2008

“Frustrated” Lewis Pairs: Applications in olefin polymerization and small molecule activation

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"Frustrated" Lewis Pairs: Applications in Olefin Polymerization and Small Molecule Activation

by

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A Dissertation
Submitted to the Faculty 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
September 2008

Your file Votre référence
ISBN: 978-0-494-47112-8
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ISBN: 978-0-494-47112-8

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Abstract

Recent work in the Stephan Group has identified the concept of "frustrated" Lewis pairs, in which traditional Lewis acid-base adducts of sterically demanding phosphines and the borane, $B(C_6F_5)_3$ are not formed and alternative reactivity can occur.

Compounds derived from "frustrated" Lewis pair chemistry have been investigated as novel co-catalysts for ethylene polymerization. The phosphonium borates of the form, $[HPR_3][B(C_6F_5)_4]$, $[R_2PHC_6F_4BF(C_6F_5)_2]$ and $[R_2PHC_4H_8OB(C_6F_5)_3]$, have been shown to be effective protic activators for the generation of electrophilic cationic Ti metal centers of the form, $[CpTiMe(NP^tBu_3)]$. The derivatization of the perfluoroaryl-linked phosphonium borates to form the perfluoroaryl-link phosphino-boranes of the form, $R_2PC_6F_4B(C_6F_5)_2$, provides a unique family of potential Lewis acidic co-catalysts. These compounds were found to be excellent co-catalysts, as the interaction of the Lewis basic phosphine with the cationic Ti center increases ion-pair separation, resulting in a more active catalytic system.

Investigations of Lewis basic phosphine additives to the polymerization of ethylene using $CpTiMe(NP^tBu_3)/B(C_6F_5)_3$ systems resulted in the observation that the addition of sterically bulky phosphines, such as P^tBu_3 and PCy_3, increased the observed polymerization activity. It has been proposed that this phenomenon is a result of the greater ion-pair separation, due to interaction of the phosphine with the Ti metal center. This provides a novel way to view the active catalyst system and the methods involved with enhancement and activity optimization.

The synthesis of the sterically bulky phosphine-functionalized monomers, $^tBu_2P(CH_2)_3CHCH_2$, and the polymerization of these monomers was investigated. The

phosphine functionalized monomer was co-polymerized with 1-hexene, albeit in low percent yield and low incorporation of the functionality. Investigations of the potential inhibition pathways indicated that the co-polymerizations and homo-polymerizations of the phosphine-functionalized monomers are inhibited by reactivity with the co-catalyst, intermolecular coordination of the phosphine functionality, and intramolecular coordination of the phosphine.

Sterically frustrated Lewis pairs of bulky phosphines and the borane, $B(C_6F_5)_3$ exhibit unprecedented reactivity with olefins, affording both intermolecular additions as well as intramolecular cyclizations. The expansion of the reactivity of the olefin activation is hindered by the nucleophilic aromatic substitution reactions.

These studies demonstrate the application of the concept of "frustrated" Lewis Pairs to the polymerization and activation of olefins.

Dedication

This work is dedicated to my mom,

who has always been there to give me a band-aid or read through the gobbledygook

Acknowledgements

There are numerous people whom I would like to thank. I hope that I have always let everyone who has made a difference to my life and my work, know how thankful I am. I would like to thank my parents, John and Patti McCahill, for all of your support along the way. I would like to thank my grandparents and my brother, for always being there for me. I would like to thank Gregory Welch, for your tolerance and patience, and for your help. I would like to thank Jason Masuda for his help in the beginning and his willingness to teach. I would like to thank Stephen Geier, Preston Chase, Sharonna Greenberg and Patti McCahill for reading my thesis and all your helpful suggestions. I would also like to thank Mike Fuerth for all the NMR help. I would like to thank Shamola Labeodan and Preston Chase for synthesis of phosphonium-borate co-catalysts. Additionally, I would like to thank Gregory Welch for conducting X-ray crystallographic studies and synthesis. Finally, I would like to thank my supervisor Dr. Douglas Stephan, for always being optimistic (sometimes a realist needs to see the glass half full) and for letting me follow where the chemistry led.

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List of Abbreviations, Nomenclature and Symbols

Å	Angstrom
Abs coeff	absorption coefficient
br	broad
^{n}Bu	*n*-butyl C_4H_9
calcd	calculated
CCD	charge-coupled device
CGC	Constrained Geometry Catalysts
Cp	cyclopentyl, C_5H_9
Cy	cyclohexyl, C_6H_{11}
°C	degrees Celsius
D_{calc}	calculated density
d	doublet
equiv.	equivalents
Et	ethyl, C_2H_5
FI	Fenokishi-Imin Haiishi
FLP	"frustrated" Lewis pair
g	grams
GOF	goodness of fit
GPC	Gel Permeation Chromatography
hr	hour
Hz	Hertz
^{i}Bu	*iso*-butyl
^{i}Pr	*iso*-propyl
J	coupling constant
L	liter
m	multiplet
M	mol L^{-1}
m	*meta*
MAO	methylaluminumoxane
Me	methyl CH_3

Mes	mesityl ($C_6H_2Me_3$-2,4,6)
mg	milligram
MHz	megahertz
M_n	number average molecular weight
min	minute
mL	milliliter
mmol	millimole
NAS	Nucleophilic Aromatic Substitution
NMR	nuclear magnetic resonance
o	*ortho*
ORTEP	Oak Ridge thermal ellipsoid plot
p	*para*
Ph	phenyl C_6H_5
ppm	parts per million
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
T*i*BAl	Tri-*iso*-butylaluminum
TMS	trimethylsilyl
wt %	weight percent
μmol	micromole

Chapter 1: Introduction

1.1 Polymerization of Ethylene by Early Transition Metals

In the 1930's Imperial Chemical Industries reported the free radical process for the production of highly branched, low density polyethylene. The many uses of this material were quickly discovered and this process is still in use today.[1]

In the early 1950's, a leap into the arena of highly active *catalytic* olefin polymerization was independently initiated by the groundbreaking work of Ziegler and Natta. These findings, in part, have lead to the widespread use of polyolefins today. In the initial report by Zeigler, a catalyst system based on titanium halides and alkylaluminum compounds which was demonstrated to polymerize ethylene at high activities (10^5 kg polymer/mol Ti) at pressures and temperatures much lower than the free radical processes.[2] Separately, Natta also reported a similar system that could polymerize alpha-olefins in a stereoregular fashion.[3] These heterogeneous systems are collectively known as Ziegler-Natta catalysts and are still in use today; modern systems typically consist of $TiCl_4$ supported on $MgCl_2$ and $AlEt_3$.[1]

1.2 Homogeneous Single-Site Metallocenes

The next major breakthrough in olefin polymerization occurred with the development of soluble, single-site metallocene-based catalysts.[4,5] Unlike the heterogeneous Ziegler-Natta systems, the specific nature of the polymerization site could be designed *a priori*, rationally modified based on ligand design principles and be probed using mechanistic investigations.[6] These initial metallocene catalyst systems developed were based on a

Cp_2TiCl_2 pre-catalyst and a Et_2AlCl co-catalyst. Further studies demonstrated that the formation of the active catalyst species occurred through ligand exchange between Cp_2TiCl_2 and Et_2AlCl to form the complex $Cp_2TiEtCl$, which forms an adduct with the aluminium species, which polarized the Ti-Cl bond, and the insertion of ethylene occurs into the Ti-R bond.[7-10] This process is illustrated in Figure 1.1.

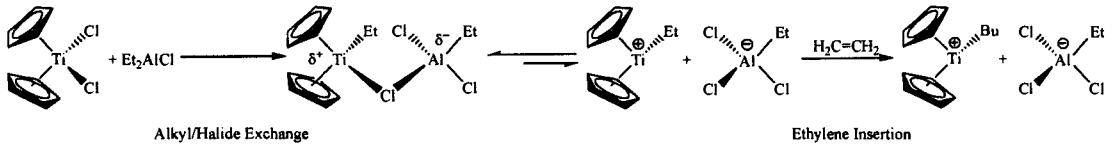


Figure 1.1 Alkyl/Halide Exchange and Ethylene Insertion

Although these systems provided mechanistic insight into the early transition metal catalyzed polymerization of ethylene, the polymerization activities of these systems were lower than those observed for the heterogeneous Ziegler-Natta systems. Numerous attempts were carried out to increase the effectiveness of these systems. Reichert and Meyer[11] reported a surprising increase in activity upon the addition of water to a $Cp_2TiEtCl/EtAlCl_2$ system. Subsequent studies led to the suggestion that the addition of water led to a dimeric aluminumoxane system, which would be a stronger Lewis acid and therefore, a better activator than previous aluminium co-catalysts utilized.[12] These results led to the development of the highly effective activator, methylaluminumoxane, MAO.[13-15] The discovery of MAO led to the rejuvenation of single-site catalysts and the development of novel pre-catalysts and co-catalysts.

1.3 Co-catalysts for Early Metal Olefin Polymerization

1.3.1 MAO

MAO is prepared via the controlled hydrolysis of $AlMe_3$ to give an oligomeric species consisting of –Al(Me)-O- subunits. Although the exact structure of MAO is not fully understood,[16,17] the generation of the active species for olefin polymerization occurs through halide for methyl exchange at the pre-catalyst and subsequent alkyl/halide abstraction,[18,19] as described for aluminium activators. This activation mechanism is illustrated in Figure 1.2.

Figure 1.2 Activation Mechanism for MAO

Although MAO was found to be an excellent co-catalyst, there are numerous disadvantages to its use. Due to the unknown structure of the co-catalyst, the nature of the active polymerization species is not well understood. Also, there are a limited number of active sites, necessitating the use of MAO in ratios of up to 1000:1. This has led to the development of new co-catalysts with well defined structures which allow for structure/activity relationships of the pre-catalyst and co-catalyst to be explored.

1.3.2 Perfluoroaryl Boranes

Although the synthesis of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was first reported in 1964[20], it was not until 1991 when Marks[21] and Ewen[22] independently reported the combination of metallocene dialkyls and $B(C_6F_5)_3$ to produced a catalyst which is highly

effective for olefin polymerization. The active species is formed by alkyl abstraction of a methyl group by the strongly Lewis acidic borane[21,23] as illustrated in Figure 1.3

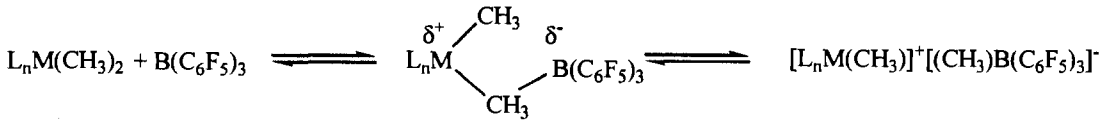


Figure 1.3 Activation Mechanism for $B(C_6F_5)_3$

Since this seminal report, not only has the use of $B(C_6F_5)_3$ in olefin polymerization grown rapidly, but the design of numerous perfluoroarylboranes and their effectiveness as activators for olefin polymerization been investigated[24]. Notably, the research groups of Marks[25-32] and Piers[33-43] have developed novel borane co-catalysts. Investigations of the impact of the electronic and steric properties of these boranes and the subsequent influence of these properties on the ability of the compounds to act as activators for olefin polymerization have been conducted. In general, for the perfluoroaryl boranes the increased Lewis acidity leads to increased polymerization activity.[24,44]

1.3.3 Trityl and Ammonium Borates

In the effort to design non-coordinating ions to minimize the cation-anion interactions, the development of effective co-catalysts employing then trityl cation, $[Ph_3C]^+$, which is a powerful alkyl abstracting agent, and the ammonium cation, $[R_3NH]^+$, which can cleave the M-alkyl bond via protonation, in combination with the relatively non-coordinating anion, $[B(C_6F_5)_4]^-$, have been developed.[21,45-48] The formation of the active species via these routes are illustrated in Figure 1.4

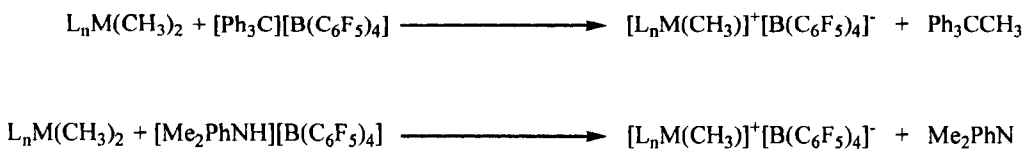


Figure 1.4 Activation Mechanisms For $[Ph_3][B(C_6F_5)_4]$ and $[Me_2PhNH][B(C_6F_5)_4]$

Modifications of the borate-based activators have also been explored to improve the stability and solubility of these activators.[49,50]

1.3.4 Role of the Anion in Polymerization Mechanism

In addition to the formation of the active metal center, the anion play a significant role in the polymerization process. There are numerous experimental[51] and theoretical[52-54] studies that suggest the anion must be considered in the propagation mechanism, as illustrated in Figure 1.5. Therefore the displacement of the anion must occur for monomer coordination and insertion to proceed.

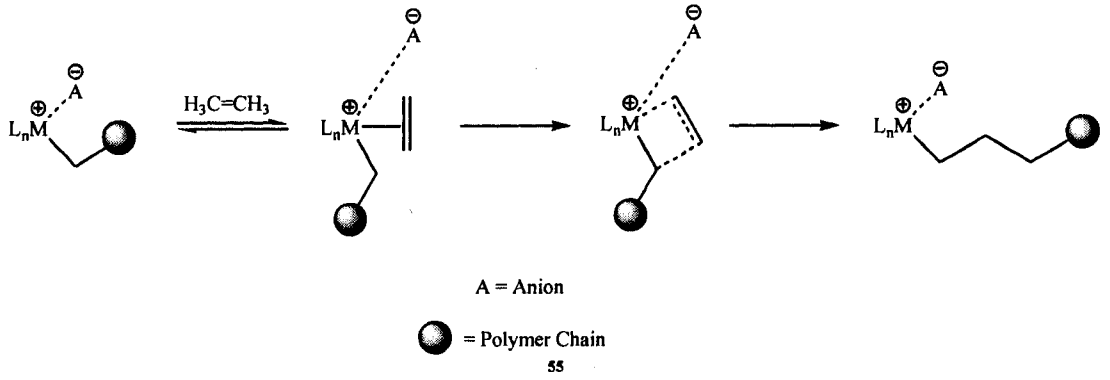


Figure 1.5 Propagation Mechanism

1.3.4.1 Stabilization of Ion-Pairs

Although the development of weakly or non-coordinating ions has been targeted[56], there is evidence that cation-anion interactions stabilize the chemically reactive cationic metal center.[24] Therefore, in designing a catalyst system the pre-catalyst-co-catalyst structure-activity relationship and the optimization of this relationship for olefin polymerization must be considered.

1.4 Pre-catalysts for Early Metal Olefin Polymerization

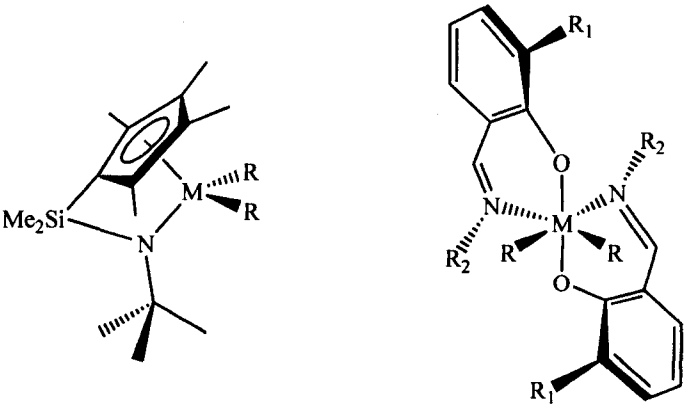
As discussed previously, the discovery of MAO led to the resurgence of studies of homogeneous, single-site catalyst systems. Not only has the modification of metallocence pre-catalyst been extensively studied,[57-59] but also the design of non-metallocene pre-catalyst systems.[60-63] Additionally, the use of non-Group IV transition metal systems has been investigated and has been reviewed elsewhere.[60,64-66] As with the co-catalyst, the pre-catalyst selected has a dramatic impact on the polymerization activity and resultant polymer properties.

1.4.1 Metallocene Pre-catalysts

As discuss previously, the metallocene framework has been modified and the ancillary ligands used to control the electronic and steric properties of the catalyst system, which has shown to have an impact on the polymerization activity and polymer properties. Rational modification of these systems has led to the ability to control the stereoselective polymerization of alpha-olefins.[67-69]

1.4.2 Alternative Group IV Pre-catalysts

As addressed earlier, there are numerous reported ligand frameworks for the development of Group IV, most specifically Ti and Zr, pre-catalyst systems and this work has been extensively reviewed. Of these pre-catalyst systems the Constrained Geometry catalysts (CGC) and the Fenokishi-Imin Haiishi (FI) catalysts have had a large impact on the field of olefin polymerization and have industrial applications. (Figure 1.6)



CGC Pre-catalyst **FI Pre-catalyst**

M = Ti, Zr
R = CH_3, Cl
R1, R2 = alkyl, aryl

Figure 1.6 CGC and FI Pre-catalysts

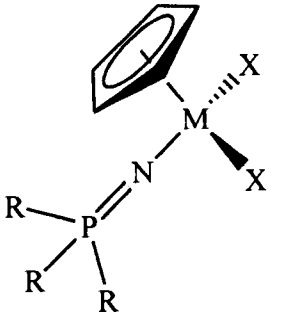
The CGC ligand systems were first reported by Bercaw and co-workers[70] and Okuda.[71] Subsequently, catalysts systems based on the CGC ligand system were patented by both the Dow Chemical Company[72] and Exxon Mobil Corporation.[73] These systems have been extensively investigated both experimentally[60,61,74] and theoretically.[75-77]

The FI catalyst systems were developed by Fujita and co-workers at Mitsui Chemicals,[78] and are noted for their high olefin polymerization activity. Modifications of this ligand framework have also been extensively investigated. [63,79-81]

The high polymerization activities observed for both the CGC and FI catalysts have been attributed to the greater exposure of the metal center, providing more space for olefin binding.

1.4.3 Group IV Phosphinimide Pre-catalysts

Another class of pre-catalysts which have found industrial applications are the group IV phosphinimide systems, developed Stephan and co-workers.[82] As illustrated in Figure 1.7



M = Ti, Zr
X = alkyl, halide
R = alkyl, aryl

Figure 1.7 Group IV Phosphinimide Pre-catalysts

These catalyst systems have been found to exhibit polymerization activities comparable to the metallocene and CGC systems, and have been patented by NOVA Chemicals Corp.[83-85] The phosphinimide functionality was chosen as an ancillary ligand due to the steric and electronic similarities of the $[NPR_3]^-$ ligand with Cp^-.[86]

The steric analogy of the $[NPR_3]^-$ ligand with Cp^- is based on a similar rationale described by Wolczanski and co-workers for the triox, $[OCR_3]^-$, ancillary ligand.[87] As illustrated in Figure 1.8. Although the cone angle at the metal center is similar, the steric bulk of the ligand is removed form the metal providing a more open metal center, and therefore, the rationale for the increase in polymerization activity is similar to the CGC and FI catalyst systems.

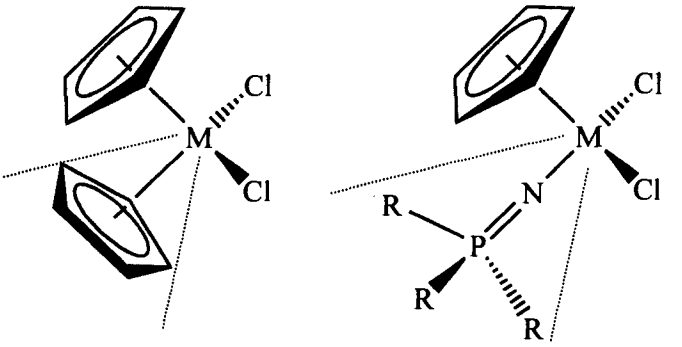


Figure 1.8 Steric Analogy of $[Cp]^-$ and $[NPR_3]^-$

The electronic analogy of the $[NPR_3]$- functionality was first proposed by Dehnicke.[88,89] The electronic analogy of the $[NPR_3]^-$ ligand to the $[Cp]^-$ ligand is based on the ability of the phosphinimide ligand to donate π-electron density to the metal centre.

Since the initial report of the high polymerization activities observed for the Group IV phosphinimide pre-catalysts, the Stephan Group has continued to develop catalyst systems involving the phosphinimide ligand framework, and numerous experimental[86,90-92] and theoretical[93] investigations have expanded the scope and understanding of this ligand system and how modifications of the steric and electronic properties of the $[NPR_3]^-$ ligand affect the polymerization activity.

1.5 Scope and Objectives of this Work

The investigation of group IV catalyst systems continues to be an area of interest and the development of novel pre-catalysts and co-catalysts continues to be explored. Recent work in the Stephan Group has identified a novel method of the synthesis of phosphonium-borates through the utility of "frustrated" Lewis pairs, in which traditional Lewis acid-base adducts of sterically demanding phosphines and the borane, $B(C_6F_5)_3$ are not formed and alternative reactivity can occur.

The utility of the compounds derived from "frustrated" Lewis pair chemistry to act as activators for olefin polymerization employing the pre-catalyst system, $CpTiMe_2(NP^tBu_3)$ is explored.

The extension of this "frustrated" Lewis pair concept as it applies to the Lewis acidic Ti cation, $[CpTiMe(NP^tBu_3)]^+$ in the presence of Lewis basic phosphines during ethylene polymerization is also probed.

Based on these results a phosphine functionalized monomer was designed, and the co-polymerizations of this monomer with 1-hexene were explored. Additionally, the reactive pathways which inhibit polymerization of these monomers investigated.

Finally, the reactivity of "frustrated" Lewis pairs of sterically demanding phosphines and the borane, $B(C_6F_5)_3$, towards olefinic substrates was investigated.

