg. Chim. Acta.*, 2002, **335**, 43-51.
376. H. U. Steinberger, B. Ziemer and M. Meisel, *Acta Crystallogr. C*, 2001, **57**, 835-837.
377. F. Schaper and H. H. Brintzinger, *Acta Crystallogr. E*, 2002, **58**, O77-O78.

378. K. R. Kumar, C. Hall, A. Penciu, M. J. Drewitt, P. J. McInenly and M. C. Baird, *J. Polym. Sci. Pol. Chem.*, 2002, **40**, 3302-3311.
379. K. R. Kumar, A. Penciu, M. J. Drewitt and M. C. Baird, *J. Organomet. Chem.*, 2004, **689**, 2900-2904.
380. J. Ugolotti, S. Hellstrom, G. J. P. Britovsek, T. S. Jones, P. Hunt and A. J. P. White, *Dalton T.*, 2007, 1425-1432.
381. W. J. Evans, *Inorg. Chem.*, 2007, **46**, 3435-3449.

Appendix A

Graphs dipiciting results from kinetic experiments in the absence of MesCN



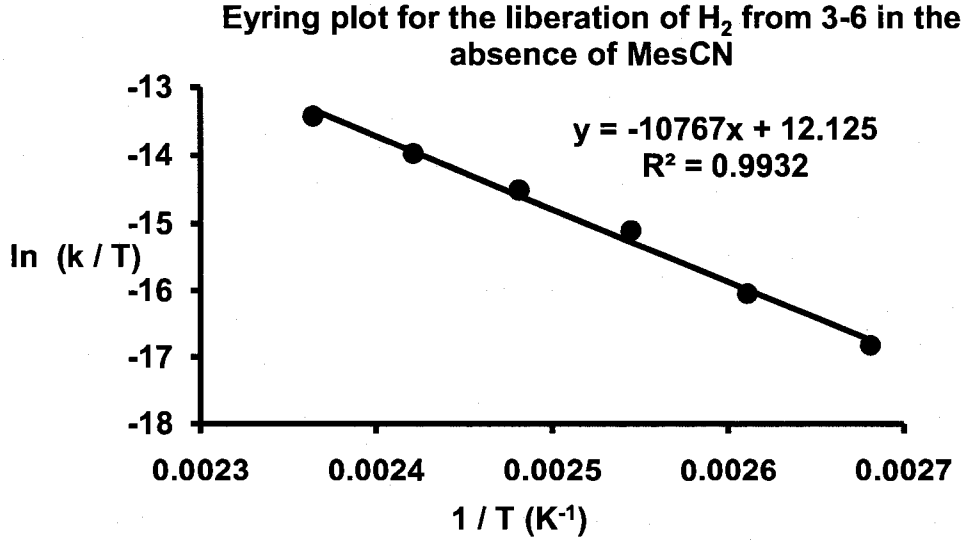


Figure A.1 Kinetic graphs. (**Top**) First order plots for the loss of H_2 from **3-6** in the absence of MesCN at varying concentrations in C_6H_5Br at 140 °C. (**Bottom**) Eyring plot over a temperature range from 100 °C to 150 °C for the loss of H_2 from **3-6** in the absence of MesCN.