Chapter 2: The Utility of Compounds Derived from "Frustrated" Lewis Pair Chemistry as Activators for Olefin Polymerization

2.1 Introduction

The discovery by Marks[21] and Ewan[22] that the strongly Lewis acidic borane, $B(C_6F_5)_3$, in combination with group IV metallocene alkyls, could act as an efficient olefin polymerization catalyst has led to the rational design and development of new, and more effective co-catalysts and contributed significantly to a deeper understanding of the catalyst/co-catalyst system. Over the past few years, the research groups of Marks[25-32], Piers,[35-43,94,95] and others,[96-99] have continued to develop novel perfluoroarylborane and *bis*-borane co-catalysts. Alteration of the Lewis acidic co-catalysts for the polymerization of olefins has been shown to have a dramatic impact on catalyst activity, life-time, and stability, as well as the properties of resultant polymers.[44,100-106] The importance of the co-catalyst is not only limited to formation of a catalytically active species from its catalyst precursor, but the resultant cation-anion interactions have been shown to have a vital role in the polymerization.[24]

Recently, the Stephan Group has identified the concept of "frustrated" Lewis pairs which involves donor and acceptor sites which are precluded from formation of Lewis acid-base adduct formation by steric congestion.[107,108] In some of these systems Lewis acid-base adducts are not formed and nucleophilic attack at a carbon *para* to B followed by fluoride transfer results in the formation of the zwitter-ionic phosphonium-borates $[R_2PH(C_6F_4)BF(C_6F_5)_2]$ as illustrated in Figure 2.1.[108] Derivatization of these compounds

yields a series of phosphonium-borates, phosphino-boranes and cationic phosphonium-boranes.[108,109]

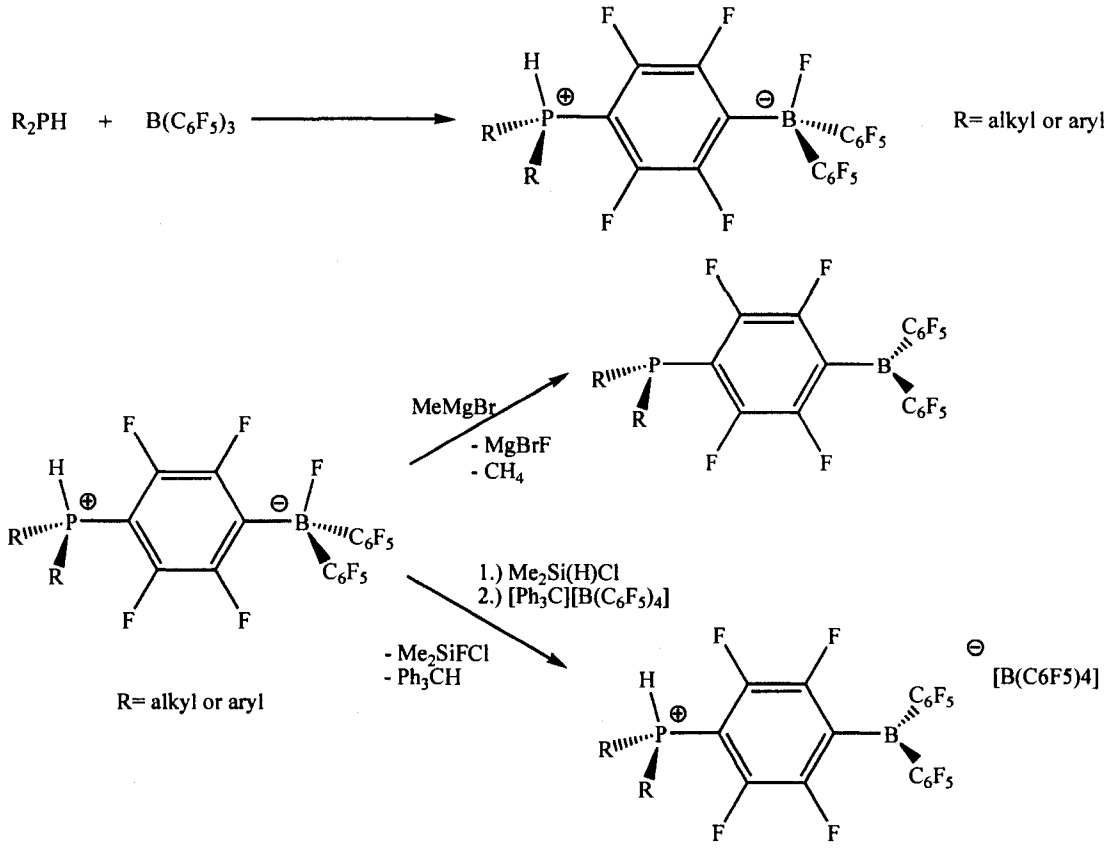


Figure 2.1 Synthesis of Phosphonium-borates, Phosphino-boranes and Cationic Phosphonium-boranes

In related reactions employing $(THF)B(C_6F_5)_3$ and phosphines, it is generally observed that relatively smaller Lewis basic phosphines simply replace THF, thereby forming traditional Lewis acid-base adducts[110]. However, reactions of sterically demanding phosphines and $(THF)B(C_6F_5)_3$ follow an alternate path, giving rise to nucleophilic ring opening of THF and yielding butoxy-tethered phosphonium-borates $[R_2HPC_4H_8OB(C_6F_5)_3]$, as illustrated in Figure 2.2 [111].

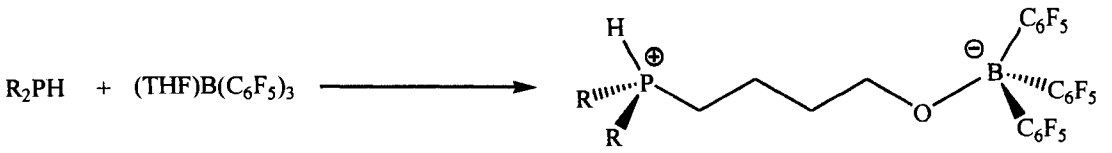


Figure 2.2 THF ring opening of $(THF)B(C_6F_5)_3$ with HPR_2

In these reactions, compounds resulting from reaction of sterically demanding phosphines with $B(C_6F_5)_3$, either in the presence, or absence of THF, can be viewed as novel olefin polymerization co-catalysts. In this chapter the polymerization of ethylene using the pre-catalyst $CpTiMe_2[NP^tBu_3]$ and activators derived from the reactions of "frustrated" Lewis pairs is investigated.

2.2 Experimental

2.2.1 General Considerations

All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres inert atmosphere glovebox. ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopic data were acquired on a Bruker Avance 300 MHz spectrometer at 300 K unless otherwise noted. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are referenced from $SiMe_4$ using the residual proton or carbon peak of the solvent. $^{31}P\{^1H\}$, ^{11}B, and ^{19}F NMR spectra were referenced to external 85% H_3PO_4, $BF_3{\cdot}Et_2O$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz, both as absolute values.

2.2.2 Solvents

Toluene was purified employing Grubbs-type column systems manufactured by Innovative Technologies. Proteo- and deuterated bromobenzene were purchased from Aldrich and Cambridge Isotopes Laboratories, and dried over CaH_2, freeze-pump-thaw degassed (3 times) and vacuum distilled prior to use.

2.2.3 Reagents

Ethylene was purchased from BOC Gases and dried over Q5 copper deoxygenation material and 3 Å molecular sieves. MeOH was purchased from Aldrich Chemical Co.; HCl was purchased from EM Science; $[Me_2PhNH][B(C_6F_5)_4]$ was purchased from Strem Chemical Inc.: All were used as received. $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, Al^iBu_3 (T*i*BAl), and $CpTiCl_2(NP^tBu_3)$ were generously donated by NOVA Chemicals Corp. and used without further purification. $CpTiMe_2[NP^tBu_3]$,[82] $[Cy_3PH][B(C_6F_5)_3]$[112] (**2.1**) and $[^tBu_3PH][B(C_6F_5)_4]$[112] (**2.3**) and were prepared via literature methods. $[Mes_3PH][B(C_6F_5)_4]$ (**2.2**)[113], $Cy_2PHC_6F_4BF(C_6F_5)_2$ (**2.4**), $Mes_2PHC_6F_4BF(C_6F_5)_2$ (**2.5**) ^{t}BuMesPHC$_6$F$_4$BF(C$_6$F$_5$)$_2$ (**2.6**), $^tBu_2PHC_6F_4BF(C_6F_5)_2$ (**2.7**), $Mes_2PHC_6F_4BCl(C_6F_5)_2$ (**2.8**), $^tBu_2PHC_4H_8OB(C_6F_5)_3$ (**2.9**), $Mes_2PHC_4H_8OB(C_6F_5)_3$ (**2.10**), $^tBu_2PC_6F_4B(C_6F_5)_2$ (**2.11**), ^{t}BuMesPC$_6$F$_4$B(C$_6$F$_5$)$_2$ (**2.12**), $Mes_2PC_6F_4B(C_6F_5)_2$ (**2.13**), $[Mes_2PHC_6F_4B(C_6F_5)_2][B(C_6F_5)_4]$ (**2.14**) and $Cy_3PC_6F_4BF(C_6F_5)_2$ (**2.15**) were prepared as reported.[108,109,111,114]

2.2.3.1 Small Scale Preparation and Characterization of Ion-pairs

[CpTiMe(NP^{t}Bu$_3$)][B(C$_6$F$_5$)$_4$] + Ph$_3$CCH$_3$ (2.16): To an orange solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.055 g, 0.059 mmol) in C$_6$D$_5$Br (0.4 mL) was added dropwise a solution of CpTiMe$_2$(NP^{t}Bu$_3$) (0.021 g, 0.058 mmol) in C$_6$D$_5$Br (0.3 mL). The solution was allowed to stir for 5 minutes. Quantitative product formation was observed by NMR. **^{1}H NMR** (C$_6$D$_5$Br, 300 MHz, 300 K): δ 7.18 -7.09 (m, 15 H, *Ph*CCH$_3$), 6.09 (s, 5H, Cp), 2.07 (s, 3H, PhCC*H$_3$*), 1.18 (d, $^3J_{HP}$ = 14 Hz, 30 H, ^{t}Bu, Ti*Me*). **^{11}B NMR** (C$_6$D$_5$Br, 96 MHz, 300 K): δ -16.7 (s). **^{13}C NMR** (C$_6$D$_5$Br, 75 Hz, 300 K): δ 149.0 (s, quaternary, Ph), 148.6 (d, $^1J_{C\text{-}F}$ = 236 Hz, *C*F), 138.4 (d, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 136.5 (d, $^1J_{C\text{-}F}$ = 242 Hz, *C*F), 128.8 (s, CH, Ph), 127.96 (s, CH, Ph), 136.0 (s, CH, Ph), 116.10 (s, Cp), 61.2 (s, Ti*Me*), 52.5 (s, quaternary, Ph$_3$*C*CH$_3$), 41.1 (d, $^1J_{C\text{-}p}$ = 41 Hz, quaternary, ^{t}Bu$_3$), 30.5 (s, Ph$_3$C*C*H$_3$), 28.9 (s, ^{t}Bu$_3$) **^{19}F NMR** (C$_6$D$_5$Br, 282 MHz, 300 K): δ -132.29 (s, 8F, *ortho*-C$_6$*F$_5$*), -162.67 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C$_6$*F$_5$*), -166.47 (t, 8F, $^3J_{F\text{-}F}$ = 17 Hz, *meta*-C$_6$*F$_5$*). **^{31}P {^{1}H} NMR** (C$_6$D$_5$Br, 121 MHz, 300 K): δ 55.8 (s)

[CpTiMe(NP^{t}Bu$_3$)][^{t}Bu$_2$P(C$_6$F$_4$)BMe(C$_6$F$_5$)$_2$] (2.17): To a yellow solution of ^{t}Bu$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (0.080 g, 0.125 mmol) in hexanes (3 mL) was added dropwise a faint yellow solution of CpTiMe$_2$(NP^{t}Bu$_3$) (0.050 g, 0.125 mmol) in hexanes (5 mL) at room temperature. Immediate precipitation of a yellow solid was observed. The mixture was stirred for 5 minutes followed by removal of all volatiles *in vacuo* to give the product as a brown solid. Yield 115 mg (92%). **^{1}H NMR** (C$_6$D$_5$Br, 300 MHz, 300 K): δ 6.12 (s, 5H, Cp), 1.23 (d, 18H, $^3J_{HP}$ = 13 Hz, ^{t}Bu$_2$P), 1.12 (s, 3H, B*Me*), 1.12 (d, 27H, $^3J_{HP}$ = 14

Hz, ^{t}Bu$_3$PN), 0.85 (s, 3H, Ti*Me*). **^{11}B NMR** (C_6D_5Br, 96 MHz, 300 K): δ -14.4 (br s). **^{13}C {^{1}H} NMR** (C_6D_5Br, 75 MHz, 300 K): δ 148.7 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 138.4 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 137.6 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 114.1 (s, Cp), 53.0 (s, Ti*Me*), 41.1 (d, $^1J_{CP}$ = 42 Hz, ^{t}Bu$_3$P), 32.6 (d, $^1J_{CP}$ = 27 Hz, ^{t}Bu$_2$P), 30.4 (d, $^2J_{CP}$ = 14 Hz, ^{t}Bu$_2$P), 29.1 (s, ^{t}Bu$_3$P), 11.2 (s, B*Me*). **^{19}F NMR** (C_6D_5Br, 282 MHz, 300 K): δ -124.58 (br, 1F, C_6F_4), -131.09 (br, 1F, C_6F_4), -132.38 (br, 4F, *ortho*-C_6F_5), -132.76 (br, 2F, C_6F_4), -160.99 (br, 2F, *para*-C_6F_5), -166.06 (br, 4F, *meta*-C_6F_5). **^{19}F NMR** (C_6D_5Br, 282 MHz, 243 K): δ -123.66 (s, 1F, C_6F_4), -132.20 (m, 4F, *ortho*-C_6F_5), -132.60 (m, 1F, C_6F_4), -133.13 (m, 1F, C_6F_4), -133.56 (m, 1F, C_6F_4), -160.76 (br, 2F, *para*-C_6F_5), -164.26 (m, 4F, *meta*-C_6F_5). **^{31}P {^{1}H} NMR** (C_6D_5Br, 121 MHz, 300 K): δ 50.8 (P^{t}Bu$_3$), 21.23 (br d, $^3J_{PF}$ = 90 Hz, P^{t}Bu$_2$). **^{31}P {^{1}H} NMR** (C_6D_5Br, 121 MHz, 243 K): δ 50.1 (P^{t}Bu$_3$), 17.60 (d, $^3J_{PF}$ = 95 Hz, P^{t}Bu$_2$).

[CpTiMe(NP^{t}Bu$_3$)][Mes$_2$P(C$_6$F$_4$)BMe(C$_6$F$_5$)$_2$] (2.18): To an orange solution of Mes$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (0.100 g, 0.131 mmol) in hexanes (3 mL) was added dropwise a faint yellow solution of CpTiMe$_2$(NP^{t}Bu$_3$) (0.047 g, 0.131 mmol) in hexanes (5 mL) at room temperature. Immediate precipitation of a yellow solid was observed. The mixture was stirred for 5 minutes and filtered. The resultant yellow-brown solid was dried under vacuum for 12 hours. Yield 115 mg (78%). **^{1}H NMR** (C_6D_5Br, 300 MHz, 300 K): δ 6.71 (s, 4H, P(C$_6$*H*$_2$)$_2$), 6.12 (s, 5H, Cp), 2.32 (s, 12H, P(C$_6$H$_2$*Me-2,6*)$_2$), 2.16 (s, 6H, P(C$_6$H$_2$*Me-4*)$_2$), 1.18 (s, 3H, B*Me*), 1.14 (br s, 27H, ^{t}Bu), 0.85 (s, 3H, Ti*Me*). **^{11}B NMR** (C_6D_5Br, 96 MHz, 300 K): δ -14.5 (br s). **^{13}C {^{1}H} NMR** (C_6D_5Br, 75 MHz, 300 K): partial δ 148.5 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 147.1 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 142.6 (d, $^2J_{C\text{-}P}$ =

12 Hz, quaternary, Mes), 138.0 (s, quaternary, Mes), 137.7 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 136.6 (dm, $^{1}J_{C\text{-}F}$ = 240 Hz, *C*F), 130.1 (s, CH Mes), 114.1 (s, Cp), 52.80 (br s, Ti*Me*), 41.2 (br, ^{t}Bu), 28.7 (br, ^{t}Bu), 22.6 (d, $^{3}J_{C\text{-}P}$ = 18 Hz, C_6H_2*Me-2,6*), 20.9 (s, C_6H_2*Me-4*), 10.5 (br s, B*Me*). **^{19}F NMR** (C_6D_5Br, 282 MHz, 300 K): δ -132.24 (br, 6F, *ortho*-C_6F_5, C_6F_4), -135.37 (br, 2F, C_6F_4), -164.08 (br, 2F, *para*-C_6F_5), -166.47 (br, 4F, *meta*-C_6F_5). **^{19}F NMR** (C_6D_5Br, 282 MHz, 243 K): δ -132.57 (m, 5F, *ortho*-C_6F_5, C_6F_4), -133.52 (s, 1F, C_6F_4), -133.73 (s, 1F, C_6F_4), -136.10 (s, 1F, C_6F_4), -164.06 (m, 2F, *para*-C_6F_5), -166.66 (m, 4F, *meta*-C_6F_5). **^{31}P {^{1}H} NMR** (C_6D_5Br, 121 MHz, 300 K): δ 50.6 (br, P^{t}Bu$_3$), -50.2 (br, $PMes_2$). **^{31}P {^{1}H} NMR** (C_6D_5Br, 121 MHz, 243 K): δ 49.0 (br, P^{t}Bu$_3$), -51.9 (t, $^{3}J_{PF}$ = 37 Hz, $PMes_2$).

[(THF)CpTiMe(NP^{t}Bu$_3$)][^{t}Bu$_2$P(C_6F_4)BMe(C_6F_5)$_2$] (2.19): The compound [CpTiMe(NP^{t}Bu$_3$)][^{t}Bu$_2$P(C_6F_4)BMe(C_6F_5)$_2$] (0.050 g, 0.05 mmol) was dissolved in THF (5 mL) at room temperature. The solution was stirred for 5 minutes followed by removal of all volatiles *in vacuo* to give the product as a brown-green solid. Yield 52 mg (97%). **^{1}H NMR** (C_6D_5Br, 300 MHz, 300 K): δ 6.09 (s, 5H, Cp), 3.64 (br s, 4H, THF), 1.63 (br s, 4H, THF),v1.23 (d, 18H, $^{3}J_{HP}$ = 12 Hz, ^{t}Bu$_2$P), 1.21 (s, 3H, B*Me*), 1.15 (d, 27H, $^{3}J_{HP}$ = 14 Hz, ^{t}Bu$_3$P), 0.93 (s, 3H, Ti*Me*). **^{11}B NMR** (C_6D_5Br, 96 MHz, 300 K): δ -14.9 (br s). **^{13}C {^{1}H} NMR** (C_6D_5Br, 75 MHz, 300 K): δ 149.1 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 137.5 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *C*F), 137.6 (dm, $^{1}J_{C\text{-}F}$ = 250 Hz, *C*F), 113.2 (s, Cp), 68.40 (s, THF), 52.2 (s, Ti*Me*), 41.1 (d, $^{1}J_{CP}$ = 44 Hz, ^{t}Bu$_3$P), 32.5 (d, $^{1}J_{CP}$ = 28 Hz, ^{t}Bu$_2$P), 29.3 (d, $^{2}J_{CP}$ = 16 Hz, ^{t}Bu$_2$P), 29.0 (s, ^{t}Bu$_3$PN), 10.8 (s, B*Me*). **^{19}F NMR** (C_6D_5Br, 282 MHz, 300 K): δ -124.97 (m, 1F, C_6F_4), -131.89 (m, 1F, C_6F_4), -132.03 (d, 4F, $^{3}J_{FF}$ = 22 Hz, *ortho*-C_6F_5), -

132.22 (s, 1F, C_6F_4), -132.43 (dd, 1F, $^3J_{FP}$ = 113 Hz, $^3J_{FF}$ = 23 Hz, C_6F_4), -160.99 (t, 2F, $^3J_{FF}$ = 23 Hz, *para*-C_6F_5), -166.06 (t, 4F, $^3J_{FF}$ = 24 Hz, *meta*-C_6F_5). **^{31}P {^{1}H} NMR** (C_6D_5Br, 121 MHz, 300 K): δ 50.8 (P^tBu_3), 19.6 (dd, $^3J_{PF}$ = 120 Hz, $^3J_{PF}$ = 20 Hz P^tBu_2).

[(THF)CpTiMe(NP^{t}Bu$_3$)][Mes$_2$PC$_6$F$_4$BMe(C$_6$F$_5$)$_2$] (2.20): To an orange solution of $Mes_2P(C_6F_4)B(C_6F_5)_2$ (0.100 g, 0.131 mmol) in hexanes (3 mL) was added dropwise a faint yellow solution of $CpTiMe_2(NP^tBu_3)$ (0.047 g, 0.131 mmol) in hexanes (5 mL) at room temperature. Immediate precipitation of a yellow solid was observed. The mixture was stirred for 30 minutes followed by addition of THF (1 mL). The resulting yellow-orange solution was stirred at room temperature for 12 hours at which time all volatiles were removed *in vacuo* to give the product as a yellow solid. Yield 140 mg (89%). **^{1}H NMR** (C_6D_5Br, 300 MHz, 300 K): δ 6.69 (s, 4H, $P(C_6H_2)_2$), 6.09 (s, 5H, Cp), 3.61 (br s, 4H, THF), 2.25 (s, 12H, $P(C_6H_2Me\text{-}2,6)_2$), 2.16 (s, 6H, $P(C_6H_2Me\text{-}4)_2$), 1.59 (br s, 4H, THF), 1.22 (s, B*Me*), 1.11 (d, $^3J_{HP}$ = 14 Hz, ^{t}Bu), 0.88 (s, Ti*Me*). **^{11}B NMR** (C_6D_5Br, 96 MHz, 300 K): δ -14.9 (br s). **^{13}C {^{1}H} NMR** (C_6D_5Br, 75 MHz, 300 K): δ 149.2 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 148.8 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *C*F), 147.2 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 142.7 (d, $^2J_{C\text{-}P}$ = 16 Hz, quaternary, Mes), 137.9 (s, quaternary, Mes), 137.3 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F), 136.6 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *C*F), 130.2 (s, CH Mes), 114.1 (s, Cp), 112.8 (d, $^1J_{C\text{-}P}$ = 70 Hz, quaternary, Mes), 76.1 (br s, THF), 52.1 (s, Ti*Me*), 40.9 (d, $^1J_{CP}$ = 41 Hz, ^{t}Bu), 28.9 (s, ^{t}Bu), 22.8 (s, THF), 22.7 (d, $^3J_{C\text{-}P}$ = 16 Hz, $C_6H_2Me\text{-}2,6$), 21.0 (s, $C_6H_2Me\text{-}4$), 10.8 (br s, B*Me*). **^{19}F NMR** (C_6D_5Br, 282 MHz, 300 K): δ -131.31 (d, $^3J_{F\text{-}F}$ = 24 Hz, 4F, *ortho*-C_6F_5), -131.60 (m, 2F, C_6F_4), -134.86 (m, 2F, C_6F_4), -163.62 (m, 2F, *para*-C_6F_5), -

166.15 (m, 4F, *meta*-C_6F_5). **$^{31}P\{^1H\}$ NMR** (C_6D_5Br, 121 MHz, 300 K): δ 51.1 (P^tBu_3), -50.0 (t, $^3J_{PF}$ = 37 Hz, $PMes_2$).

2.2.4 Polymerization Protocol

There are numerous factors that may affect polymerization results obtained using the Buchi reactor system. To ensure results obtained were comparable routine standards were run to evaluate reproducibility of the system. These polymerization results and analysis are outlined in Appendix A.

2.2.4.1 Description of Polymerization Reactor Set-up

Polymerizations were performed in a 1 L Buchi reactor system. Following assembly, the reactor vessel and solvent storage unit were refilled with nitrogen via 4 refill/evacuation cycles over at least 90 minutes. Approximately 600 mL of toluene was transferred to the solvent storage container from the purification column. The solvent was then purged with dry nitrogen for 20 minutes and transferred to the reactor vessel by differential pressure. In the reactor vessel, the solvent was stirred at 1500 ± 5 RPM and the temperature was kept constant at 30 ± 2 °C. Ethylene was introduced into the reactor vessel via five vent/refill cycles.

2.2.4.2 Description of Catalyst and Co-catalyst Preparation

The pre-catalyst, co-catalyst and scrubber stock solutions were freshly prepared and loaded into syringes in a glovebox and then transferred to the reactor immediately before injection to limit the possibility of catalyst decomposition. As an example, a

polymerization experiment using $CpTiMe_2(NP^tBu_3)$ as the catalyst, $B(C_6F_5)_3$ as the co-catalyst, and T*i*BAl as the scrubber will be used to describe the preparation of the stock solutions.

Catalyst Solution: $CpTiMe_2(NP^tBu_3)$ (0.013 g, 0.036 mmol) was weighed into a vial. Toluene (10.380 g, 12.0 mL) was added, forming a clear, light yellow solution. 1.0 mL (0.003 mmol $CpTiMe_2(NP^tBu_3)$) of the solution was transferred to a syringe for injection into the reactor.

Co-Catalyst Solution: $B(C_6F_5)_3$ (0.012 g, 0.024 mmol) was weighed into a vial. Toluene (10.380 g, 12.0 mL) was added, forming a clear, colourless solution. 1.5 mL (0.003 mmol $B(C_6F_5)_3$, 1 equivalent) of the solution was transferred to a syringe for injection into the reactor.

Scrubber Solution: 0.4 mL of a 25.2 weight % solution of T*i*BAl in heptanes (0.36 mmol Al*i*-Bu_3) was added to toluene (15.260 g, 17.64 mL) producing a clear, colourless solution. 3.0 mL (0.06 mmol, 20 equivalents) of the solution was transferred to a syringe for injection into the reactor.

2.2.4.3 Description of Polymerization Experiments

Note: The injection sequence is the same for all polymerizations, unless otherwise specified. The prepared solution of T*i*BAl (3.0 mL) was injected into the reaction vessel through the catalyst injection inlet and allowed to stir for 5 min. The prepared $CpTiMe_2(NP^tBu_3)$ solution (1.0 mL) was then injected into the reaction vessel followed immediately by injection of the $B(C_6F_5)_3$ solution (1.5 mL). The mixture was stirred at 1500 ± 5 RPM at 30 °C under 2 atm of dynamic ethylene flow for 10 minutes.

Temperature and ethylene flow rate were recorded manually at regular intervals. After 10 minutes, polymerization was stopped by closing the ethylene inlet valve and venting the reactor. Stirring was stopped, and the reactor disassembled.

2.2.4.4 Description of Polymer Recovery and Work-up

The contents of the reactor were emptied into a 4 L beaker that contained approximately 100 mL of 10% HCl (v/v) in MeOH. The polymer that precipitated was then collected by filtration, washed with toluene and acetone, and dried overnight. Resulting polymer was weighed and polymerization activity calculated according to Equation 2.1:

Equation 2.1: Polymerization Activity

$$Activity\ (g\ mmol^{-1}\ hr^{-1}\ atm^{-1}) = \frac{mass\ of\ polymer\ (g)}{amount\ of\ catalyst\ (mmol)\ x\ time\ (hr)\ x\ pressure\ of\ ethylene\ (atm)}$$

Each polymerization was carried out in duplicate to ensure reproducibility. The average polymerization of these two trials was reported and the percent difference of the trials calculated according to Equation 2.2:

Equation 2.2 Percent Difference

$$\%\ Difference = \frac{|activity\ trial\ \#1 - activity\ trial\ \#2|\ (g)}{average\ activity\ (g)}\ x\ 100$$

2.3 Results and Discussion

2.3.1 Polymerizations of Ethylene using Phosphonium-Borate Co-catalysts

Ammonium cations (R_3NH) have been found to readily cleave metal-alkyl bonds via protonolysis.[47,48,115] Due to this reactivity, ion-pairs of the type $[HNRR'_2][B(C_6F_5)_4]$ (R= alkyl and aryl) have proven to be effective co-catalysts for olefin polymerization.[47] Investigations of the perfluoroaryl phosphonium-borates derived from "frustrated" Lewis pair chemistry have demonstrated that the phosphonium cation can be readily deprotonated to give anionic phosphino-borates.[109] These results prompted the examination of the utility of perfluoroaryl and alkoxy linked phosphonium-borates as protic activators for olefin polymerization. In parallel with these studies, a series of standard unlinked phosphonium-borates were tested for polymerization activity. The range of compounds evaluated are illustrated in Figure 2.3

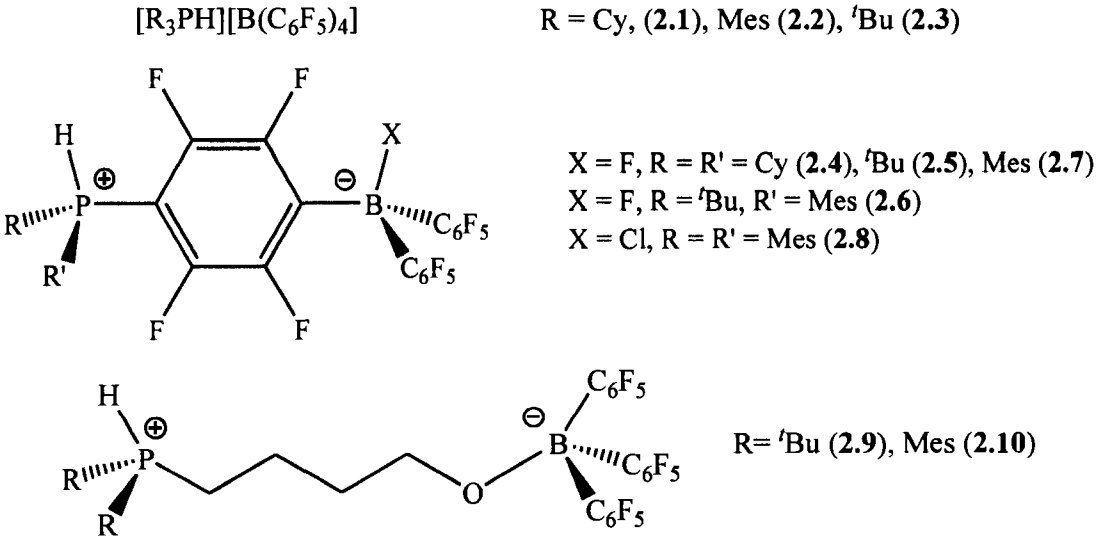


Figure 2.3 Phosphonium-Borate Compounds Tested

The polymerization activity and the mechanistic evaluation of the catalyst systems employing the co-catalyst listed in Figure 2.3 will be discussed in three classes: 1) unlinked, 2) perfluoroaryl-linked and 3) alkoxy-linked phosphonium-borates.

2.3.1.1 Unlinked Phosphonium-Borates as Activators

It is proposed that **2.1 – 2.3** would activate the Ti pre-catalyst through a protonation mechanism. Cleavage of one of the Ti-Me bonds by the phosphonium of $[R_3PH][B(C_6F_5)_4]$ releases methane, free phosphine (R_3P) and yields the desired ion-pair, as illustrated in Figure 2.4. Here a 3-coordinate cationic Ti center is countered by the weakly coordinating anion, $[B(C_6F_5)_4]^-$. This polymerization process is initiated by olefin coordination to Ti followed by migratory insertion into the adjacent Ti-Me bond. It is believed that employing sterically bulky phosphonium cations, resulting free phosphine generated after protonation of the Me group will be too large to coordinate to Ti and inhibit the reaction.[116]

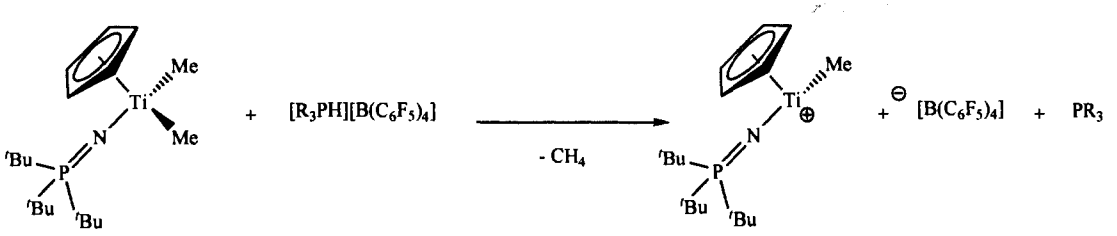


Figure 2.4 Activation of $CpTiMe_2(NP^tBu_3)$ with Unlinked Phosphonium-Borates

Compounds **2.4 – 2.8** were tested as for their ability to act as co-catalysts for ethylene polymerization and the results are documented in Table 2.1. In evaluating the effectiveness of the phosphonium-borates as activators for ethylene polymerization, the

activities were compared to polymerizations using $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ and $[Me_2PhNH][B(C_6F_5)_4]$.

Table 2.1 Polymerization Results for Unlinked Phosphonium-Borates

Co-catalyst	Activity[b]	Activity[b]	Average Activity[b]	% Difference
$B(C_6F_5)_3$	8215	9331	8773	13
$[Ph_3C][B(C_6F_5)_4]$	7670	7252	7461	6
$[Me_2PhNH][B(C_6F_5)_4]$	2831	3231	3031	13
$[Cy_3PH][B(C_6F_5)_4]$ **(2.1)**	7641	5584	6613	31
$[Mes_3PH][B(C_6F_5)_4]$ **(2.2)**	6225	5799	6012	7
$[^tBu_3PH][B(C_6F_5)_4]$ **(2.3)**	350	310	330	12

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (5 μmol/L), 1 equiv. co-catalyst, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}

From the results in Table 2.1, it is clear that all of the noted unlinked phosphonium borates are effective co-catalysts that produce active catalyst systems in combination with $CpTiMe_2(NP^tBu_3)$. The relative activities using **2.1** and **2.2** are comparable to catalyst derived from $CpTiMe_2(NP^tBu_3)$ and $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$. The relative activities of **2.1** and **2.2** are higher than those derived using $[Me_2PhNH][B(C_6F_5)_4]$. This increased activity may be the result of free amine coordination to the Ti metal center.[117,118] Catalyst systems formed using co-catalyst **2.3**, however, were found to have much lower activities. The ion-pairs generated from the use of **2.1 – 2.3** should be analogous to the ion-pair generated using $[Ph_3C][B(C_6F_5)_4]$; a mono-methyl Ti cation and a $B(C_6F_5)_4$ anion. The similar activities observed with **2.1** and **2.2** suggest that the active species is consistent with the species generated employing $[Ph_3C][B(C_6F_5)_4]$, indicating that the free phosphine does not coordinate to the cationic metal center and inhibit polymerization.

Clearly, steric bulk at the P center prevents any coordination to the Ti cation. Previous and ongoing work in the Stephan Group has demonstrated that sterically bulky phosphines do not interact with Lewis acids in a traditional donor-acceptor fashion.[107,116,119,120] Considering P^tBu_3 has similar steric bulk to both PCy_3 and $PMes_3$ (Table 2.2), it was surprising that utilization of **2.3** produced a relatively less active catalyst system. These results suggest that acidity is a factor in the ability of the phosphonium to protonate the Me group and generate the active catalyst species.

Table 2.2 Cone Angles and pKa values of Cy_3P, $^tBu_3P$ and Mes_3P

Phosphine	**Cone Angle**[121]	**pKa**[122]
PCy_3	170°	9.7
P^tBu_3	182°	11.4
$PMes_3$	212°	N/A
$(P(o\text{-tolyl})_3)^a$	$(194°)^a$	$(3.1)^a$

[a] Cone Angles and pKa for $P(o\text{-tolyl})_3$ is given to use for comparison since the pKa of $PMes_3$ will be similar.

To further investigate the activation mechanism, stoichiometric reactions were carried out and monitored via multi-nuclear NMR spectroscopy. To a stirring solution of **2.1** or **2.2** in C_6D_5Br, 1 equivalent of $CpTiMe_2(NPtBu_3)$ in C_6D_5Br was added resulting in immediate evolution of gas. The ^{31}P and ^1H NMR spectroscopy showed complete deprotonation of the phosphine and generation of the expected catalytically active species, $[CpTiMe(NP^tBu_3)][B(C_6F_5)_4]$ (**2.16**). Resonances attributed to free phosphine (11.1 and 35.5 ppm for PCy_3 and $PMes_3$, respectively) and the base free cation $[CpTiMe(NP^tBu_3)]^+$ (55.9 ppm) was observed in the ^{31}P NMR spectra of both reactions

confirming that these bulky phosphines are too large to coordinate to the present cationic Ti centers.

A third experiment was carried out between **2.3** and $CpTiMe_2(NPtBu_3)$ in C_6D_5Br in a similar fashion to those described above. The ^{31}P NMR spectrum showed resonances at 62.1 ppm and 60.0 ppm in an approximate 1:1 ratio, attributed to both P^tBu_3 and HP^tBu_2, respectively, thus indicating only partial deprotonation of the phosphine. Additionally, only one resonance in the ^{31}P NMR spectra was observed from the ligand $^tBu_3PN$. The incomplete activation of the pre-catalyst species results in formation of the Me-bridged dimer, $[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-}Me)][B(C_6F_5)_4]$, which has been previously reported.[123] This dimer is presumed to be a poor olefin polymerization catalyst due to the inaccessibility of the cationic Ti center, thus explaining low activity observed in the present case.

These results show that the both the sterics and electronics of the phosphines play a vital role in the ability of the phosphonium-borates to generate a catalytically active titanium center. Not only must the phosphonium be sterically bulky in order to prevent the corresponding phosphine from coordinating to Ti, but the PH moiety must be sufficiently acidic to fully protonate one of the Ti-Me bonds.

2.3.1.2 Perfluoroaryl Linked Phosphonium-Borates as Activators

Compounds **2.4 – 2.8** contain both a PH moiety and an anionic borate fragment and thus should be active co-catalysts similar to those noted in section 2.3.1.1. A possible reaction pathway for the generation of active catalyst systems is shown in Figure 2.5. Protonation of one of the Ti-Me groups releases methane and yields the desired ion-pair consisting of the cationic titanium center and the anionic phosphino-borate.

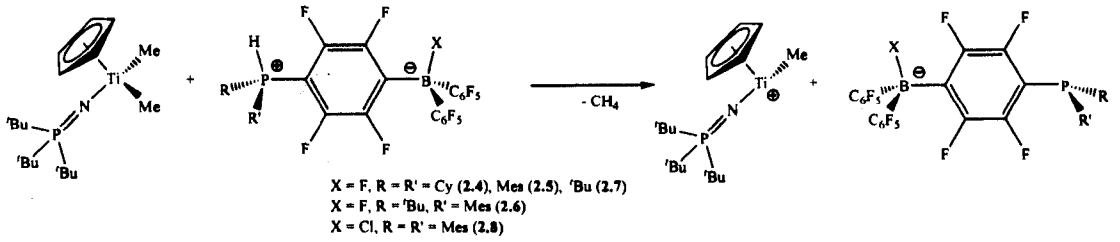


Figure 2.5 Activation of $CpTiMe_2(NP^tBu_3)$ with Perfluoroaryl Linked Phosphonium-Borates

Compounds **2.4 – 2.8** were tested for their ability to act as co-catalysts for ethylene polymerization. The polymerizations were conducted in duplicate, and the results of this testing are shown in Table 2.3.

Table 2.3 Polymerization Results for the Perfluoroaryl Phosphonium-Borates

Co-catalyst	Activity[b]	Activity[b]	Average Activity[b]	% Difference
$B(C_6F_5)_3$	8215	9331	8773	13
$[Ph_3C][B(C_6F_5)_4]$	7670	7252	7461	6
$Cy_2PHC_6F_4BF(C_6F_5)_2$ **(2.4)**	4762	4255	4507	11
$Mes_2PHC_6F_4BF(C_6F_5)_2$ **(2.5)**	10363	12801	11582	21
$^tBuMesPHC_6F_4BF(C_6F_5)_2$ **(2.6)**	4876	5174	5025	6
$^tBu_2PHC_6F_4BF(C_6F_5)_2$ **(2.7)**	3468	2324	2896	40
$Mes_2PHC_6F_4BCl(C_6F_5)_2$ **(2.8)**	649	496	573	27

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (5 μmol/L), 1 equiv. co-catalyst, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}

The catalyst systems derived from the phosphonium-fluoroborates (**2.4 – 2.6**) showed activities comparable to $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$. Consistent with the results from the unlinked systems, the activity of polymerizations with **2.7** exhibited a lower activity

than polymerizations using **2.4** and **2.5** as activators. Additionally, the activity determined when **2.6** was employed was found to be less than with **2.5** but higher than with **2.7**. Overall the trend seems to follow that as the acidity of the PH moiety increases, so does the activity of the catalyst systems. This indicates that protonation of one of the Ti-Me bonds and generation of active Ti species, is the most important factor in generating active catalyst systems.

To further investigate activation of $CpTiMe_2(NPtBu_3)$ with the phosphonium-fluoroborates, stoichiometric small scale reactions were carried out and monitored by multi-nuclear NMR spectroscopy. Initial studies using **2.5** showed incomplete deprotonation of the phosphorus, but also cleavage of the B-F and indicated the formation of a B-Me species. Complete identification of the products was not possible due to multiple product formation. To investigate the B-F cleavage and potential products a series of reactions of $Cy_3PC_6F_4BF(C_6F_5)_2$ (**2.15**) with $CpTiMe_2(NP^tBu_3)$ and $[CpTiMe(NP^tBu_3)][B(C_6F_5)_4]$ (**2.16**) were performed. Mixing of **2.15** with $CpTiMe_2(NP^tBu_3)$ resulted in no reaction, as expected. This indicates that B-F cleavage and fluoride for methyl exchange at boron occur only after the formation of the cationic Ti center. Confirming this, NMR studies of the reaction of **2.15** with $[CpTiMe(NP^tBu_3)][B(C_6F_5)_4]$ show immediate B-F cleavage and B-Me formation. Further attempts to isolate and determine the products of this reaction were unsuccessful.

Recently, Marks and coworkers[124,125] have reported the use of $[Ph_3C][FM(C_6F_5)_3]$, where M = B and Al, as co-catalysts for olefin polymerization. Stoichiometric studies of these activators and the Zr pre-catalyst, $Me_2C(Cp)(Flu)ZrMe_2$ indicated B-F cleavage and the formation of B-Me. In these studies no products were isolated and a bridging Zr-F-Zr was proposed.

Since the activities of the polymerizations using **2.4** – **2.6** are comparable to those using $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ it is reasonable to suggest that the B-F cleavage is slower than ethylene coordination and insertion. However, the chloro-derivative **2.8** is a poor co-catalyst, which is due to more rapid Cl transfer to the Ti-center.

These results demonstrate that the compounds derived from *para*-nucleophilic aromatic substitution of $B(C_6F_5)_3$ by sterically demanding phosphines are active co-catalysts for the polymerization of ethylene with the pre-catalyst $CpTiMe_2(NP^tBu_3)$. Although catalytically active, investigations of the nature of the active species in the absence of the olefinic substrate are difficult due to B-F and B-Cl cleavage and transfer of the halide to the Ti cation.

2.3.1.3 Alkoxy Linked Phosphonium-Borates as Activators

As in unlinked and perfluoroaryl linked phosphonium-borates, **2.9** and **2.10** are also believed to activate the Ti pre-catalyst through cleavage of one of the Ti-Me groups via protonolysis, releasing methane and yielding the desired ion-pair consisting of the cationic titanium center and the anionic phosphino-borate, illustrated in Figure 2.6.

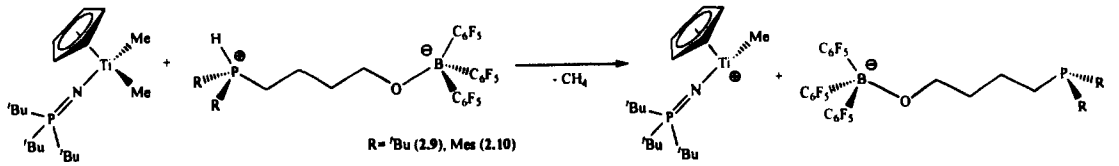


Figure 2.6 Activation of $CpTiMe_2(NP^tBu_3)$ with Alkoxy Linked Phosphonium-Borates

Compounds **2.9** and **2.10** were tested for their ability to act as co-catalysts for ethylene polymerization. The polymerizations were conducted in duplicate, and the results are shown in Table 2.4. In evaluating the effectiveness of the phosphonium-borates as activators for olefin polymerization the activities were compared to polymerizations using $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$.

Table 2.4 Polymerization Results for Alkoxy-Linked Phosphonium-Borates

Co-catalyst	**Activity[b]**	**Activity[b]**	**Average Activity[b]**	**% Difference**
$B(C_6F_5)_3$	8215	9331	8773	13
$[Ph_3C][B(C_6F_5)_4]$	7670	7252	7461	6
$^tBu_2PHC_4H_8OB(C_6F_5)_3$ **(2.9)**	90	105	98	15
$Mes_2PHC_4H_8OB(C_6F_5)_3$ **(2.10)**	13482	15579	14534	14

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (5 μmol/L), 1 equiv. co-catalyst, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}

Consistent with previous experimental results **2.10** was found to be an effective activator for the olefin polymerization using $CpTiMe_2(NP^tBu_3)$, with activities comparable to using $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$. Similarly, the compound **2.9** was found to be a poor activator, due to a reduced acidity of the PH moiety which inhibits the ability of the compound to protonate a Ti-Me bond.

It has been demonstrated that the adducts of $B(C_6F_5)_3$ with H_2O or alcohols (ROH) are strong Bronsted acids that are capable of cleaving metal-alkyl bonds of Cp_2ZrMe and give rise to catalytic species of the form, $[Cp_2ZrMe][ROB(C_6F_5)]$, which are active for olefin polymerization[126-128]. Further studies by Baird and coworkers suggested the ligand exchange and formation of Zr-OR species.[129]

Although **2.10** was found to be an effective activator, it is proposed that at industrially relevant conditions, cleavage of the B-OR bond and ligand exchange to form the less active Ti-OR species would also occur. This destroys the active catalyst, and therefore would not be an appropriate choice as an activator at elevated temperatures.

2.3.2 Phosphino-Boranes as Activators

The phosphino-boranes derived from "frustrated" Lewis pair chemistry present a unique family of potential activators that have a Lewis basic phosphine as part of the activating species. As seen in the studies of the phosphonium-borates and, as demonstrated in other studies in the Stephan Group, no coordination of sterically demanding phosphines to the Ti center of the catalyst species is observed. This prompted the investigation the bifunctional phosphino-boranes as co-catalysts. The phosphino-boranes investigated are shown in Figure 2.7. It is proposed that activation of the Ti pre-catalyst would proceed in a similar manner as the activation using $B(C_6F_5)_3$, through methyl-abstraction to form the methyl borate anion, as illustrated below.

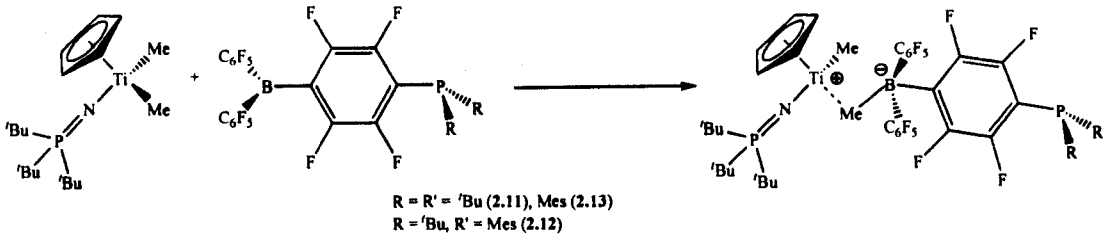


Figure 2.7 Activation of $CpTiMe_2(NP^tBu_3)$ with Phosphino-Boranes

Compounds **2.11** – **2.13** were tested as for their ability to act as co-catalysts for ethylene polymerization. The polymerizations results are shown in Table 2.5. In evaluating the effectiveness of the series of phosphino-boranes for olefin polymerization

the activities were compared to polymerizations using $B(C_6F_5)_3$. Contrary to the results obtained using protic activators, the trend observed was the more basic the pendant phosphine the better the activator.

Table 2.5 Polymerization Results for Phosphino-Boranes[a]

Co-catalyst	1 Activity[b]	2 Activity[b]	Average Activity[b]	% Difference
$B(C_6F_5)_3$	8215	9331	8773	13
$^tBu_2PC_6F_4B(C_6F_5)_2$ **(2.11)**	18589	17286	17938	7
$^tBuMesPC_6F_4B(C_6F_5)_2$ **(2.12)**	9448	8934	9191	6
$Mes_2PC_6F_4B(C_6F_5)_2$ **(2.13)**	4070	5516	4793	30

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (5 μmol/L), 1 equiv. co-catalyst, 20 equiv. *T*iBAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}

Assuming the activation pathway depicted in Figure 2.7 the observation that **2.13** is less active then $B(C_6F_5)_3$ is consistent with the relatively lower Lewis acidity at B determined experimentally.[108] The reduced Lewis acidity at B renders the compound to be a weaker methyl abstractor, and consequently yields a less active metal center. Surprisingly, these results show that the **2.11** is significantly more active than $B(C_6F_5)_3$, despite the reduced Lewis acidity at B compared to $B(C_6F_5)_3$. This is contrary to the belief that the more Lewis acidic the B site typically results in a better the activator[24,36]. A possible explanation for the almost doubled activity could be a transient interaction of the phosphine moiety with the Ti cation. One could envision a weak Ti-P contact displacing the Me-B and thereby allowing for a more open coordination site for the olefin as depicted in Figure 2.8.