Appendix B

Graphs dipiciting results from kinetic experiments in the presence of MesCN

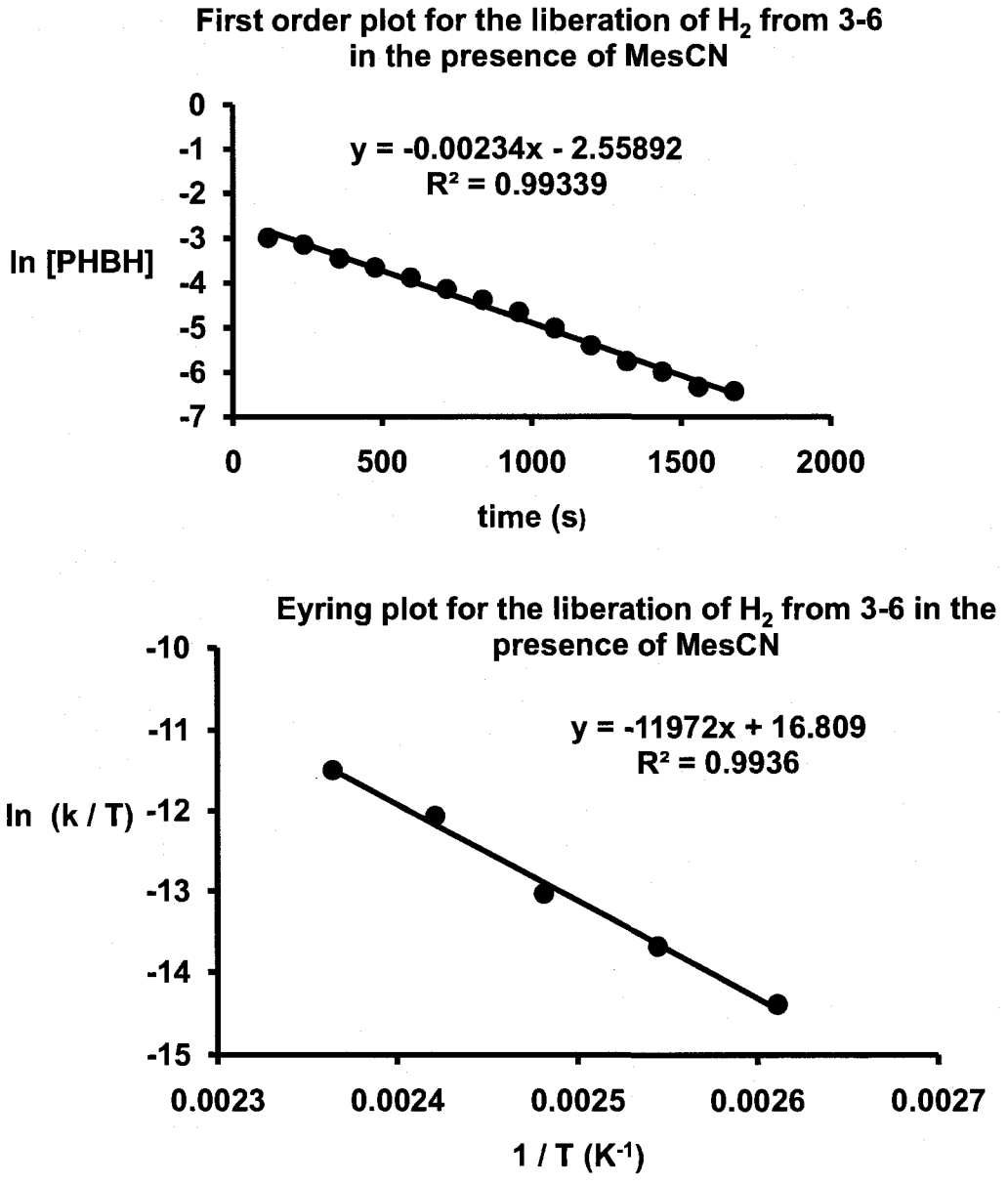


Figure B.1 Kinetic graphs. (**Top**) First order plot for the loss of H_2 from **3-6** with added MesCN at 0.04 M in C_6H_5Br at 140 °C. (**Bottom**) Eyring plot over a temperature range from 110 °C to 150 °C for the loss of H_2 from **3-6** with added MesCN.

Vita Auctoris

Gregory Charles Welch
Date of Birth: October 24, 1980
Place of Birth: Calgary, Alberta, Canada

Academic Background:

Ph.D.Candiate, Inorganic Chemistry
University of Windsor, Windsor, Ontario, Canada
Supervisor: Professor D. W. Stephan
January 2004 – present

BSc. Honors Chemistry
University of Calgary, Calgary, Alberta, Canada
Received 2003

Work Experience:

Chemistry Teaching Assistant
University of Windsor, Windsor, Ontario, Canada
January 2004 – May 2007

Student Research Scientist
NOVA Chemicals, Calgary, Alberta, Canada
NRTC New Catalysts and Polymers Division
Supervisor: Dr. Qinyan Wang
August 2003 – December 2003

NSERC Summer Research Student / Honors Research Student
University of Calgary, Calgary, Alberta, Canada
Supervisor: Professor W. E. Piers
May 2002 – August 2003

NSERC Summer Research Student
University of Calgary, Calgary, Alberta, Canada
Supervisor: Professor T. Chivers
May 2000 – August 2000

Articles Published or Accepted in Refereed Journals:

10. **Welch, G. C.**; Holtrichter-Roessmann, T.; Stephan, D. W. (2008) Thermal Rearrangement of Phosphine-$B(C_6F_5)_3$ Adducts. *Inorg. Chem.* **47**, 1904-1906.