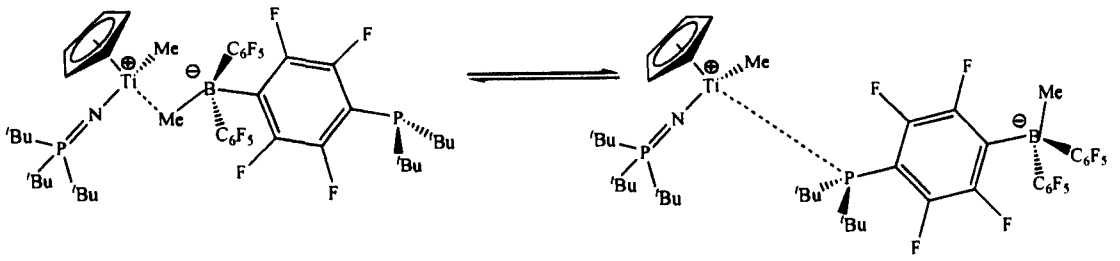


Figure 2.8 Phosphine Interaction with $[CpMeTi(NP^tBu_3)]^+$

This model for the activation and increased activity would be consistent with the trend of increasing basicity of the P center resulting in an increase in activity. To probe this interaction, stoiciometric reactions of $CpTiMe_2(NP^tBu_3)$ and **2.11** and **2.13** were conducted.

The reaction of $CpTiMe_2(NP^tBu_3)$ and $B(C_6F_5)_3$ has been previously described[82,123]. For the resulting compound, $[CpTiMe(NP^tBu_3)][MeB(C_6F_5)_3]$, the ^{1}H-NMR spectra shows only one Me peak for the Ti-Me and B-Me groups. This data is consistent with the rapid exchange of the Ti and B bound Me groups which is not slowed even on cooling to -80 °C. In contrast, the ^{1}H-NMR spectra of $[CpTiMe(NP^tBu_3)][^tBu_2P(C_6F_4)BMe(C_6F_5)_2]$ (**2.17**) shows two distinct Me signals at 1.22 and 0.88 ppm, corresponding to the B-Me and Ti-Me groups, respectively. The assignment of these resonances was confirmed by ^{1}H-^{13}C HSQC experiments that correlated the ^{1}H NMR signals of the B-Me and Ti-Me groups to ^{13}C NMR resonances at 10.7 and 50.4, respectively. An ^{1}H-^{1}H EXSY experiment showed these Me groups were not be in exchange. The ^{31}P NMR spectrum of **2.17** showed a slight broadening of the signal attributed to the co-catalyst species (broad doublet at 21.2 ppm). Upon addition of an excess of the Lewis base THF to the reaction mixture, **2.19** was formed. The ^{31}P NMR

peak for **2.19** was resolved as a doublet of doublets, characteristic of the independently-generated anionic phosphino-borane. Splitting of this signal arises from distinct coupling to the *ortho*-fluorines of the C_6F_4 bridge. These results indicate that in the ion pair **2.17**, there likely exists a weak interaction between the Ti center and the P of the borate. Upon addition of THF, a THF molecule coordinates to the Ti center, which eliminates any sort of Ti-P interaction, and results in a separated ion-pair. With respect to the increased activity observed for the olefin polymerization experiments, the pendent P moiety prevents formation of a close Ti-Me-B interaction allowing for faster propagation of the polymer chain.

Similar results were observed in the formation of **2.18** and **2.20**. The ^{1}H-NMR spectra of $[CpTiMe(NP^tBu_3)][Mes_2P(C_6F_4)BMe(C_6F_5)_2]$ (**2.18**) showed two distinct Me signals at 1.18 and 0.85 ppm, corresponding to the B-Me and Ti-Me groups, respectively. The assignment of these resonances was confirmed by ^{1}H-^{13}C HSQC experiments which correlated the ^{1}H NMR signals of the B-Me and Ti-Me groups to ^{13}C NMR resonances at 10.5 and 52.8, respectively. Additionally, a ^{1}H-^{1}H EXSY experiment demonstrated that these Me groups are not exchanging. The ^{31}P NMR spectrum of **2.18** showed a slight broadening of the signal attributed to the co-catalyst species (broad singlet at -50.2 ppm). Upon addition of excess Lewis base THF to the reaction mixture **2.20** was formed. The peak in the ^{31}P NMR spectrum for **2.20** was resolved as a triplet, characteristic of the independently generated anionic phosphino-borate. Although the activity determined when **2.18** was used was significantly less than $B(C_6F_5)_3$, it is expected to show similar, if not higher activities. Impurities or the hydroscopic nature of **2.18** may have led to the decreased activity observed.

2.3.3 Cationic Phosphonium-Borates as Activators

The use of the cationic boranes (**2.14**) presents an interesting activation system, as it has potential for a dual activation for activation through protonation and/or methyl abstraction, as illustrated in Figure 2.9

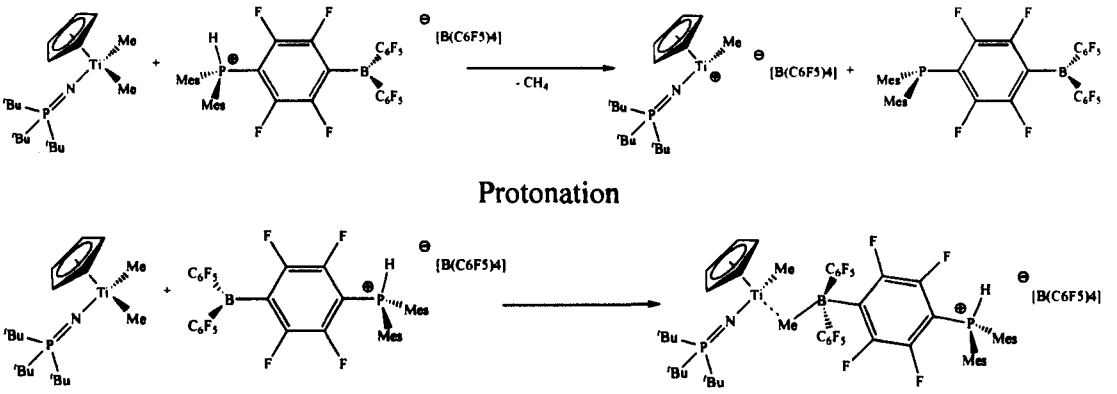


Figure 2.9 Activation of $CpTiMe_2(NP^tBu_3)$ by Cationic Phosphonium-Boranes

Compound **2.14** was tested as an activator for ethylene polymerization. The polymerization results are documented in Table 2.6

Table 2.6 Polymerization Results for Cationic Phosphonium-Borates[a]

Co-catalyst	Equiv. of Co-catalyst	1 Activity[b]	2 Activity[b]	Average Activity[b]	% Difference
$B(C_6F_5)_3$	1	8215	9331	8773	13
$[Ph_3C][B(C_6F_5)_4]$	1	7670	7252	7461	6
$[Mes_2PHC_6F_4B(C_6F_5)_2][B(C_6F_5)_4]$ (**2.14**)	1	5592[c]	5886[c]	5739	5
$[Mes_2PHC_6F_4B(C_6F_5)_2][B(C_6F_5)_4]$ (**2.14**)	0.5	6879[c]	6444[c]	6662	7

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (5 μmol/L), 1 equiv. co-catalyst, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}
[c] Reactor swollen with polymer

The results in Table 2.6 show that **2.14** had a comparable activity to $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$, using either 1 or 0.5 equivalents. This is initially surprising, as **2.14** is effectively a cationic borane and has been shown to have a more Lewis acidic B center than $B(C_6F_5)_3$.[108] In theory, this should generate a more separated ion-pair and therefore a more active catalyst system. However, the presence of the multiple anionic species in solution may provide alternate decomposition pathways and be the result of slightly lower activities that were observed

Comparing when 1 vs. 0.5 equivalents of **2.14** was used as the co-catalyst, it is observed that 0.5 equivalents gives slightly higher activities. This outcome is consistent with the observed activities for **2.16** and **2.18**. In the case of 1 equivalent added, generation of the ion pair, $[CpTiMe(NP^tBu_3)][B(C_6F_5)_4]$ and the zwitterion, $Mes_2PHC_6F_4B(Me)(C_6F_5)_2$ is expected. With 0.5 equivalents, the formation of, $[CpTiMe(NP^tBu_3)][B(C_6F_5)_4]$, and $[CpTiMe(NP^tBu_3)][Mes_2PC_6F_4B(Me)(C_6F_5)_2]$ via both methyl abstraction and protonation would occur. Consistent with the P moiety increasing the activity through an interaction with the Ti center, these systems would be more catalytically active. While these systems may provide interesting solution NMR dynamics they are ultimately synthesized using both $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$, **2.14** is therefore impractical for industrial use as olefin polymerization activator because the observed activity is not significantly greater than that observed in a polymerization system that utilizes $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$.

2.4 Summary and Conclusions

In this chapter it was demonstrated that compounds derived from "frustrated" Lewis pair chemistry can be used as efficient activators for the polymerization of ethylene using $CpTiMe_2(NP^tBu_3)$. For the unlinked, perfluoroaryl and alkoxy-linked phosphonium-borates both the sterics and the electronics of the phosphine play an essential role in the ability of phosphonium-borate to generate a catalytically active titanium center. Not only must the phosphonium be sterically bulky in order to prevent the corresponding phosphine from coordinating to Ti, but the PH moiety must be sufficiently acidic to fully protonate one of the Ti-Me bonds. With respect to the phosphino-boranes, the presence of the phosphine in an activating species increases ion-pair separation through the interaction of the Ti metal center and the phosphine, this results in an increase in activity. The cationic phosphonium-boranes can act as a dual activator through both methyl abstraction and protonation. To further evaluate the effectiveness of these activators a range of pre-catalysts should be tested to fully understand the impact of activators derived from "frustrated" Lewis pair chemistry.

Chapter 3: The Effect of Phosphine Additives on Olefin Polymerization

3.1 Introduction

In Chapter 2 it was demonstrated that the Lewis acidic boranes of the form $R_2PC_6F_4B(C_6F_5)_2$ generated catalyst systems with $CpTiMe_2(NP^tBu_3)$ that exhibited ethylene polymerization activities higher than those derived from the parent borane, $B(C_6F_5)_3$. It was proposed that the observed increased activity was a result of a greater ion-pair separation resulting from interaction of the phosphine moiety with the Ti cation of $[CpTiMe(NP^tBu_3)][R_2P(C_6F_4)BMe(C_6F_5)_2]$.

Previous investigations conducted by the Stephan Group have demonstrated that small donor molecules stabilize Ti(IV) cations through direct coordination of the donor to Ti yielding species of the form, $[CpTiMe(NP^tBu_3)PR_3][XB(C_6F_5)_3]$, where X= Me or C_6F_5 and R = Me, ^{n}Bu and Ph. However, previous efforts to isolate the donor stabilized compounds with sterically bulky phosphines (R = Cy, ^{t}Bu and *o*-tolyl) revealed no evidence of phosphine binding to Ti and in some cases the free phosphine was observed in solution NMR spectroscopic studies[116,123].

The cationic group IV metal-alkyl complexes, which are highly active for olefin polymerization, are sensitive to the presence of nucleophilic reagents. In general, in the polymerization process, the presence of nucleophilic additives or impurities leads to irreversible catalyst deactivation resulting in a decreased polymerization activity through quenching of the active cationic metal center. There are, however, documented studies of addition of Lewis bases to olefin polymerization. Chien and co-workers reported the addition of the Lewis bases; THF, ethyl benzoate and acetonitrile, to ethylene-propylene

co-polymerizations.[130] Their studies revealed that as the molar ratio of Lewis base is increased, there is a dramatic decrease in the polymerization activity. Damiani and co-workers have also reported the use of ethyl benzoate as an additive in the polymerizations of ethylene and propylene. [131,132] Their results also indicate a decrease in polymerization activity with the increased molar ratio of ethyl benzoate added. These results demonstrate how Lewis bases poison catalysts through coordination of the base to the active metal center.

In contrast, there are examples of donor systems that do not negatively impact polymerization. The immobilization of the catalyst system, $[Cp_2ZrMe][B(C_6F_5)_4]$, on a poly(4-vinylpyridine) support resulted in a catalyst system with an higher polymerization activity of ethylene.[133] Recently, Gibson and co-workers reported the modification of phenoxy-amide ligands to incorporate pendant donors, which did not coordinate to the neutral Ti and Zr complexes. The incorporation of these pendant groups, specifically phosphines, resulted in the increased polymerization activity of Ti and Zr complexes.[134] Bochmann and co-worker have also reported Zr salicylaldiminato complexes incorporating pendant phosphines, which do not coordinate to the metal center. Introduction of these phosphines resulted in no impact on the ethylene polymerization activity.[135] In summary, the use of non-coordinating phosphine groups has been shown to either have a no impact or can result in a benefit on the polymerization activity for Ti and Zr catalysts.

Based on the observation that sterically bulky phosphines do not coordinate to the Ti center of $[CpTiMe(NP^tBu_3)]^+$, it was theorized that the addition of phosphines to catalysts mixtures would aid in separation of the cation-anion interaction, thereby resulting in generation of a more active Ti center while also weakly stabilizing the Ti

center, without quenching reactivity. In this chapter the impact of the addition of Lewis basic phosphines, with varying electronic and steric properties, on the polymerization of ethylene using the pre-catalyst $CpTiMe_2(NP^tBu_3)$ and co-catalysts, $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$, will be investigated.

3.2 Experimental

3.2.1 General Considerations

All preparations were performed under an atmosphere of dry O_2-free N_2 employing either Schlenk-line techniques or a Vacuum Atmospheres inert atmosphere glovebox.

3.2.2 Solvents

Toluene was purified employing Grubbs-type column systems manufactured by Innovative Technologies.

3.2.3 Reagents

Ethylene was purchased from BOC gases and dried over Q5 copper deoxygenation material and 3 Å molecular sieves. MeOH and $PMes_3$ were purchased from Aldrich Chemical Co.; HCl was purchased from EM Science; PEt_3, P^nBu_3, PPh_3, PCy_3, P^tBu_3 and $P(o\text{-tolyl})_3$ were purchased from Strem Chemicals, Inc.; all were used as received. $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, Al^iBu_3 (T*i*BAl), and $CpTiCl_2[NP^tBu_3]$ were generously donated by NOVA Chemicals Corp. and were used without further purification. $CpTiMe_2[NP^tBu_3]$[82] was prepared in accordance with literature methods.

3.2.4 Polymerization Protocol

There are numerous factors that can affect polymerization results obtained using the Buchi reactor system. To ensure that the results obtained were comparable, routine standards were run to evaluate the reproducibility of the system. These polymerization results and analysis are outlined in Appendix A.

The description of the polymerization set-up is described in section 2.2.4.1. The description of the polymer work-up and polymerization activity calculation (Equation 2.1) and percent difference calculation (Equation 2.2) are outlined in section 2.2.4.4

3.2.4.1 Description of Catalyst and Co-catalyst Preparation

The pre-catalyst, phosphine, co-catalyst and scrubber stock solutions were freshly prepared, loaded into syringes in a glovebox, and then transferred to the reactor immediately before injection in order to limit possibility of catalyst decomposition. An example polymerization experiment using $CpTiMe_2(NP^tBu_3)$ as the catalyst, 10 equivalents of P^tBu_3 as additive, 1 equivalent of $B(C_6F_5)_3$ as co-catalyst, and 20 equivalents of T*i*BAl as the scrubber will be used to describe how the stock solutions were prepared.

Catalyst Solution: $CpTiMe_2(NP^tBu_3)$ (0.012 g, 0.032 mmol) was weighed into a vial. Toluene (15.570 g, 18.0 mL) was then added to form a clear, light yellow solution. 1.0 mL (0.0018 mmol $CpTiMe_2(NP^tBu_3)$) of the solution was transferred to a syringe for injection into the reactor.

Phosphine Solution: P^tBu_3 (0.015 g, 0.072 mmol) was weighed into a vial. Toluene (6.920 g, 8.0 mL) was added to form a clear, colorless solution. 2.0 mL (0.018 mmol

P^tBu_3, 10 equivalents) of the solution was transferred to a syringe for injection into the reactor.

Co-Catalyst Solution: $B(C_6F_5)_3$ (0.011 g, 0.022 mmol) was weighed into a vial. Toluene (15.570 g, 18.0 mL) was added to form a clear, colourless solution. 1.5 mL (0.0018 mmol $B(C_6F_5)_3$, 1 equivalent) of the solution was transferred to a syringe for injection into the reactor.

Scrubber Solution: 0.2 mL of a 25.2 weight % solution of T*i*BAl in heptanes (0.18 mmol Al*i*-Bu_3) was added to toluene (12.836 g, 14.84 mL) to produce a clear, colourless solution. 3.0 mL (0.036 mmol T*i*BAl, 20 equivalents) of the solution was transferred to a syringe for injection into the reactor.

3.2.4.2 Description of Polymerization Experiments

The injection sequence used was the same for all polymerizations unless otherwise noted. The prepared solution of T*i*BAl (3.0 mL) was injected into the reaction vessel through the catalyst injection inlet and allowed to stir for 5 min. The prepared $CpTiMe_2[NP^tBu_3]$ solution (1.0 mL) was injected into the reaction vessel followed immediately by injection of the P^tBu_3 solution (2.0 mL) and the $B(C_6F_5)_3$ solution (1.5 mL). The mixture was stirred at 1500 ± 5 RPM at 30° C under 2 atm of dynamic ethylene flow for 10 minutes. Temperature and ethylene flow rate were recorded manually at regular intervals. After 10 minutes, polymerization was stopped by closing the ethylene inlet valve and venting the reactor. Stirring was stopped, and the reactor was disassembled.

3.3 Results and Discussion

3.3.1 Polymerization of Ethylene with Phosphine Additives

To investigate the effect of adding tertiary phosphines to the polymerization of ethylene using $CpTiMe_2(NP^tBu_3)$ and $B(C_6F_5)_3$, a range of phosphines were selected that had varying steric and electronic properties. The phosphines used for this study, their corresponding cone angle and pKa are shown in Table 3.1.

Table 3.1 Phosphine Additives and Respective Cone Angle and pKas

Phosphine	Cone Angle[121]	pKa[122]
PEt_3	132°	8.7
P^nBu_3	132°	8.4
PPh_3	145°	2.7
PCy_3	170°	9.7
P^tBu_3	182°	11.4
P(*o*-tolyl)$_3$	194°	3.1
$PMes_3$	212°	N/A

3.3.1.1 Polymerization Results

Initially, the impact of adding 10 equivalents of each phosphines was investigated. Results are shown in Table 3.2. In evaluating the influence of the phosphine additives, the resulting polymerization activities were compared to polymerizations conducted in the absence of phosphine.

Table 3.2 Polymerization in Presence of 10 Equivalents PR_3[a]

Phosphine	Activity[b]	Activity[b]	Average Activity[b]	% Difference
None	Multiple Runs Performed[c]		14460[c]	30[c]
PEt_3	6835	8002	7418	16
P^nBu_3	10760	8737	9748	21
PPh_3	9005	11923	10489	27
PCy_3	22083	21793	21938	1
P^tBu_3	52530	44267	48398	17
P(*o*-tolyl)$_3$	12933	10903	11918	17
$PMes_3$	20803	17675	19239	16

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 10 equiv. phosphine, 1 equiv. $B(C_6F_5)_3$, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C

[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}

[c] See Appendix A for results and calculations

The observed polymerization activities indicate a dependence on the size of phosphine additive used. As illustrated in Figure 3.1, the polymerization activity of $CpTiMe_2(NP^tBu_3)/B(C_6F_5)_3$ catalysts system decreases, if only slightly, upon addition of 10 equivalents of one of the relatively smaller phosphines; PEt_3, P^nBu_3 and PPh_3. There was, however, a remarkable increase in activity upon addition of 10 equivalents of P^tBu_3 and PCy_3, with the P^tBu_3 additive resulting in an observed activity over *3 times* more than that with no additive. No appricaible change in activity is observed when 10 equivalents of the ultra bulky phosphines P(*o*-tolyl)$_3$ and $PMes_3$ were used as additives.

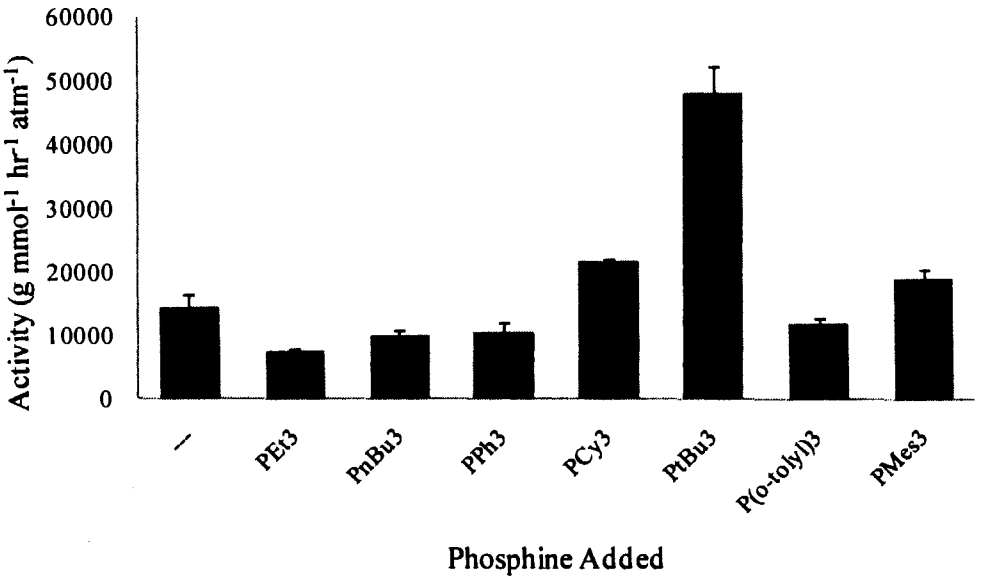


Figure 3.1 Bar Graph Depicting the Ethylene Polymerization Activity of the $CpTiMe_2(NP^tBu_3)/B(C_6F_5)_3$ in the Presence of 10 Equivalents Phosphine

In examining the role of the phosphine as an additive in ethylene polymerization, potential reactivity of the phosphine in the reactor system must be considered. There were three possible reaction pathways available for the phosphine in the reactor 1) Reaction of the added phosphine with the T*i*BAl used as a scrubber, via P-Al coordination; 2) Reaction with $B(C_6F_5)_3$ via adduct or "frustrated" Lewis pair type reactivity, resulting in a species inactive for metal-alkyl activation, and 3) Reaction with Ti cation, $[CpTiMe(NP^tBu_3)]^+$, either through coordination to the metal center, which decreases the activity of the polymerization, or though an interaction with the Ti cation, which could potentially result in an increase activity as reported in Chapter 2 with the use of $R_2PC_6F_4B(C_6F_5)_2$ as the co-catalyst. To further investigate the role of the phosphine, as it relates to the active catalyst system, the amount of phosphine was varied.

3.3.1.2 Polymerizations with PEt_3 and P^nBu_3 added

The first phosphines investigated for their impact on polymerization process were the relatively small and basic phosphines, PEt_3 and P^nBu_3, which have been shown to form the donor stabilized cation ($[CpMeTi(NP^tBu_3)P^nBu_3][MeB(C_6F_5)_3],$).[123] Polymerizations where conducted with 2, 10, 20 and 50 mole ratio of phosphine to Ti. The results are shown in Table 3.3.

Table 3.3 Polymerization Results for the Addition of PEt_3 and P^nBu_3

Phosphine	Equivalents	Activity[b]	Activity[b]	Average Activity[b]	% Difference
None	**0**	**Multiple Runs Performed**		**14460[c]**	**30[c]**
PEt_3	**2**	**10393**	**8943**	**9668**	**15**
	10	**6835**	**8002**	**7418**	**16**
	20	**5507**	**4348**	**4928**	**24**
	50	**No Polymer Recovered**			
P^nBu_3	**2**	9138	10805	9972	17
	10	10760	8737	9748	21
	20	8988	8213	8601	9
	50	No Polymer Recovered			

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 1 equiv. B(C6F5)3, 20 equiv. TiBAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g mmol-1 hr-1 atm-1
[c] See Appendix A for results and calculations

As shown in Table 3.3, and illustrated in Figure 3.2 as the concentration of phosphine was increased there was a decrease in the polymerization activity. At 50 equivalents of phosphine added no polymer was recovered.

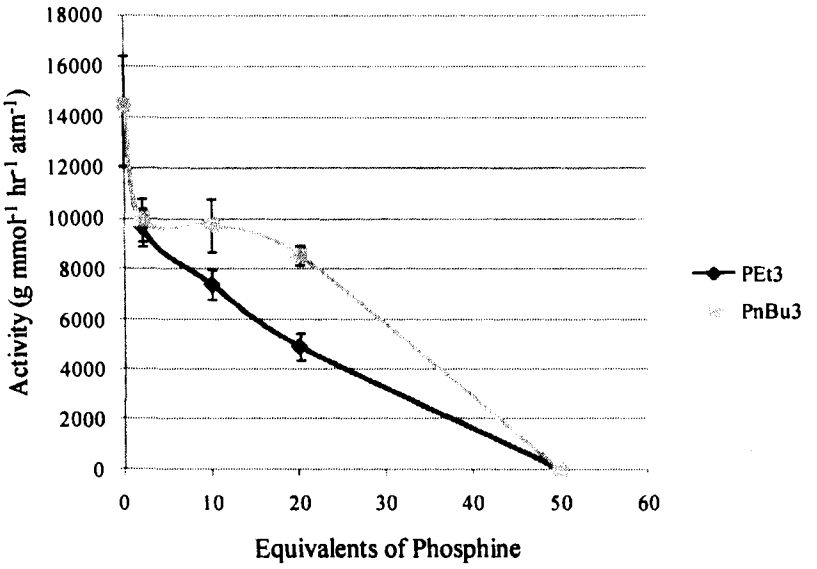


Figure 3.2 Activity of Polymerization as a Function of the Amount of Phosphine Added

At low mole ratios of phosphine/Ti, the actual influence of the added phosphine may be underestimated due to reactivity with TiBAl. It is presumed that these phosphines form traditional Lewis adducts with Al.[136,137] At higher phosphine concentrations, the decreased activity could be attributed to two factors: 1) the reactivity of PEt_3 or P^nBu_3 and $B(C_6F_5)_3$ forming the Lewis acid-Lewis base adducts, which would be inactive for methyl abstraction; or 2) the formation of the stabilized cation $[CpTiMe(NP^tBu_3)PR_3][MeB(C_6F_5)_3]$ which would also be inactive for olefin polymerization. Considering the order of addition employed, the $B(C_6F_5)_3$ is added to a mixture of $CpTiMe_2(NP^tBu_3)$ and the phosphine, either factor could be the reason a decrease in activity was observed.

3.3.1.3 Polymerizations with PPh_3 Added

The influence of the relatively small and less basic phosphine, PPh_3 on reactivity was then considered. The results of the polymerization of ethylene using 2, 10, 20 and 50 equivalents of PPh_3 are listed in Table 3.4.

Table 3.4 Polymerization Results with PPh_3 Additive

Phosphine	Equivalents	Activity[b]	Activity[b]	Average Activity[b]	% Difference
None	**0**	**Multiple Runs Performed**		**14460[c]**	**30[c]**
PPh_3	**2**	**13582**	**9338**	**11460**	**37**
	10	**9005**	**11923**	**10489**	**27**
	20	**13743**	**10643**	**12193**	**25**
	50	**8807**	**11577**	**10192**	**27**

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 1 equiv. $B(C_6F_5)_3$, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}
[c] See Appendix A for results and calculations

As illustrated in Figure 3.3, the polymerization activity decreases only slightly upon the addition of PPh_3, even at high P/Ti molar concentrations. These results are initially surprising given the fact that the donor stabilized cation $[CpTiMe(NP^tBu_3)PPh_3]^+$ [123] and the Lewis acid-base adduct $Ph_3PB(C_6F_5)_3$ [138] have been previously reported.

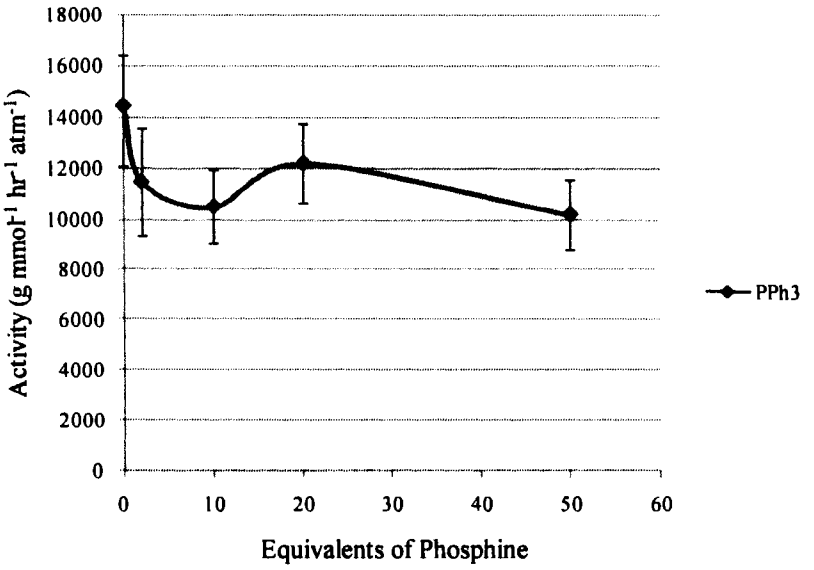


Figure 3.3 Polymerization Activity as a Function of Equivalents of PPh_3

Although coordination of the PPh_3 to the Ti cation occurs, adduct formation is likely reversible due to the increased lability of PPh_3 compared to that of PEt_3 or P^nBu_3, resulting from the increased steric crowding and decreased basicity, therefore ethylene coordination and insertion must compete with adduct formation. It was been previously reported by Brintzinger and co-workers that for zirconocene cations, coordination of a Lewis base to the cationic metal center decreases with increasing steric bulk and/or decreasing basicity.[139] Additionally, the reactivity of PPh_3 and $B(C_6F_5)_3$ to form the Lewis acid-Lewis base adduct does not impact the formation of the cation, as the donor stabilized cation has been reported to be formed via reaction of the adduct $Ph_3PB(C_6F_5)_3$ with $CpTiMe_2(NP^tBu_3)$, through phosphine dissociation and Me abstraction.[116,123] Therefore, although initially surprising, the addition of PPh_3, even at high molar ratios to Ti, has very little impact on the polymerization activity of the $CpTiMe_2(NP^tBu_3)/B(C_6F_5)_3$ system.

3.3.1.4 Polymerizations with PCy_3 Added

The next phosphine considered was the sterically bulky, relatively basic phosphine PCy_3. As discussed in Chapter 2, using the co-catalysts $[Cy_3PH][B(C_6F_5)_4]$, PCy_3 does not coordinate to the cation, $[CpMeTi(NP^tBu_3)]^+$. However, PCy_3 is known to rapidly react with $B(C_6F_5)_3$ to give $Cy_3PC_6F_4BF(C_6F_5)_2$,[108,116] which is has no mode for Ti-Me bond activation (Chapter 2) and therefore reduction in the amount of the catalytically active species could be expected.

Table 3.5 Polymerization Results for the Use of PCy_3 Additive

Phosphine	Equivalents	Activity[b]	Activity[b]	Average Activity[b]	% Difference
None	0	Multiple Runs Performed[c]		14460[c]	30[c]
PCy_3	2	9485	12800	11143	30
	10	22084	21793	21938	1
	20	23745	24162	23953	2
	50	6175	8407	7291	31

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 1 equiv. $B(C_6F_5)_3$, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}
[c] See Appendix A for results and calculations

As shown in Figure 3.4, upon addition of 10 and 20 mole equivalents of PCy_3 there is a doubling of the polymerization activity. This increase is attributed to a weak non-bonding interaction of the PCy_3 with the Ti cation, increasing the ion-pair separation of the cation and the Me-B anion. Although with the addition of 2 equivalents of PCy_3 there was no increase in activity, the effectiveness of the phosphine could have been diminished due to PCy_3-T*i*BAl interactions.

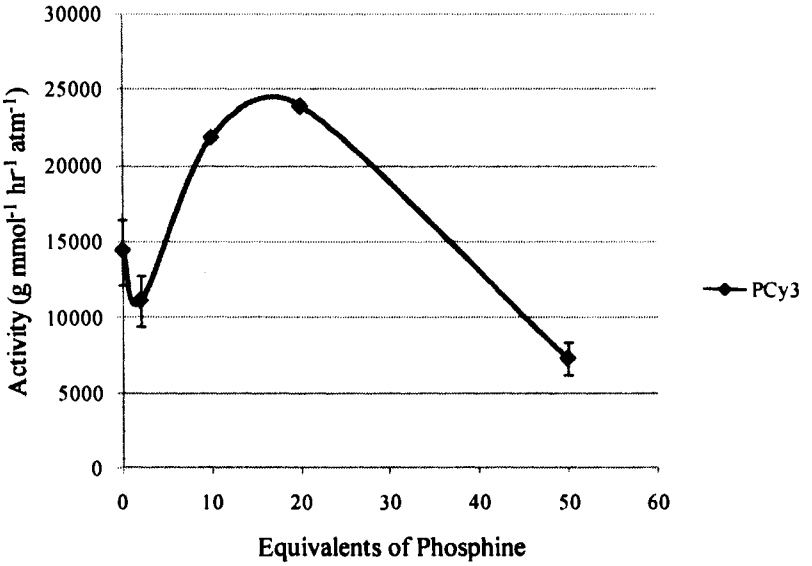


Figure 3.4 Polymerization Activity as a Function of PCy_3 Added

As the concentration of PCy_3 is increased to 50 molar equivalents, there is a dramatic decrease in activity, presumably due to increased competition of *para*-nucleophilic aromatic substitution of the $B(C_6F_5)_3$ with methyl abstraction. Based on these results, the effect of the added phosphine, PCy_3, is an increase in polymerization activity due to ion-pair separation through a weak Ti-P non-bonding interaction. This effect was diminished at high phosphine concentrations, likely as a result of formation of the inactive species $Cy_3PC_6F_4BF(C_6F_5)_2$.

3.3.1.5 Polymerizations with P^tBu_3 Added

Addition of the sterically bulky, basic phosphine, P^tBu_3, which has also been shown to not coordinate to the cation, $[CpTiMe(NP^tBu_3)]^+$, was also investigated. P^tBu_3, however, has been shown to not react with $B(C_6F_5)_3$ to form a traditional adduct.[140] Polymerization results are shown in Table 3.6

Table 3.6 Polymerization Activity with P^tBu_3 Additives

Phosphine	Equivalents	Activity[b]	Activity[b]	Average Activity[b]	% Difference
None	0	Multiple Runs Performed[c]		14460[c]	30[c]
P^tBu_3	2	22937	29502	26219	25
	10	52530	44267	48398	17
	20	29900	33575	31738	12
	50	28185	27438	27812	3

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 1 equiv. $B(C_6F_5)_3$, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}
[c] See Appendix A for results and calculations

As illustrated in Figure 3.5, upon addition of even 2 mole equivalents of P^tBu_3 there was a doubling of the polymerization activity. When 10 equivalents were added there was a 3 times higher activity observed than when no phosphine was added. Similar to the results found for the activator $^tBu_2PC_6F_4B(C_6F_5)_2$, it is proposed that a weak noncovalent interaction of P with the Ti cation increases ion-pair separation, resulting in an enhanced activity.

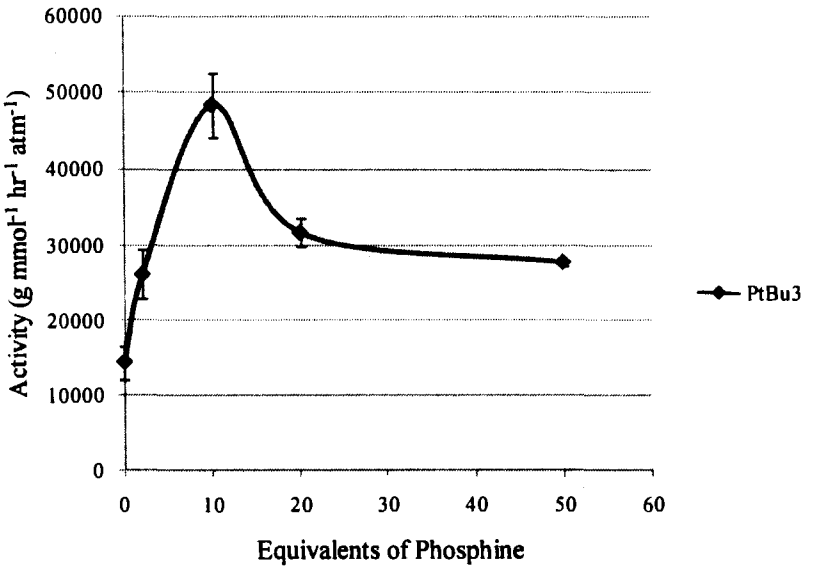


Figure 3.5 Polymerization Activity as a Function of P^tBu_3 Added

Although the effectiveness of P^tBu_3 addition decreases at 20 and 50 equivalents added, the catalyst systems were still 2 times more active than when no phosphine is added. While P^tBu_3 does not react with $B(C_6F_5)_3$ alone, a decrease of the impact of adding P^tBu_3 may be due to "frustrated" Lewis pair interactions of P^tBu_3 and $B(C_6F_5)_3$ in presence of olefins.[120] This unique activity will be discussed in further detail in Chapter 5.

3.3.1.6 Polymerizations with P(o-tolyl)$_3$ and PMes$_3$ Added

The use of P(*o*-tolyl)$_3$ and $PMes_3$ as additives were also investigated. These are very sterically encumbered, but relatively less basic than PCy_3 and P^tBu_3. Polymerization results with the use of P(*o*-tolyl)$_3$ and $PMes_3$ as additives are shown in Table 3.7

Table 3.7 Polymerization Results with P(*o*-tolyl)$_3$ and PMes$_3$ Additives

Phosphine	Equivalents	Activity[b]	Activity[b]	Average Activity[b]	% Difference
None	0	Multiple Runs Performed[c]		14460[c]	30[c]
P(*o*-tolyl)$_3$	2	14158	12898	13528	9
	10	12933	10903	11918	17
	20	12182	15705	13943	25
	50	14300	12632	13466	12
PMes$_3$	2	17500	16303	16902	7
	10	20803	17675	19239	16
	20	17248	17332	17290	0
	50	11988	14752	13370	21

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 1 equiv. $B(C_6F_5)3$, 20 equiv. TiBAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g mmol-1 hr-1 atm-1
[c] See Appendix A for results and calculations

As illustrated in Figure 3.6 addition of P(*o*-tolyl)$_3$ and PMes$_3$ does not have a significant impact on the polymerization activities. Even using a large molar excess of either phosphine, results in activities comparable to polymerizations with the use of no phosphine additives. P(*o*-tolyl)$_3$ and PMes$_3$ do not coordinate to the Ti cation, and do not react with $B(C_6F_5)_3$, even in the presence of olefin. (Discussed further in Chapter 5)

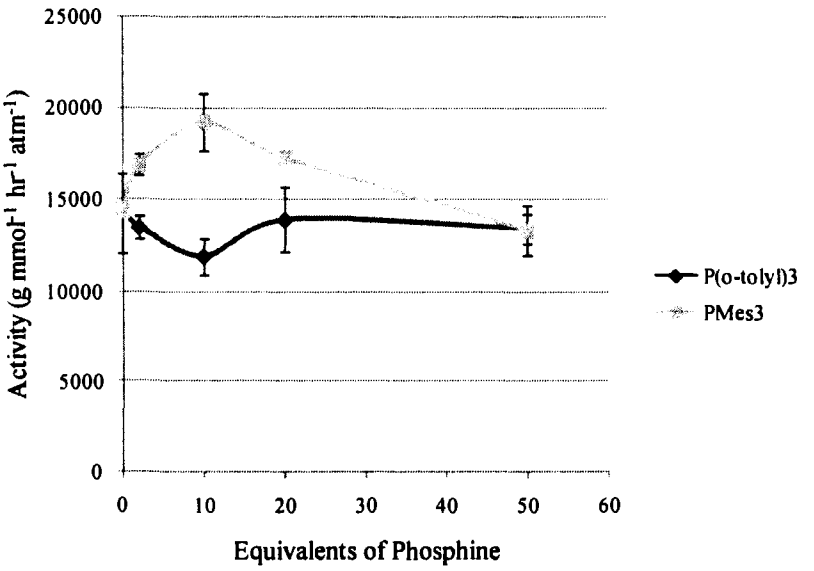


Figure 3.6 Polymerization Activity as a Function of Phosphine Added

The reduced impact of the addition of P(*o*-tolyl)$_3$ and PMes$_3$ compared to PCy$_3$ and P^{t}Bu$_3$ is consistent with the decreased interaction with the Ti cation based on decreased basicity of the phosphine. Similar to the results obtained in Chapter 2 with the use of $R_2PC_6F_4B(C_6F_5)_2$ as co-catalysts, the decreased activity of polymerization is proportional to the decrease in basicity (activity of ^{t}Bu$_2$PC$_6$F$_4$B(C$_6$F$_5$)2 > Mes$_2$PC$_6$F$_4$B(C$_6$F$_5$)$_2$).

Overall, the addition of the phosphine additives P(*o*-tolyl)$_3$ and PMes$_3$, has little influence on the polymerization activity of the CpMe$_2$Ti(NP^{t}Bu$_3$)/B(C$_6$F$_5$)$_3$ system.

3.3.1.7 Polymerizations with [Ph$_3$C][B(C$_6$F$_5$)$_4$] Activation

As reported and discussed in Chapter 2, the phosphines, PCy$_3$, P^{t}Bu$_3$ and PMes$_3$ resulted in no coordination to [CpTiMe(NP^{t}Bu$_3$)][B(C$_6$F$_5$)$_4$] and the use of the activators [R$_3$PH][B(C$_6$F$_5$)$_4$], where R = Cy and Mes, resulted in activities comparable to the activation using [Ph$_3$C][B(C$_6$F$_5$)$_4$]. To examine the effect of adding a large mole ratio of

P/Ti, 20 molar equivalents of the phosphines; PEt_3, P^tBu_3 and $PMes_3$, were added to the polymerization of ethylene employing $CpTiMe_2(NP^tBu_3)$ activated with $[Ph_3C][B(C_6F_5)_4]$. Results are shown in Table 3.8.

Table 3.8 Polymerization Results for Trityl Activations[a]

Phosphine	Activity[b]	Activity[b]	Average Activity[b]	% Difference
None	7847	8475	8161	8
PEt_3	Trace amounts of polymer recovered			
P^tBu_3	8288	8338	8313	1
$PMes_3$	6717	5845	6281	14

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 20 equiv. phosphine, 1 equiv. co $[Ph_3C][B(C_6F_5)_4]$, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}

As illustrated the addition of PEt_3 results in a decrease in the activity, only trace amounts of polymer was recovered (< 1 g). The decreased reactivity is due to the formation of either of the adducts, $[CpTiMe(NP^tBu_3)PEt_3]^+$ or $[Ph_3PCPh_3]^+$. The addition of 20 equivalents of P^tBu_3 and $PMes_3$, resulted in polymerization activities comparable to those observed in the absence of phosphines, P^tBu_3 and $PMes_3$, have been shown to not coordinate to the cation, $[CpTiMe(NP^tBu_3)]^+$.

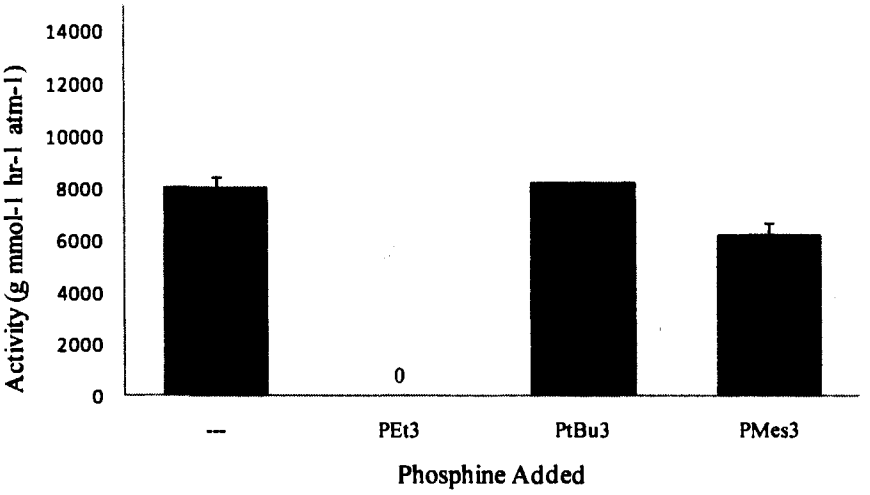


Figure 3.7 Bar Graph Depicting the Ethylene Polymerization Activity of the $CpMe_2Ti(NP^tBu_3)/[Ph_3C][B(C_6F_5)_4]$ in the Presence of 20 Equivalents Phosphine

When the polymerization was activated using $[Ph_3C][B(C_6F_5)_4]$, the larger anion $[B(C_6F_5)_4]^-$, presumably results in greater cation-anion separation.[24] Thus when the sterically bulky phosphines are added to the catalytic system, affiliation of the Lewis base with the cation has a lesser effect on the ion-pairing and therefore on the resulting polymerization activity.

3.3.1.8 General Overview of the Role of Phosphine Additives in the Polymerization of Ethylene

The observation that sterically bulky Lewis base can enhance the ethylene polymerization activity is initially surprising and appeared to be counter-intuitive, as the addition of a donor was expected to sequester Ti cations and preclude polymerization. Thus, despite the absence of a direct bonding interaction, the phosphine additive clearly alters the active site. It is reasonable to propose that the electrostatic attraction of the Ti-

cation and the sterically demanding Lewis base results in association in solution, especially when considering the results from Chapter 2. This proposition was evaluated employing molecular mechanics calculations. Models based on crystallographic data for the two fragments $[CpTiMe(NP^tBu_3)]^+$ and P^tBu_3 were employed to calculate the total energy as a function of approach of P^tBu_3 on a vector towards the vacant coordination site of Ti. These computations reveal that the minimum energy corresponds to a Ti-P separation of 4.2 Å.