9. Chase, P. A.; **Welch, G. C.**; Jurca, T.; Stephan, D. W. Metal-Free Catalytic Hydrogenation. *Angew. Chem. Int. Edn. Engl.* **46**, 8050-8053 (2007). *Cover Article, VIP, Featured in C&EN News*
8. **Welch, G. C.**; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. Tuning Lewis Acidity Using The Reactivity of "Frustrated Lewis Pairs": Facile Formation of Phosphine-boranes and Cationic Phosphonium-boranes. *Dalton Trans.* **31**, 3407-3414 (2007). *Cover Article*
7. McCahill, J. S. J.; **Welch, G. C.**; Stephan, D. W. Reactivity of "Frustrated Lewis Pairs": Three Component Reactions of Phosphines, a Borane, and Olefins. *Angew. Chem. Int. Edn. Engl.* **46**, 4968-4971 (2007). *VIP*
6. **Welch, G. C.**; Stephan, D. W. Facile Heterolytic Cleavage of Dihydrogen by Phosphines and Boranes. *J. Am. Chem. Soc.* **129**, 1880-1881 (2007).
5. **Welch, G. C.**; San Juan, R.; Masuda, J. D.; Stephan, D. W. Reversible, Metal Free Hydrogen Activation. *Science* **314**, 1124-1126 (2006). *Featured in C&EN News **84**, 21 (2006)*
4. Carbrera, L.; **Welch, G. C.**; Wei, P.; Masuda, J. D.; Stephan, D. W. Pyridine and Phosphine Reactions with $[CPh_3][B(C_6F_5)_4]$. *Inorg. Chim. Acta.* **359**, 3066-3071 (2006). *Invited for the special 'Professor Brian James' issue*
3. **Welch, G. C.**; Masuda, J. D.; Stephan, D. W. Phosphonium-Borate Zwitterions, Anionic Phosphines, and Dianionic Phosphonium-Dialkoxides via Tetrahydrofuran Ring-Opening Reactions. *Inorg. Chem.* **45**, 478-480 (2006).
2. **Welch, G. C.**; Piers, W. E.; Parvez, M.; McDonald, R. Neutral and Cationic Organoaluminum Complexes Utilizing a Novel Anilido Phosphinimine Ligand. *Organometallics* **23**, 1811-1818 (2004).
1. Hayes, P. H.; **Welch, G. C.**; Emslie, D.; Noack, C.; Piers, W. E., Parvez, M. A New Chelating Anildio-Imine Donor Related to ß-Diketiminato Ligands for Stabilization of Organoyttrium Cations. *Organometallics* **22**, 1577-1579 (2003).

Patents:

1. Doug Stephan, Greg Welch, Preston Chase: US Provisional Applications 60/865,684 filed Nov 14, 2006 and 60/896,557 filed March 23, 2007 (patent filed Nov 14, 2007)

Selected Presentations:

5. **Welch, G. C.**; McCahill, J. S. J.; Chase, P. A.; Stephan, D. W. "Frustrated Lewis Pairs": From Lewis acid-base adducts to the reversible activation of dihydrogen. Invited Seminar, DIC Young Investigators Symposium. 236rd ACS National Meeting, Philadelphia, PA, United States, Aug 17-21, 2008.
4. **Welch, G. C.**; Stephan, D. W. "Frustrated Lewis Pairs": Hydrogen Activation. Invited Lecture, University of Michigan, Ann Arbor, MI, United States, June 24, 2007.
3. **Welch, G. C.**; Stephan, D. W. Cooperative reactivity of phosphines and boranes: The reversible metal free activation of dihydrogen. Poster, 233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007.

2. **Welch, G. C.**; Cabrera, L.; Hollink, E.; Stephan, D. W. Facile routes to anionic phosphines, cationic boranes, and phosphino-boranes. Poster, 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006.
1. **Welch, G. C.**; Cabrera, L.; Hollink, E.; Stephan, D. W. Reactions of the Lewis acid $B(C_6F_5)_3$ with secondary phosphines and phosphides: Nucleophilic aromatic substitution and THF ring opening. Poster, 38th Inorganic Discussion Weekend, University of Western Ontario, London, ON, Canada, Nov 4-6, 2005.

Selected Scholarships, fellowships, and other awards received:

8. ACS DIC Young Investigators Award, $1000, Awarded 2008
7. NSERC PDF 2 Year Research Award (National), $80000 over 2 years, Awarded 2008
6. NSERC PGS-D 3 Year Research Award (National), $63000 over 3 years, Awarded 2006
5. University of Windsor, Presidents Excellence Award (Institutional), $3000, Awarded 2006
4. University of Windsor, Doctoral Tuition Scholarship (Institutional), Awarded 2006
3. University of Windsor, Graduate Tuition Scholarship (Institutional), Awarded 2005
2. NSERC Undergraduate Research Award (Institutional), Awarded 2002
1. NSERC Undergraduate Research Award (Institutional), Awarded 2000

Permanent Address:

111 Silvercrest Cr NW
Calgary, AB, Canada
T3B 3T8

403-286-3086