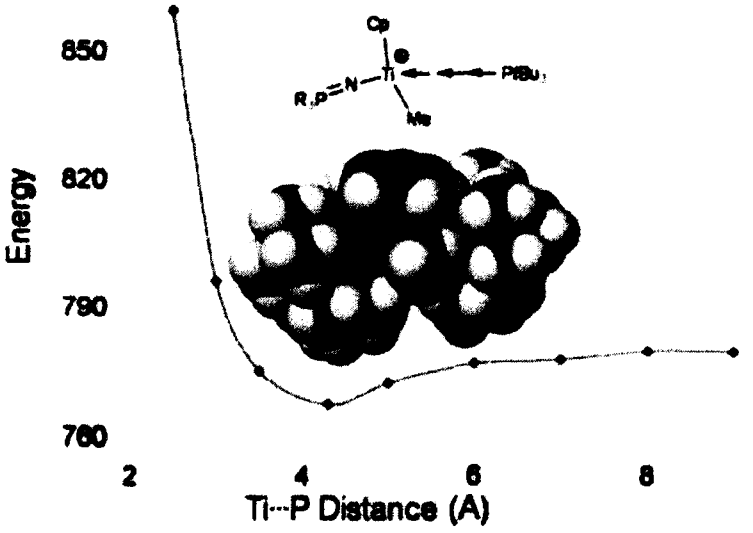


Figure 3.8 Plot of Total Energy vs Ti-P Distance and Space-filling Diagram of the Minimum Energy Conformation of $[CpTiMe(NP^tBu_3)]^+$ and P^tBu_3 with Ti-P Distance of 4.2 Å.

These results support the view that steric demands preclude dative Ti-P bonding in the case of the sterically demanding P^tBu_3. It is noteworthy that previous computational studies have shown the most significant energy barrier to insertion of ethylene into the growing polymer chain is cation-anion separation.[54,141,142] Thus, it is also reasonable to

suggest that the electrostatic interaction of the sterically demanding phosphines and the Ti-cation may also crowd the cation which causes a greater anion-cation separation.

Maximum polymerization activity is achieved with the addition of 10 equivalents of P^tBu_3. This maximum corresponds to a 3 fold increase in the activity compared to the catalytic system in the absence of phosphine. Conventionally, in the development of more active catalyst systems, the synthetic modification of the catalyst[74,81,143] or co-catalyst[24,144] is targeted. Although these modifications may result in the enhancement of the polymerization activity they are usually synthetically challenging and associated with an increase in cost in both materials and highly qualified personnel. The enhancement of activity by the addition of the phosphine is a significant finding as we have shown the system can be simply modified to yield higher activities by the addition of the commercially available P^tBu_3. This dramatic increase in activity is observed with a relatively minimal cost and time associated with system development and improvement. This provides a novel way to view the active catalyst system and the methods involved with enhancement and activity optimization.

Recently, Bravaya and co-workers[145] have reported similar observations of the polymerization of propylene using *rac*-$Me_2SiInd_2ZrMe_2$/$[Ph_3C][B(C_6F_5)_4]$ systems in the presence of the Lewis bases; Me_2NPh and NPh_3. Similar to this proposed explanation of the observed increase of activity in the presence of a Lewis base, they suggest the weakening of cation-anion interactions and a reduction of the energy formation of the active centers due to the steric congestion of the cation provided by the affiliation of the bulky Lewis base.

Further studies of the general utility of Lewis basic additives in other catalytic systems should be carried out as this may involve optimization to determine the most

advantageous steric/electronic properties of the added Lewis base for each unique catalytic system.

3.4 Summary and Conclusions

In this chapter the use of phosphine additives in the polymerization of ethylene was investigated. Sterically bulky phosphines, P^tBu_3 and PCy_3, increase the polymerization activity of the $CpTiMe_2(NP^tBu_3)/B(C_6F_5)_3$ system. These observations are conceptually related to main group "frustrated" Lewis acid-base pairs that have been recently described.[107,140] In those cases, unusual reactivity and catalytic behaviour have been derived from the combination of Lewis acids and bases which are too sterically encumbered to quench each other. In a similar fashion, this description applies to highly Lewis acidic Ti-cations in the presence of sterically demanding phosphines. Thus, the observed activity enhancement described herein can be identified as another example of the unique reactivity of "frustrated" Lewis pairs. Following these findings, this novel transition metal "frustrated" Lewis pair concept, based on Ti and Zr cations and bulky phosphines, has been investigated and demonstrated to affect hydrogen and olefin activation.[113] Current studies on these systems continue to be examined in the Stephan Group. Significantly, the use of additives to alter the polymerization activity presents another method of controlling the polymerization that does not involve the synthetic alteration of the catalysts/co-catalyst systems.

Chapter 4: Towards the Polymerization of Pendant Phosphine Monomers

4.1 Introduction

The development of single site catalysts for the polymerization of ethylene and other α-olefins has been a major area of research for the past quarter of a century. The specific tuning of defined metal complexes allows strict control over the microstructure of polyolefins produced.[60,68] This rational catalyst development, although extensively studied, continues to be a motivating objective in numerous research endeavors. A driving force behind some of these investigations is the expansion of these systems to incorporate functional moieties into the polymer, to enhance or change the polymer properties and range of applications.[146]

There are two main approached to the synthesis of functional polyolefins; chain-end functionalization and in-chain functionalization.[147-149] Chain-end functionalizations is achieved through generating chain-end unsaturation and further reactivity or terminal functionalization of polymers. In-chain functionalization is typically achieved through post-polymerization reactivity; the use of groups to protect the functionality during the polymerization or direct polymerization. Of the methods for in-chain functionalization direct polymerization is preferred, since it requires no modification post-polymerization. Therefore, numerous studies have been carried out to incorporate the functional moieties directly during the polymerization process. Furthermore, it is desirable to add these moieties in a controlled manner without compensation of any desirable properties.

Functional monomers that have been shown to be directly polymerized using Group IV catalysts include weakly-interacting main group functionalized monomers, such as silicon,[150,151] halogen,[152] and nitrogen[151,153] containing monomers. Although the direct polymerization of functional monomers has been demonstrated using group IV transition metal catalysts the polymerization of many polar monomers has been limited due to the electrophilic nature of the catalysts and subsequent poisoning of the catalyst by means of coordination of the functional group to the metal center.

Previous efforts in the Stephan group to isolate the donor stabilized cations, $[CpTiMe(NP^tBu_3)(PR_3)]^+$ with sterically bulky phosphines (R = Cy, ^{t}Bu and *o*-tolyl) revealed no evidence of phosphine binding to Ti and in some cases the free phosphine was observed in solution NMR spectroscopic studies[116,123]. Additionally, as outlined in Chapter 3, the addition of sterically bulky phosphines to ethylene polymerizations using $CpTiMe_2(NP^tBu_3)$ and $B(C_6F_5)_3$ resulted in an enhancement of polymerization activity. This prompted us to look at the potential of the polymerization of olefins containing pendant phosphine monomers.

In this chapter the potential for the polymerization of α-olefins with pendant phosphines is examined and the potential inhibition pathways of the polymerization of these monomers are discussed.

4.2 Experimental

4.2.1 General Considerations

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 were purified employing a Grubbs' type column system manufactured by Innovative Technology. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance-300 spectrometer. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P NMR spectra were referenced to 85% H_3PO_4. Chemical shifts are reported in ppm and coupling constants in Hz. $^{13}C\{^1H\}$ NMR analyses of polymers were acquired using with a 10 s delay between scans.

4.2.2 Solvents

Toluene, hexanes and diethyl ether were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. Uninhibited THF was purchased from EDM and dried over Na/benzophenone and distilled prior to use. Deuterated benzene (C_6D_6) was purchased from Cambridge Isotopes Laboratories, dried over Na/benzophenone, freeze-pump-thaw degassed (3 times) and vacuum distilled prior to use.

4.2.3 Reagents

HP^tBu_2, $Br(CH_2)_3CHCH_2$, $Br(CH_2)_4CH_3$, $Br(CH_2)_9CH_3$ and anhydrous MeOH were purchased from Aldrich Chemical Company, $[Me_2PhNH][B(C_6F_5)_4]$ was purchased from Strem Chemical Inc.; all were used as received. 1-Hexene was purchased from Aldrich Chemical Company and distilled from Na/benzophenone. $^tBu_2PLi$ was prepared by treating HP^tBu_2 with 1 equivalent of ^{n}BuLi in toluene and collecting the precipitate. $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, and $CpTiCl_2(NP^tBu_3)$ were generously donated by NOVA Chemicals Corp. and were used without further purification. $CpTiMe_2[NP^tBu_3]$[82] was prepared via literature methods.

4.2.3.1 Synthesis of Phosphines

$^tBu_2P(CH_2)_3CHCH_2$: A solution of $Br(CH_2)_3CHCH_2$ (4.829 g 32.40 mmol) in THF (5 mL) was added to a solution of $^tBu_2PLi$ (4.392g, 28.87 mmol) in THF (50 mL) cooled to 0 °C. The solution was stirred and warmed to room temperature for 12 hours. The solvent was removed *in vacuo* and hexanes was added to precipitate LiBr. The solution was filtered through celite and vacuum distilled (58 – 62 °C) to yield a clear liquid. Yield 4.894 g (78.9%). **^{1}H NMR** (C_6D_6, 300 MHz, 300 K) δ: 5.71 – 5.85 (m, 1H, $PCH_2CH_2CH_2CHCH_2$), 4.97 – 5.08 (m, 2H, $PCH_2CH_2CH_2CHCH_2$), 2.13 (quartet, 2H, $^3J_{H\text{-}H}$ = 7 Hz, $PCH_2CH_2CH_2CHCH_2$), 1.65 (sextet, 2H, $^3J_{H\text{-}H}$ = 7 Hz, $PCH_2CH_2CH_2CHCH_2$), 1.22 – 1.33 (m, 2H, $PCH_2CH_2CH_2CHCH_2$), 1.07 (d, 18H, $^3J_{H\text{-}P}$ = 10 Hz, P^tBu_2). **^{13}C{^{1}H} NMR** (C_6D_6, 75 MHz, 300 K) δ: 139.2 (s, $PCH_2CH_2CH_2CHCH_2$), 115.3 (s, $PCH_2CH_2CH_2CHCH_2$), 36.0 (d, $^3J_{C\text{-}P}$ = 13 Hz, $PCH_2CH_2CH_2CHCH_2$), 31.6 (d, $^1J_{C\text{-}P}$ = 23 Hz, P^tBu_2), 30.6 (s, $PCH_2CH_2CH_2CHCH_2$), 30.2 (d, $^2J_{C\text{-}P}$ = 15 Hz, P^tBu_2), 21.4

(d, $^{1}J_{C\text{-}P}$ = 22 Hz, P$CH_2CH_2CH_2CHCH_2$). **$^{31}P\{^{1}H\}$ NMR** (C_6D_6, 121 MHz, 300 K) δ: 27.8 (s).

[^{t}Bu$_2$PH((CH$_2$)$_3$CHCH$_2$)][B(C$_6$F$_5$)$_4$] + Me$_2$PhN: A solution of $^{t}Bu_2P(CH_2)_3CHCH_2$ (0.021 g, 0.100 mmol) in C_6D_5Br (0.5 mL) was added to a solution of [Me_2PhNH][$B(C_6F_5)_4$] (0.079 g, 0.100 mmol) in C_6D_5Br. Quantitative product formation was observed by NMR. **^{1}H NMR** (C_6D_5Br, 300 MHz, 300 K): δ 7.22 (t, $^{3}J_{H\text{-}H}$ = 7 Hz, 2H, Ph), 6.75 (t, 1H, $^{3}J_{H\text{-}H}$ = 7 Hz, Ph), 6.65 (d, 2H,$^{3}J_{H\text{-}H}$ = 8 Hz, Ph), 5.50 – 5.54 (m, 1H, $^{t}Bu_2PH((CH_2)_3CHCH_2)$, 4.96 – 5.08 (m, 2H, $^{t}Bu_2PH((CH_2)_3CHCH_2)$, 4.22 (d, 1H $^{1}J_{H\text{-}P}$ = 444 Hz, P*H*), 2.69 (s, 6H, Me_2), 1.93 – 1.95 (m, 2H, $^{t}Bu_2PH((CH_2)_3CHCH_2)$, 1.29 – 1.61 (m, 4H, $^{t}Bu_2PH((CH_2)_3CHCH_2)$, 0.87 (d, 18H, $^{3}J_{H\text{-}P}$ = 17 Hz, $^{t}Bu_2$) **$^{11}B\{^{1}H\}$ NMR** (C_6D_5Br, 96 MHz, 300 K): δ -16.7 (s). **^{19}F NMR** (C_6D_5Br, 282 MHz, 300 K): δ -132.37 (s, 8F, *ortho*-C_6F_5), -162.76 (t, 4F, $^{3}J_{F\text{-}F}$ = 19 Hz, *para*-C_6F_5), -166.46 (t, 8F, $^{3}J_{F\text{-}F}$ = 18 Hz, *meta*-C_6F_5). **$^{31}P\{^{1}H\}$ NMR** (C_6D_5Br, 121 MHz, 300 K): δ 52.4 (s). **^{31}P NMR** (C_6D_5Br, 121 MHz, 300K): δ 53.2 (d, $^{1}J_{P\text{-}H}$ = 438 Hz).

^{t}Bu$_2$P(CH$_2$)$_4$CH$_3$: A solution of $Br(CH_2)_4CH_3$ (0.977 g 6.47 mmol) in THF (5 mL) was added to a solution of $^{t}Bu_2PLi$ (1.003 g, 6.59 mmol) in THF (50 mL) cooled to 0 °C. The solution was stirred and warmed to room temperature for 12 hours. The solvent was removed *in vacuo* and hexanes was added to precipitate LiBr. The solution was filtered through celite and vacuum distilled (50 - 63 °C) to yield a clear liquid. Yield 0.707 g (50.5 %). **^{1}H NMR** (C_6D_6, 300 MHz, 300 K) δ: 1.27 – 1.54 (m, 8H, $(CH_2)_4$), 1.11 (d, 18H, $^{3}J_{H\text{-}P}$ = 11 Hz, P$^{t}Bu_2$), 0.97 (t, 3H, $^{3}J_{H\text{-}H}$= 7 Hz, CH_3). **$^{13}C\{^{1}H\}$ NMR** (C_6D_6, 75

MHz, 300 K) δ: 34.4 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, $PCH_2CH_2\mathit{C}H_2CH_2CH_3$), 31.5 (d, $^{1}J_{C\text{-}P}$ = 23 Hz, P^tBu_2), 31.0 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, $PCH_2\mathit{C}H_2CH_2CH_2CH_3$), 30.1 (d, $^{2}J_{C\text{-}P}$ = 14 Hz, P^tBu_2), 23.2 (s, $PCH_2CH_2CH_2\mathit{C}H_2CH_3$) 22.0 (d, $^{1}J_{C\text{-}P}$ = 22 Hz, $P\mathit{C}H_2CH_2CH_2CH_2CH_3$), 14.68 (s, $PCH_2CH_2CH_2CH_2\mathit{C}H_3$). **$^{31}P\{^{1}H\}$ NMR** (C_6D_6, 121 MHz, 300 K) δ: 27.8 (s).

$^tBu_2P(CH_2)_9CHCH_2$: A solution of $Br(CH_2)_9CH_3$ (3.198 g 13.71 mmol) in THF (5 mL) was added to a solution of $^tBu_2PLi$ (2.076 g, 13.71 mmol) in THF (50 mL) cooled to 0 °C. The solution was stirred and warmed to room temperature for 12 hours. The solvent was removed *in vacuo* and hexanes was added to precipitate LiBr. The solution was filtered through celite and dried *in vacuo* to yield a clear liquid. Yield2.696 g (65.9 %) **^{1}H NMR** (C_6D_6, 300 MHz, 300 K) δ: 5.73 – 5.87 (m, 1H, $CH_2C\mathit{H}(CH_2)_9P^tBu_2$), 4.98 – 5.09 (m, $C\mathit{H}_2CH(CH_2)_9P^tBu_2$), 1.99 (quartet, 2H, $CH_2CHC\mathit{H}_2(CH_2)_8P^tBu_2$), 1.29 – 1.66 (m, 14H, $CH_2CHCH_2(CH_2)_8P^tBu_2$), 1.16 (d, 18H, $^{3}J_{H\text{-}P}$ = 11 Hz, P^tBu_2). **$^{13}C\{^{1}H\}$ NMR** (C_6D_6, 75 MHz, 300 K) partial δ: 139.5 (s, $CH_2\mathit{C}H(CH_2)_9P^tBu_2$), 114.8 (s, $\mathit{C}H_2CH(CH_2)_9P^tBu_2$), 34.5 (s, $CH_2CH(CH_2)_9P^tBu_2$), 32.2 (d, $^{2}J_{C\text{-}P}$ = 13 Hz, $CH_2CH(\mathit{C}H_2)_9P^tBu_2$), 31.5 (d, $^{1}J_{C\text{-}P}$ = 23 Hz, P^tBu), 31.5 (s, $CH_2CH(\mathit{C}H_2)_9P^tBu_2$), 22.1 (d, $^{1}J_{C\text{-}P}$ = 23 Hz, $CH_2CH(\mathit{C}H_2)_9P^tBu_2$). **$^{31}P\{^{1}H\}$ NMR** (C_6D_6, 121 MHz, 300 K) δ: 27.8 (s).

4.2.4 Polymerization Procedures

4.2.4.1 Polymerization of 1-Hexene

A 20 mL vial with a propylene top closure with TFE/silicone septum was equipped with a magnetic stir bar. 0.673 g of 1-hexene (8 mmol), 0.015 g of $CpMe_2Ti(NP^tBu_3)$ (0.04 mmol) and 6 mL of toluene were added to the vial. The vial was then immersed in

a bath of desired temperature, and stirred for 5 minutes at the polymerization temperature. A syringe containing 0.020 g of $B(C_6F_5)_3$ (0.04 mmol) dissolved in 4 mL of toluene was then brought out of the glovebox and its contents injected into the vial. After a desired time interval, polymerizations were quenched by injection of 1 mL of MeOH. Volatiles were removed *in vacuo*. 1 mL of toluene was added and 5 mL MeOH was added to precipitate the polymer. The polymer was washed 2 times with 5 mL MeOH and dried *in vacuo*.

4.2.4.2 Co-polymerizations of 1-Hexene with $^tBu_2P(CH_2)_3CHCH_2$

A 20 mL vial with a propylene top closure with TFE/silicone septa was equipped with a magnetic stir bar. 0.640 g of 1-hexene (7.6 mmol), 0.086 g of $^tBu_2P(CH_2)_3CHCH_2$ (0.4 mmol), 0.015 g of $CpMe_2Ti(NP^tBu_3)$ (0.04 mmol) and 6 mL of toluene were added to the vial. The vial was then immersed in a bath of desired temperature, and stirred for 5 minutes at the polymerization temperature. A syringe containing 0.020 g of $B(C_6F_5)_3$ (0.04 mmol) dissolved in 4 mL of toluene was then brought out of the glovebox and its contents injected into the vial. After a desired time interval, polymerizations were quenched by injection of 1 mL of MeOH. Volatiles were removed *in vacuo*. 1 mL of toluene was added and 5 mL MeOH was added to precipitate the polymer. Polymer was washed 2 times with 5 mL MeOH and dried *in vacuo*.

4.2.4.3 Co-polymerizations with Phosphine Added After 5 Minutes

A 20 mL vial with a propylene top closure with TFE/silicone septa was equipped with a magnetic stir bar. 0.640 g of 1-hexene (7.6 mmol) and 0.015 g of $CpMe_2Ti(NP^tBu_3)$ (0.04 mmol) and 4 mL of toluene were added to the vial. The vial was

then immersed in a bath of desired temperature, and stirred for 5 minutes at the polymerization temperature. A syringe containing 0.020 g of $B(C_6F_5)_3$ (0.04 mmol) dissolved in 4 mL of toluene was then brought out of the glovebox and its contents injected into the vial. After 5 minutes 0.086 g of $^tBu_2P(CH_2)_3CHCH_2$ (0.4 mmol) in 2 mL of toluene was added. After a desired time interval, polymerizations were quenched by injection of 1 mL of MeOH. Volatiles were removed *in vacuo*. 1 mL of toluene was added and 5 mL MeOH was added to precipitate the polymer. The polymer was washed 2 times with 5 mL MeOH and dried *in vacuo*.

4.2.4.4 Molecular Weight Determination

Molecular weight determinations were performed using a Waters Breeze system GPC using THF as eluent. The detector used was a Waters model 410 refractive index detector at 35°C, and molecular weights were calibrated using narrow polystyrene standards (Polymer Laboratories Inc.). The samples were prepared by dissolving the polymer in THF (0.1% w/v) then filtering through a 0.45 μm filter.

4.3 Results and Discussion

4.3.1 Monomer Design and Synthesis

In designing an appropriate phosphine containing monomer for the polymerization with $CpTiMe_2(NP^tBu_3)/B(C_6F_5)_3$ system, the previous studies by Waymouth and co-workers of the polymerization of amine functionalized olefin[151,154] were considered. The

observed polymerization activities in the homo-polymerization of substituted 5-amino-1-pentenes are illustrated in Figure 4.1.

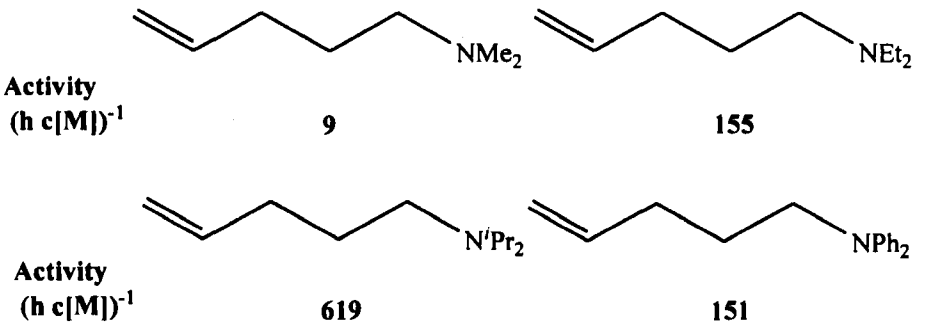


Figure 4.1 Polymerization of Substituted 5-amino-1-pentenes

Their results showed that the steric bulkiness of the amine substituents had a significant impact on the activity, with the ^{i}Pr substituted amine showing the highest activity. Additionally, it is noted that considering the basicity and bulkiness of the substituents, the steric factors are more important than the electronics of the amine. Similar results were also observed by Hakala *et al.* for the copolymerization of oxygen-functionalized olefins.[155]

In addition to the influence of the steric and electronic properties of the functional group, it has been observed that altering the length of the spacer between the functional group and the olefin has a profound impact on the polymerization. For example, reducing the spacer to 2 carbons from 3 carbons, to 4-amino-1-butene, resulted in a decreased the polymerization activity.[154] Gianni *et al.* also observed this trend for the polymerization of amino-functionalized olefins using Ziegler catalysts.[156,157] Lofgren *et al.* have also reported the increased incorporation of oxygen-functionalized monomers into the polyethylene chain with the increase of the spacer group.[158]

Considering these previous reports and our own results of the polymerization of ethylene in the presence of sterically bulky phosphines, we developed the phosphine with the pendant olefinic substituent, $^tBu_2P(CH_2)_3CHCH_2$. The synthesis of the phosphine-functionalized olefin is illustrated in Figure 4.2.

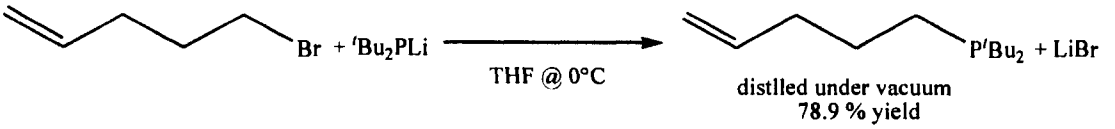


Figure 4.2 Synthesis of $^tBu_2P(CH_2)_3CHCH_2$

4.3.2 Co-polymerizations of 1-Hexene and $^tBu_2P(CH_2)_3CHCH_2$

To investigate the polymerization of $^tBu_2P(CH_2)_3CHCH_2$, co-polymerizations of the monomer with 1-hexene were carried out and compared to the polymerization of 1-hexene. The results are listed in Table 4.1.

Table 4.1 Co-polymerization of 1-Hexene and $^tBu_2P(CH_2)_3CHCH_2$[a]

Ratio 1-Hexene:Phosphine[b]	Isolated Yield[c] (%)	Molecular Weight (M_n)[d]	Incorporation of Phosphine[e] (%)
100:0	94	7980	N/A
99:1	93	7740	Not able to determine
95:5	21	1140	4
90:10	21	2650	5

[a]Polymerization Conditions: Catalyst – $CpTiMe_2(NP^tBu_3)$ (0.16 mmol), 1 equiv. $B(C_6F_5)_3$, polymerization time – 16 hours, polymerization temperature – 0 °C
[b]16 mmol of total monomer
[c]Yield based on total monomer
[d]Determined by GPC
[e]Determined by $^{13}C\{^1H\}$ NMR spectroscopy

These results illustrate that, upon increased concentration of phosphine-functionalized monomer, there was a drastic decrease in the isolated yield of the polymer recovered and the molecular weight of the polymer. Furthermore, attempted homo-polymerizations of the phosphine-functionalized monomer and co-polymerizations with a high phosphine concentration resulted in no isolation of polymer.

The co-polymers produced from the polymerization of 5 and 10 mole percent of $^{t}Bu_2P(CH_2)_3CHCH_2$, resulted in polymers with an approximate 5 % incorporation of the phosphine monomer. A representative example of the $^{13}C\{^{1}H\}$ NMR spectra of the polymers and corresponding peak assignments are shown in Figure 4.3. To estimate the percent incorporation of the phosphine monomer, the ratio of the carbons of the CH_3 of the hexane (B1) and the CH_3 of the ^{t}Bu were compared.

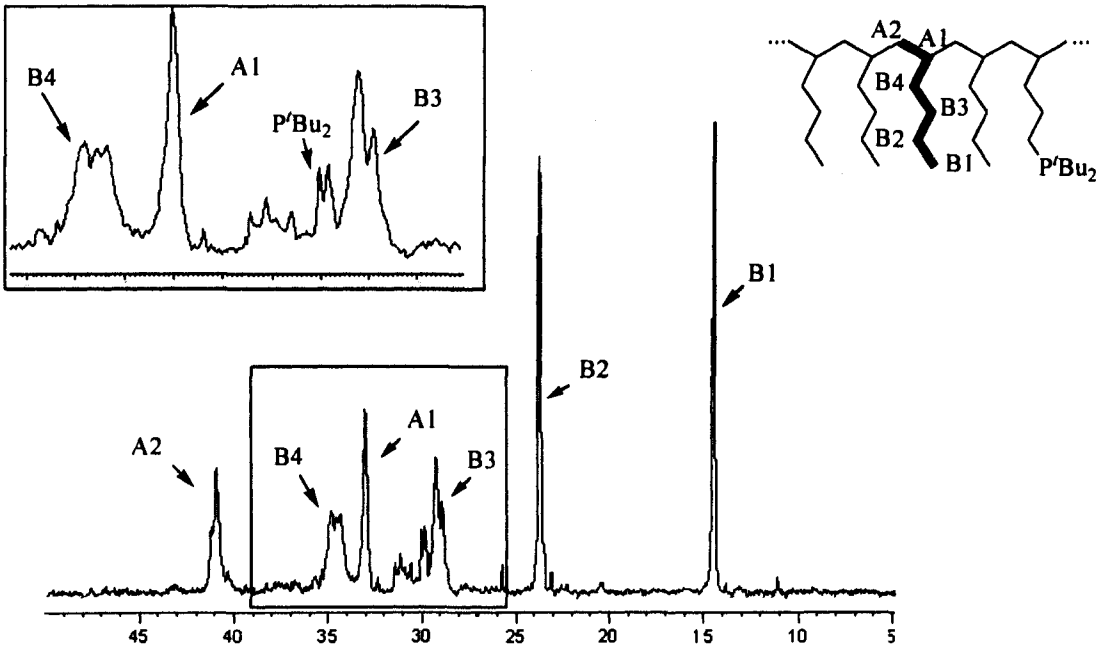


Figure 4.3 $^{13}C\{^{1}H\}$ Peak Assignment of Copolymers

It is clear that addition of the phosphine containing monomer results in a significant decrease in activity, and attempts to homo-polymerize the phosphine functionalized monomer, or polymerizations at high concentrations yielded no polymer. This led us to investigate the potential modes of polymerization inhibition.

4.3.3 Potential Inhibition Pathways

In examining the catalyst system there are three potential inhibition pathways which could result in a decreased activity. These inhibition pathways include 1) reactions with the co-catalyst, causing the co-catalyst to be inactive and unable to produce the cationic Ti center; 2) intermolecular co-ordination or interaction of the phosphine to the cationic Ti center; and 3) intramolecular coordination or interaction of the phosphine. Each of these inhibition pathways was examined and the results discussed.

4.3.3.1 Reactions with the Co-catalysts

To examine the potential for polymerization inhibition due to reactivity of the phosphine monomer and the co-catalyst two strategies were employed. The first strategy entailed investigating the co-polymerizations using other co-catalysts. The second strategy involved studying the effect of adding the phosphine-monomer to a pre-activated catalyst system, in order to inhibit direct interaction of the phosphine with the Lewis acidic co-catalyst.

4.3.3.2 Effect of Different Co-catalysts on Co-polymerizations

The use of three different co-catalysts, $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ and $[Me_2PhNH][B(C_6F_5)_4]$ and the resultant isolated yield of the co-polymerizations was examined and results illustrated below. (Table 4.2)

Table 4.2 Effect of Co-catalyst on Co-polymerization[a]

Co-catalyst	Isolated Yield[b] (%)	Molecular Weight[c]	Incorporation of Phosphine[d] (%)
$B(C_6F_5)_3$	23.2 %	1065	3
$[Ph_3C][B(C_6F_5)_4]$	19.3 %	1125	4
$[Me_2PhNH][B(C_6F_5)_4]$	18.4 %	916	4

[a]Polymerization Conditions: Catalyst – $CpTiMe_2(NP^tBu_3)$ (0.04 mmol), 1 equiv. co-catalyst, 200 equivalents of total monomer, (8 mmol), 1-hexene:phosphine ratio 95:5, polymerization time – 5 hours, polymerization temperature –30 °C
[b]Yield based on total monomer
[c]Determined by GPC
[d]Determined by $^{13}C\{^1H\}$ NMR spectroscopy

These results indicate the isolated yield of polymer is not strongly dependent on the co-catalyst utilized. Therefore, all three co-catalysts could potentially react with the phosphine containing monomer. The potential reactivity of each co-catalyst with the phosphine functionalized monomer is discussed below.

4.3.3.2.1 Reactions of $B(C_6F_5)_3$ with $^tBu_2P(CH_2)_3CHCH_2$

As discussed in previous chapters, even if the sterics of Lewis acid-base systems preclude the formation of classical Lewis acid-base adducts, alternate reactivity can occur. Sterically bulky phosphine have been shown to effect the nucleophilic aromatic substitution of a C_6F_5 aryl ring of $B(C_6F_5)_3$ to give zwitterionic phosphonium-borates of

the form $R_3P(C_6F_4)B(C_6F_5)$ [107,114] Although P^tBu_3 is not known to react with $B(C_6F_5)_3$, a slight decrease in steric bulk (e.g. P^nBu_3 or HP^tBu_2) results in nucleophilic aromatic substitution, to give zwitterions of the form $R_2R'P(C_6F_4)BF(C_6F_5)_2$ R = R' = ^{n}Bu, R = ^{t}Bu, R = H). The reactivity of the phosphine-functionalized monomer with $B(C_6F_5)_3$ is discussed in full detail in Chapter 5.

4.3.3.2.2 Reactions of $[Ph_3C][B(C_6F_5)_4]$ with $^tBu_2P(CH_2)_3CHCH_2$

Although bulky phosphines are known to form traditional acid-base adducts with $[Ph_3C]^+$, the bulky phosphine, P^tBu_3, is known to effect the nucleophilic aromatic substitution of a Ph ring of $[Ph_3C]^+$ to yield, $[^tBu_3PC_6H_4CH(C_6H_5)_2]^+$ as illustrated in Figure 4.4.[159]

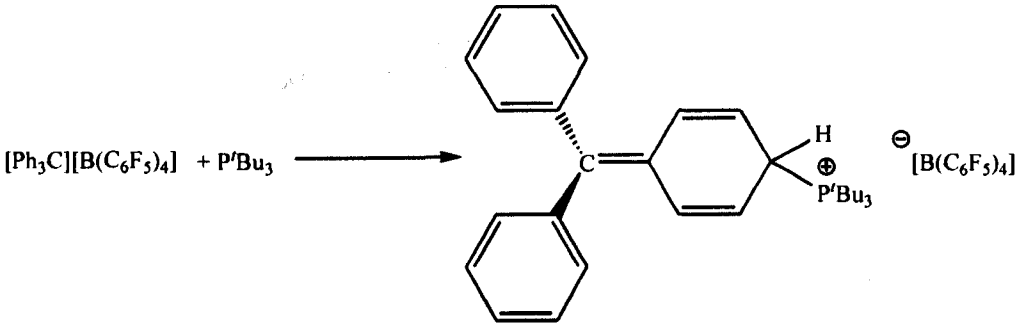


Figure 4.4 Nucleophilic Aromatic Substitution of $[Ph_3C]^+$

It is expected that reactions of $[Ph_3C][B(C_6F_5)_4]$ and $^tBu_2P(CH_2)_3CHCH_2$ will also result in nucleophilic attack at the *para*-position of an aryl ring of the trityl cation, giving the species of the form $[^tBu_2(CH_2CH(CH_2)_3)PC_6H_4CH(C_6H_5)_2][B(C_6F_5)_4]$, Therefore the formation of $[^tBu_2(CH_2CH(CH_2)_3)PC_6H_4CH(C_6H_5)_2][B(C_6F_5)_4]$ could potentially compete

with methyl abstraction of the Ti-Me bond by the trityl cation, and result in the formation of less of the catalytically active Ti cation.

4.3.3.2.3 Reactions of $[Me_2PhNH][B(C_6F_5)_4]$ with $^tBu_2P(CH_2)_3CHCH_2$

Anilinium borate is a protic activator relying on the relatively acidic NH moiety to protonate a metal-alkyl bond in order to generate an active catalyst species. The Me_2PhNH ammonium cation has a pKa of 5.1,[160] therefore in the presence of a stronger base, deprotonation of the NH to give Base-H would likely occur. In this instance the generation of the active metal center would be limited to the acidity of the newly generated Base-H bond. While not determined, it is assumed that the pKa of $^tBu_2P(CH_2)_3CHCH_2$ should fall in between than of P^tBu_3 and P^nBu_3. Considering that both P^tBu_3 and P^nBu_3 have higher pKa's than Me_2PhN and are as a result more basic, one can assume that upon reaction of $^tBu_2P(CH_2)_3CHCH_2$ with $[Me_2PhNH][B(C_6F_5)_4]$, transfer of the proton from N to P would readily occur. Indeed, an independent experiment confirmed the formation of $[^tBu_2P(H)((CH_2)_3CHCH_2)][B(C_6F_5)_4]$, and free amine Me_2PhN. The ^{31}P NMR signal of $[^tBu_2P(H)((CH_2)_3CHCH_2)]$ at 52.5 ppm was sharp indicating little to no exchange of the proton between N and P consistent with the relative pKa values. It was demonstrated in Chapter 2 that $[^tBu_3PH]$ is a poor protic activator due to a relatively strong PH bond. Therefore in the present case it is likely that generation of $[^tBu_2P(H)((CH_2)_3CHCH_2)]$ results in incomplete activation of the metal pre-catalysts and ultimately causes significant decrease in polymer recovered .

4.3.3.3 Control of Phosphine-Co-catalyst Reactivity

To investigate the extent of inhibition due to phosphine-co-catalyst interactions, polymerizations were conducted with $^{t}Bu_2P(CH_2)_3CHCH_2$ added 5 minutes after the formation of the catalytically active species $[CpTiMe(NP^{t}Bu_3)][MeB(C_6F_5)_3]$. Results are listed in Table 4.3.

Table 4.3 Control of Phosphine-Co-catalyst Reactivity Polymerization Results[a]

Ratio 1-Hexene:Phosphine	**Isolated Yield[b] (%)**	**Molecular Weight[c] (M_n)**	**Incorporation of Phosphine[d] (%)**
100:0	98.0	3230	N/A
95:5	58.9	1480	3
90:10	43.6	1590	4
75:25	36.2	1800	Not able to determine

[a]Polymerization Conditions: Catalyst – $CpTiMe_2(NP^{t}Bu_3)$ (0.04 mmol), 1 equiv. co-catalyst, 200 equivalents of total monomer, (8 mmol), 1-hexene:phosphine ratio 95:5, polymerization time – 5 hours, polymerization temperature –30 °C
[b]Yield based on total monomer
[c]Determined by GPC
[d]Determined by $^{13}C\{^{1}H\}$ NMR spectroscopy

As illustrated in the above table the isolated yields of the polymers are significantly higher than those of the polymerizations with $^{t}Bu_2P(CH_2)_3CHCH_2$ present when co-catalyst is added. However, the isolated yield decreases as the amount of $^{t}Bu_2P(CH_2)_3CHCH_2$ is increased. As the concentration is increased to 25 mole % the isolated yield is comparable to the yield of the polymerizations of 1-hexene conducted for 5 minutes (34.6 % yield). Therefore the reactivity of $^{t}Bu_2P(CH_2)_3CHCH_2$ with the co-catalyst is not the only inhibition to polymerization and other pathways should be investigated.

4.3.3.4 Intermolecular of Phosphines to Ti-cation

Another possible inhibition to polymerizations is the intermolecular coordination of the phosphine to the Ti cation shown in Figure 4.5.

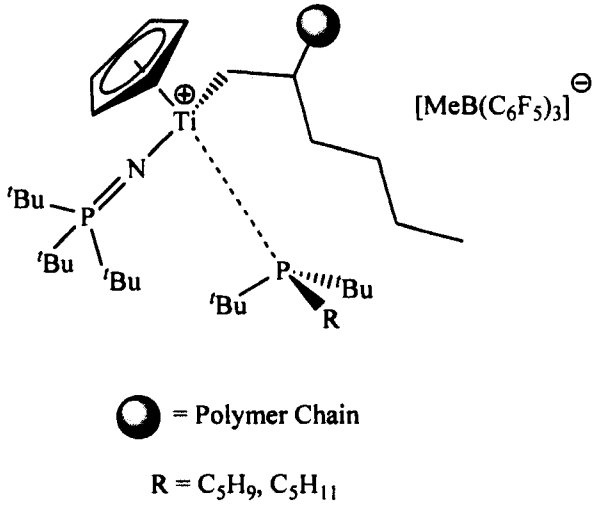


Figure 4.5 Intermolecular Coordination of Phosphine

To investigate this potential inhibition pathway, a series of polymerizations were conducted in the presence of the sterically equivalent phosphine $^tBu_2P(CH_2)_4CH_3$, which contains no olefinic group. The polymerization results are shown in Table 4.4. To ensure that phosphine reactivity with the co-catalyst, $B(C_6F_5)_3$, did not contribute to any reduced polymer recovered, the phosphine was added 5 minutes after the formation of the catalytically active species $[CpTiMe(NP^tBu_3)][MeB(C_6F_5)_3]$.

Table 4.4 1-Hexene Polymerizations with Added $^tBu_2P(CH_2)_4CH_3$[a]

Ratio 1-Hexene:Phosphine	Isolated Yield[b] (%)
100:0	98.0
100:5	64.4
100:10	57.6
100:25	54.3

[a]Polymerization Conditions: Catalyst – $CpTiMe_2(NP^tBu_3)$ (0.04 mmol), 1 equiv. co-catalyst, 200 equivalents of total monomer, (8 mmol), 1-hexene:phosphine ratio 95:5, polymerization time – 5 hours, polymerization temperature –30 °C
[b]Yield based on total monomer

As shown in Table 4.4 and illustrated in Figure 4.6, as the concentration of the phosphine increases there is a decrease in the isolated yield obtained. Also depicted in the graph is the isolated yield of a 5 minute polymerization of 1-hexene with no phosphine added (34.6%).

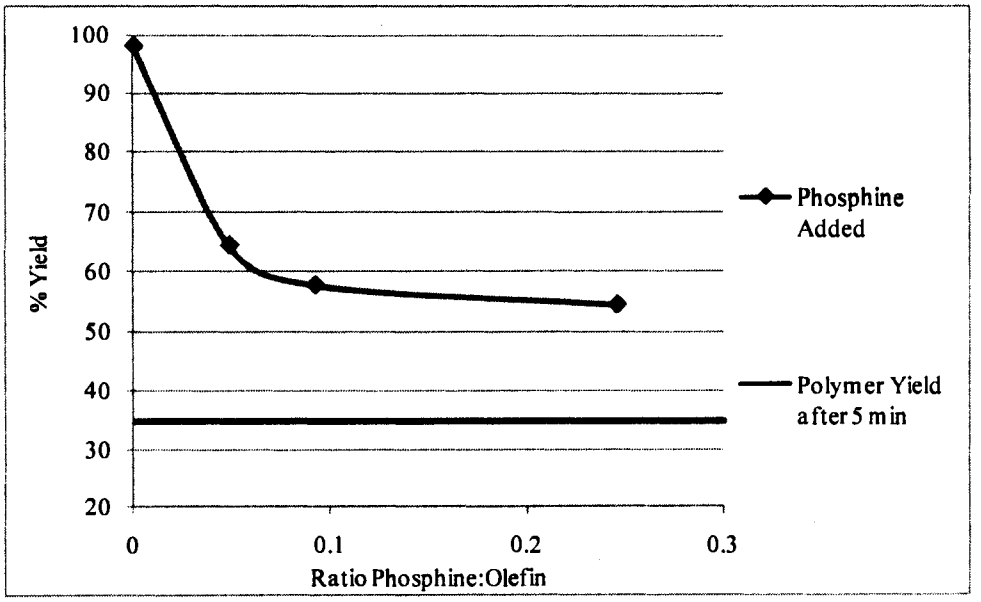


Figure 4.6 1-Hexene Polymerizations with Added $^tBu_2P(CH_2)_4CH_3$

Therefore, the intermolecular coordination of the phosphine to the Ti cation does inhibit polymerization. This result is initially surprising since P^tBu_3 was found not to inhibit ethylene polymerization; however there must be a fine line between a phosphine being small enough to coordinate to the Ti cationic metal center and being large enough to prevent coordination. Additionally, if the Ti cation is indeed interacting with the phosphine, the increased steric hindrance at the metal center may inhibit coordination of the 1-hexene. These results are consistent with the intermolecular coordination of the amine, $^iPr_2N(CH_2)_3CHCH_2$, found to inhibit the 1-hexene polymerizations using $Cp^*_2ZrMe_2/[Me_2PhNH][B(C_6F_5)_4]$ systems.[161]

4.3.3.5 Intramolecular of Phosphines to Ti-cation

There also exists potential for the intramolecular coordination of a phosphine on the polymer chain to interact with the Ti cation as depicted in Figure 4.7. Here an incorporated P chain may be flexible enough to bite back towards the electrophilic P center blocking a site for olefin coordination and insertion.

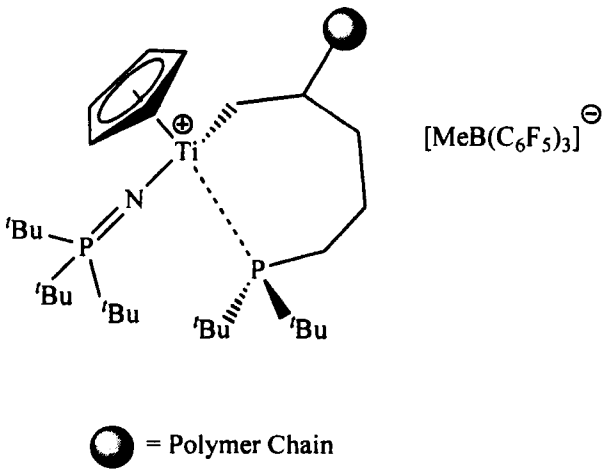


Figure 4.7 Intramolecular Coordination of Phosphine

To investigate the potential intramolecular coordination of the phosphine to the Ti cation, a series of polymerizations were conducted in the presence of $^tBu_2P(CH_2)_3CHCH_2$. The polymerization results are shown in Table 4.5. To ensure that phosphine reactivity with the co-catalyst, $B(C_6F_5)_3$, did not contribute to any reduced polymer recovered, the phosphine was added 5 minutes after the formation of the catalytically active species $[CpTiMe(NP^tBu_3)][MeB(C_6F_5)_3]$.

Table 4.5 Co-polymerization of 1-Hexene and $^tBu_2P(CH_2)_3CHCH_2$[a]

Ratio Olefin:Phosphine	Isolated Yield[b] (%)
100:0	98.0
100:5	53.2
100:10	46.5
100:25	38.5

[a]Polymerization Conditions: Catalyst – $CpTiMe_2(NP^tBu_3)$ (0.04 mmol), 1 equiv. co-catalyst, 200 equivalents of total monomer, (8 mmol), 1-hexene:phosphine ratio 95:5, polymerization time – 5 hours, polymerization temperature –30 °C
[b]Yield based on total monomer

These results were compared to the polymerizations conducted investigating intermolecular coordination. A graphical representation of these polymerization results is shown in Figure 4.8.

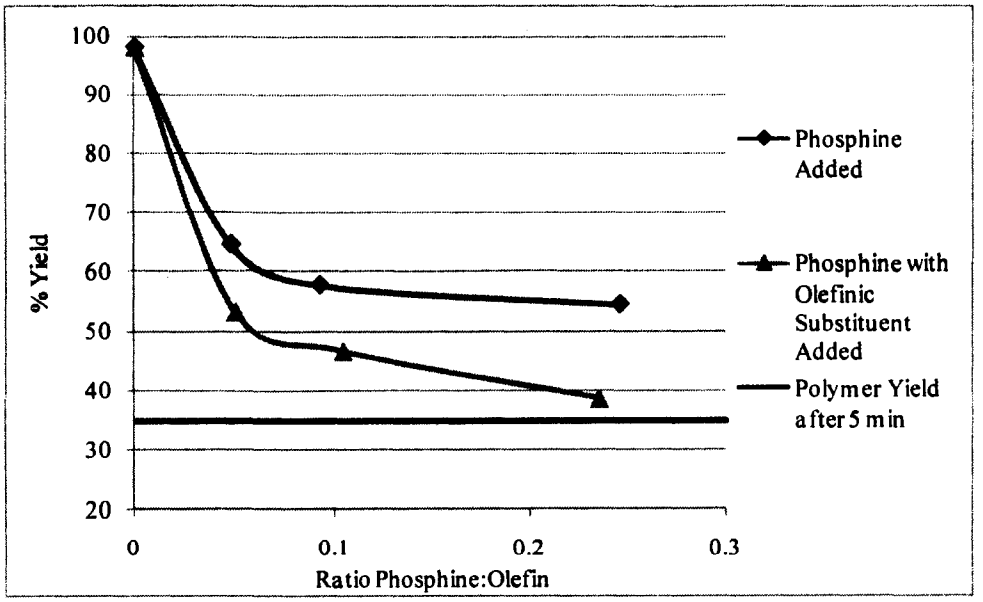


Figure 4.8 Intermolecular vs. Intramolecular Activation

As illustrated above the polymerizations with added $^{t}Bu_2P(CH_2)_3CHCH_2$ had isolated yields less than that of polymerizations with the added $^{t}Bu_2P(CH_2)_4CH_3$. This suggests that intramolecular activation plays a major role in the inhibition. These results are consistent with those observed by Waymouth and co-workers, where the aminopentene, $^{i}Pr_2N(CH_2)_3CHCH_2$, with a polymerizable group, was found to be a more potent inhibitor than the amine, $^{i}Pr_2P(CH_2)_4CH_3$, which lacks an olefinic group.[161]

4.3.3.6 Overview of Polymerization of Pendant Phosphine Monomers

Examination of the results obtained for the co-polymerization of 1-hexene and the phosphine functionalized monomer indicates that the functionality of the monomer results in polymerization inhibition through three pathways. First, interaction of $^{t}Bu_2P(CH_2)_3CHCH_2$ with the co-catalyst competes with catalyst activation, which results in the formation of fewer active sites. Second, the phosphine can coordinate with the cationic Ti center in an intermolecular fashion to inhibit monomer coordination and insertion. Third, the intramolecular interaction of the phosphine on the growing polymer chain also inhibits polymerization.

Considering the pathways of polymerization inhibition there are three strategies typically employed to avoid catalysts deactivation. These must be considered by designing a new phosphine functionalized monomer, in order to achieve higher activities and a greater incorporation of the phosphine moiety: 1) separation of the functional group from the double bond; 2) increasing the steric bulk around functional group, 3) decreasing the nucleophilicity of functional group.

The co-polymerizations of 1-hexene with an longer carbon linker between the phosphine and the olefinic group, the monomer, $^{t}Bu_2P(CH_2)_9CHCH_2$, were conducted to

see if increasing the spacer group affects the polymerization. The co-polymerization results and the comparison to the co-polymerizations using $^{t}Bu_2P(CH_2)_3CHCH_2$, are reported in Table 4.6

Table 4.6 Co-polymerizations of 1-Hexene with $^{t}Bu_2P(CH_2)_3CHCH_2$ and $^{t}Bu_2P(CH_2)_9CHCH_2$[a]

Co-monomer	Isolated Yield[b] (%)	Incorporation of Phosphine[c] (%)
$^{t}Bu_2P(CH_2)_3CHCH_2$	46.5	4
$^{t}Bu_2P(CH_2)_9CHCH_2$	50.6	9

[a]Polymerization Conditions: Catalyst – $CpTiMe_2(NP^{t}Bu_3)$ (0.04 mmol), 1 equiv. co-catalyst, 200 equivalents of total monomer, (8 mmol), 1-hexene:phosphine ratio 90:10, polymerization time – 5 hours, polymerization temperature –30 °C
[b]Yield based on total monomer
[c]Determined by $^{13}C\{^{1}H\}$ NMR spectroscopy

The use of the longer spacer between the phosphine and the olefinic group results in a slight increase in isolated yield and a greater incorporation of the phosphine functionalized monomer. These results are consistent to those of the co-polymerization nitrogen and oxygen containing functional monomers.[158,161] The use of a longer spacer between the functionality and the olefinic group reduces the intramolecular inhibition, as a 13-membered chelate is much less likely than a 7-membered chelate.

In future investigations the use of phosphine functionalized monomers with greater steric bulk and decreased nucleophilicity should be investigated. The use of Mes or *o*-tolyl substituents on the phosphine will result in greater steric protection and a reduced basicity of the phosphine compared to $^{t}Bu_2P(CH_2)_3CHCH_2$.

4.4 Summary and Conclusions

The co-polymerization of 1-hexene and phosphine-functionalized monomers using the $CpMe_2Ti(NP^tBu_3)$ catalyst systems has been demonstrated, albeit at low yields and low phosphine monomer incorporation. The co-polymerizations and homo-polymerizations of the phosphine-functionalized monomers are inhibited by reactivity with the co-catalyst, intermolecular coordination of the phosphine functionality, and intramolecular coordination of the phosphine. Future work to increase the activity of the polymerizations includes altering the sterics and nucleophilicity of the phosphine moiety.

Chapter 5: Reactivity of "Frustrated Lewis Pairs": Three Component Reactions of Phosphine, Borane and Olefins

5.1 Introduction

The formation of Lewis acid-base adducts is a classical concept in chemistry.[162] This idea is fundamental to main group chemistry, the basis of coordination chemistry of the transition metals[163] and the foundation of a variety of both stoichiometric and catalytic organic transformations.[164] In all of these cases, the observed chemistry is predicated on the interaction of a Lewis base with a Lewis acid in a donor-acceptor fashion. In recent work, the Stephan Group has been studying systems in which steric demands preclude such classical donor-acceptor interactions. Examination of sterically hindered phosphines with $B(C_6F_5)_3$ has demonstrated that in the absence of the formation of classical Lewis acid-base adducts novel reaction pathways are available. When the tertiary phosphines, PCy_3 and P^iPr, or the secondary phosphines, HP^tBu_2 and $HPMes_2$ were utilized no simple Lewis acid-base adduct formation was observed.[140] These studies indicate that steric congestion precludes coordination of the phosphine to the borane and that nucleophilic attack by the phosphine at the more accessible, electrophilic *para*-carbon of an arene ring occurs. Thus, substitution occurs with concurrent fluoride transfer to B to yield the zwitterionic compounds, $[R_3P(C_6F_4)BF(C_6F_5)_2]$ (R = Cy or ^{t}Pr) or $[R_2PH(C_6F_4)BF(C_6F_5)_2]$ (R = ^{t}Bu, Mes).[108] Similar reactivity has also been observed by Erker and co-workers in the thermal rearrangement of the phosphorus ylide adduct $(Ph_3PCHPh)B(C_6F_5)_3$ to the *para*-substituted species $[Ph_3PCHPh(C_6F_4)BF(C_6F_5)_2]$.[165] For related phosphine/borane combinations where steric demands are even greater, no

interaction between the Lewis acid and Lewis base was apparent and formation of the zwitterionic phosphonium-borates does not occur.[116,119] The reactivity of $B(C_6F_5)_3$ and phosphines is summarized in Figure 5.1.

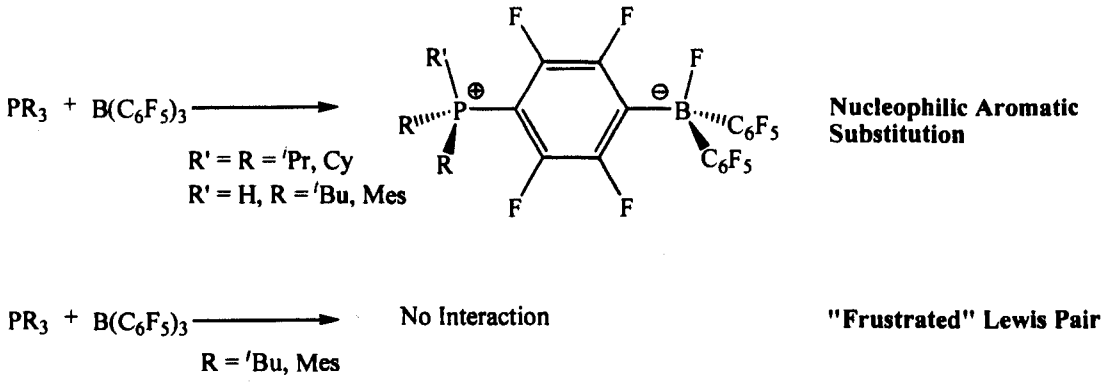


Figure 5.1 Reactivity of $B(C_6F_5)_3$ and Phosphines

In the case of the extremely sterically encumbered phosphines, P^tBu_3 and $PMes_3$, the steric frustration leaves the original Lewis acidity and basicity unquenched, therefore these centers are available for further reactivity. Initial studies showed that exposure of H_2 to simple solutions of the phosphines, P^tBu_3 or $PMes_3$ with $B(C_6F_5)_3$ resulted in heterolytic cleavage of hydrogen.[119]

In this chapter the reactivity of sterically demanding phosphines and $B(C_6F_5)_3$ with olefins to give alkyl-linked phosphonium borates is discussed. Additionally, the reactivity of phosphines containing olefinic substituents with $B(C_6F_5)_3$ is described.

5.2 Experimental

5.2.1 General Considerations

All preparations were completed 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 were purified employing a Grubbs' type column system manufactured by Innovative Technology. ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR spectroscopy were referenced to 85% H_3PO_4, BF_3, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer.

5.2.2 Solvents

Toluene, methylene chloride, hexanes and pentanes were purified employing Grubbs-type column systems manufactured by Innovative Technologies or were distilled from the appropriate drying agents under N_2. Uninhibited THF was purchased from EDM and dried over Na/benzophenone and distilled prior to use. Deuterated bromobenzene (C_6D_5Br), benzene (C_6D_6), and methylene chloride (CD_2Cl_2) were purchased from Cambridge Isotopes Laboratories, dried over Na/benzophenone (C_6D_6) or CaH_2 (C_6D_5Br and CD_2Cl_2), freeze-pump-thaw degassed (3 times) and then vacuum distilled prior to use.

5.2.3 Reagents

Ethylene and propylene was purchased from BOC gases. Ethylene was dried over Q5 copper deoxygenation material and 3 Å molecular sieves. Ethylene and propylene were passed through a dririte gas drying unit prior to use. 1-Hexene was purchased from Aldrich Chemical Company and distilled from Na/benzophenone. $PMes_3$ was purchased from Aldrich Chemical Co.; P^tBu_3, P(*o*-tolyl)$_3$ and HP^tBu_2 were purchased from Strem Chemicals, Inc.; all were used as received. Mes_2PH was prepared as reported in the literature.[166] $B(C_6F_5)_3$, was generously donated by NOVA Chemicals Corp. and used without further purification.

5.2.3.1 Reaction of $B(C_6F_5)_3$ and Phosphines with Olefins

$^tBu_3P(C_2H_4)B(C_6F_5)_3$ (5.1): To a solution of $B(C_6F_5)_3$ (0.499 g, 0.97 mmol) in C_6H_5Br (50 mL) under ethylene purge, was added a solution of $^tBu_3P$ (0.221 g, 1.09 mmol) in C_6H_5Br (2 mL). The resulting solution was purged with ethylene for 1 h and the reaction was stirred under 1 atm of ethylene at room temperature for 16 h. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 and hexanes added to precipitate a white solid. The solid was filtered and washed with hexanes several times and dried *in vacuo*. Yield 0.452 g (63%). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at 25 °C. **^1H NMR** (THF-d_8, 300 MHz, 300 K): δ 1.69-1.94 (br, m, 4H, C_2H_4), 1.43 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz, ^{t}Bu). **$^{11}B\{^1H\}$ NMR** (THF-d_8, 96 MHz, 300 K): δ -13.3. **$^{13}C\{^1H\}$ NMR** (THF-d_8, 75 MHz, 300 K): partial δ

149.1 (dm, $^1J_{C\text{-}F}$ = 238 Hz, *ortho*-C_6F_5), 139.0 (dm, $^1J_{C\text{-}F}$ = 244 Hz, *para*-C_6F_5), 137.57 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *meta*-C_6F_5), 39.9 (d, $^1J_{C\text{-}P}$ = 30 Hz, ^{t}Bu), 29.90 (s, ^{t}Bu), 19.0 (d, $^1J_{C\text{-}P}$ = 30 Hz, PCH_2), 17.6 (br, BCH_2). **^{19}F NMR** (THF-d_8, 282 MHz, 300 K): δ -132.58 (d, 6F, $^3J_{F\text{-}F}$ = 25 Hz, *ortho*-C_6F_5), -164.14 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -167.27 (t, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (THF-d_8, 121 MHz, 300 K): δ 50.0. Anal. Calcd. For $C_{32}H_{31}BF_{15}P$: C, 51.77; H, 4.21. Found: C, 51.92; H, 3.93 %.

^{t}Bu$_3$P(CH(CH$_3$)CH$_2$)B(C$_6$F$_5$)$_3$ (5.2): To a solution of $B(C_6F_5)_3$ (0.473 g, 0.92 mmol) in C_6H_5Br (50 mL) under propylene purge, was added a solution of ^{t}Bu$_3$P (0.258 g, 1.28 mmol) in C_6H_5Br (2 mL). The resulting solution was purged with propylene for 4 hours and the reaction was stirred under 1 atm of propylene at room temperature for 12 h. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 and hexanes added to precipitate a white solid. The solid was filtered and washed with hexane several times and dried *in vacuo*. Yield 0.436 g (63%). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at 25 °C **^{1}H NMR** (THF-d_8, 300 MHz, 300 K): δ 2.72 (br, 1H, PCH), 2.30 (br, 2H, BCH_2), 1.59 (d, 27H, $^3J_{H\text{-}P}$ = 13 Hz, ^{t}Bu), 1.57 (m, 3H, Me). **^{11}B{^{1}H} NMR** (THF-d_8, 96 MHz, 300 K): δ -11.6. **^{13}C{^{1}H} NMR** (THF-d_8, 75 MHz, 300 K): partial δ 149.1 (dm, $^1J_{C\text{-}F}$ = 237 Hz, *ortho*-C_6F_5), 139.1 (dm, $^1J_{C\text{-}F}$ = 230 Hz, *para*-C_6F_5), 137.5 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *meta*-C_6F_5), 41.6 (d, $^1J_{C\text{-}P}$ = 25 Hz, ^{t}Bu), 33.7 (d, $^1J_{C\text{-}P}$ = 22 Hz, PCH), 31.1 (s, ^{t}Bu), 18.92 (s, Me). **^{19}F NMR** (THF-d_8, 282 MHz, 300 K): δ -129.08 (br, s, 6F, *ortho*-C_6F_5), -162.41 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C_6F_5), -165.53 (mt, 6F, *meta*-C_6F_5). **^{31}P{^{1}H} NMR** (THF-d_8, 121 MHz, 300 K): δ 56.9. Anal. Calcd. For $C_{33}H_{33}BF_{15}P$: C, 52.40; H, 4.40. Found: C, 52.14; H, 4.36 %.

^{t}Bu$_3$P(CH(C$_4$H$_9$)CH$_2$)B(C$_6$F$_5$)$_3$ (5.3): To a solution of B(C$_6$F$_5$)$_3$ (0.496 g, 0.97 mmol) in 1-hexene (30 mL) was added a solution of ^{t}Bu$_3$P (0.211 g, 1.04 mmol) in 1-hexene (2 mL) was added. The solution was stirred at room temperature for 12 h, during which time a white precipitate formed. The solid was filtered and washed with pentanes and dried *in vacuo*. Yield 0.428 g (55%). Crystals suitable for X-ray diffraction were grown from a layered CH$_2$Cl$_2$/pentane/C$_6$D$_6$ solution at 25 °C. **^{1}H NMR** (THF-d$_8$, 300 MHz, 300 K): δ 2.84 (br m, 1H, P-C*H*), 2.40 (br m, 1H, CHC*H*$_2$), 2.12 (br m, 2H, BC*H*$_2$), 1.63 (d, 27H, $^3J_{H\text{-}P}$ = 13 Hz, ^{t}Bu), 1.53 (br m, 1H, CHC*H*$_2$), 1.02-1.34 (br m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.78 – 0.93 (m, 2H, *CH*$_2$*Me)*, 0.69 (t, 3H, $^3J_{H\text{-}H}$ = 7 Hz, *Me)*. **^{11}B{^{1}H} NMR** (THF-d$_8$, 96 MHz, 300 K): δ -13.0. **^{13}C{^{1}H} NMR** (THF-d$_8$, 75 MHz, 300 K): partial δ 149.5 (dm, $^1J_{C\text{-}F}$ = 237 Hz, *ortho*-C$_6$F$_5$), 139.2 (dm, $^1J_{C\text{-}F}$ = 244 Hz, *para*-C$_6$F$_5$), 137.8 (dm, $^1J_{C\text{-}F}$ = 256 Hz, *meta*-C$_6$F$_5$), 42.1 (d, $^1J_{C\text{-}P}$ = 24 Hz, ^{t}Bu), 40.1 (d, $^1J_{C\text{-}P}$ = 18 Hz, P*C*H), 33.9 (s, CH*C*H$_2$), 33.1 (d, $^3J_{C\text{-}P}$ = 10 Hz, CH$_2$*C*H$_2$CH$_2$), 31.5 (s, ^{t}Bu), 23.9 (s, *C*H$_2$Me), 14.0 (s, *Me*). **^{19}F NMR** (THF-d$_8$, 282 MHz, 300 K): δ -129.31 (br s, 2F, *ortho*-C$_6$F$_5$), - 130.66 (br s, 4F, *ortho*-C$_6$F$_5$), -164.22 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *para*-C$_6$F$_5$), -167.42 (t, 6F, $^3J_{F\text{-}F}$ = 23 Hz, *meta*-C$_6$F$_5$). **^{31}P{^{1}H} NMR** (THF-d$_8$, 121 MHz, 300 K): δ 58.3. Anal. Calcd. For C$_{36}$H$_{39}$BF$_{15}$P: C, 54.15; H, 4.92. Found: C, 53.93; H, 4.64%.

Mes$_2$PH(CH(C$_4$H$_9$)CH$_2$)B(C$_6$F$_5$)$_3$ (5.4): To a solution of B(C$_6$F$_5$)$_3$ (0.243 g, 0.48 mmol) in 1-hexene (10 mL) was added a solution of Mes$_2$PH (0.127 g, 0.47 mmol) in hexanes (2 mL). The solution was stirred at room temperature for 12 hours, during which time a white precipitate formed. The solid was filtered and washed with pentanes and dried *in*

vacuo. Yield 0.272 g (66.8%). Crystals suitable for X-ray diffraction were grown from a CH_2Cl_2/pentane solution at -35 °C. **^{1}H NMR** (CD_2Cl_2, 300 MHz, 300 K) δ: 7.22 (dd, 1H, $^1J_{H\text{-}P}$ = 460 Hz, $^3J_{H\text{-}H}$ = 9 Hz, P-*H*), 7.02 (br s, 4H, C_6H_2) 2.76 (br m, 1H, P-C*H*), 2.36 (s, 6H, C_6H_2*Me*-2,6), 2.35 (s, 6H, C_6H_2*Me*-2,6), 2.31 (s, 6H, C_6H_2*Me*-4), 1.93 (br m, 1H, P-CH-CH_2-CH_2-CH_2-CH_3), 1.65 (br m, 1H, P-CH-CH_2-CH_2-CH_2-CH_3), 1.30 (br m, 2H, B-CH_2), 0.89 (br m, 2H, P-CH-CH_2-CH_2-CH_2-CH_3), 0.73 (m, 2H, P-CH-CH_2-CH_2-CH_2-CH_3), 0.54 (t, 3H, $^3J_{H\text{-}H}$ = 7 Hz, P-CH-CH_2-CH_2-CH_2-CH_3). . **^{11}B{^{1}H} NMR** (CD_2Cl_2, 96 MHz, 300 K) δ: -13.6 (s). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 75 MHz, 300 K) partial δ: 148.7 (dm, $^1J_{C\text{-}F}$ = 237 Hz, *ortho*-C_6F_5), 146.2 (br s, *para*-$C_6H_2Me_3$), 144.0 (d, $^2J_{C\text{-}P}$ = 9 Hz, *ortho*-$C_6H_2Me_3$), 143.7 (d, $^2J_{C\text{-}P}$ = 9 Hz, *ortho*-$C_6H_2Me_3$), 138.7 (dm, $^1J_{C\text{-}F}$ = 244 Hz, *para*-C_6F_5), 137.2 (dm, $^1J_{C\text{-}F}$ = 256 Hz, *meta*-C_6F_5), 132.4 (d, $^3J_{C\text{-}P}$ = 10 Hz, *meta*-$C_6H_2Me_3$), 132.2 (d, $^3J_{C\text{-}P}$ = 10 Hz, *meta*-$C_6H_2Me_3$), 38.7 (d, $^1J_{C\text{-}P}$ = 27 Hz, P-*C*H-CH_2-CH_2-CH_2-CH_3), 31.4 (s, P-CH-*C*H_2-CH_2-CH_2-CH_3), 31.3 (d, $^3J_{C\text{-}P}$ = 5 Hz, P-CH-CH_2-*C*H_2-CH_2-CH_3), 23.1 (d, $^3J_{C\text{-}P}$ = 6 Hz, C_6H_2*Me*-2,6), 22.9 (s, P-CH-CH_2-CH_2-*C*H_2-CH_3), 22.7 (d, $^3J_{C\text{-}P}$ = 6 Hz, C_6H_2*Me*-2,6), 21.5 (s, C_6H_2*Me*-4), 13.66 (s, P-CH-CH_2-CH_2-CH_2-*C*H_3). **^{19}F NMR** (CD_2Cl_2, 282 MHz, 300 K) δ: -131.86 (d, 6F, $^3J_{F\text{-}F}$ = 23 Hz, *ortho*-C_6F_5), -163.20 (t, 3F, $^3J_{F\text{-}F}$ = 23 Hz, *para*-C_6F_5), - 166.86 (t, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C6F5). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz, 300 K) δ: 5.3 (s).

5.2.3.2 Synthesis of Phosphines with Pendant Olefinic Substituents

$Mes_2PCH_2CH_2CH_2CHCH_2$ – To a solution of Mes_2PLi (1.532 g, 5.66 mmol) in THF (50 mL) a solution of $BrCH_2CH_2CH_2CHCH_2$ (0.902 g, 6.05 mmol) in THF (5 mL) was added. The solution was stirred at room temperature for 14 hours. The solvent was

removed *in vacuo* and hexanes was added to precipitate LiBr. The solution was filtered through a celite plug and the solvent removed *in vacuo* to yield bright yellow oil. Yield 0.712 g (37.2%). **^{1}H NMR** (C_6D_6, 300 MHz, 300 K) δ: 6.69 (d, 4H, $^4J_{H\text{-}P}$ = 2 Hz, $C_6H_2Me_3$), 5.56 – 5.69 (m, 1H, $PCH_2CH_2CH_2CHCH_2$), 4.90 – 4.97 (m, 2H, $PCH_2CH_2CH_2CHCH_2$), 2.44 – 2.49 (m, 2H, $PCH_2CH_2CH_2CHCH_2$), 2.38 (s, 12H, C_6H_2Me-2,6), 2.08 (s, 6H, C_6H_2Me-4), 1.98 – 2.06 (m, 2H, $PCH_2CH_2CH_2CHCH_2$), 1.44 – 1.52 (m, 2H, $PCH_2CH_2CH_2CHCH_2$). **^{13}C{^{1}H} NMR** (C_6D_6, 75 MHz, 300 K) δ: 142.1 (d, $^2J_{C\text{-}P}$ = 13 Hz, *ortho*-$C_6H_2Me_3$), 138.4 (s, *para*-$C_6H_2Me_3$), 137.3 (s, $PCH_2CH_2CH_2CHCH_2$), 134.0 (d, $^1J_{C\text{-}P}$ = 23 Hz, *ipso*-$C_6H_2Me_3$), 130.3 (s, *meta*-$C_6H_2Me_3$), 115.0 (s, $PCH_2CH_2CH_2CHCH_2$), 35.5 (d, $^3J_{C\text{-}P}$ = 15 Hz, $PCH_2CH_2CH_2CHCH_2$), 27.7 (d, $^2J_{C\text{-}P}$ = 15 Hz, $PCH_2CH_2CH_2CHCH_2$), 26.9 (d, $^1J_{C\text{-}P}$ = 22 Hz, $PCH_2CH_2CH_2CHCH_2$), 23.3 (d, $^3J_{C\text{-}P}$ = 15 Hz, C_6H_2Me-2,6), 20.7 (s, C_6H_2Me-4). **^{31}P{^{1}H} NMR** (C_6D_6, 121 MHz, 300 K) δ: -22.1(s).

^{t}Bu$_2$PCH$_2$CHCH$_2$: ^{t}Bu$_2$PCl (2.410 g, 13.33 mmol) was added dropwise to a solution CH_2CHCH_2Br (13.33 mmol) in 50 mL of diethyl ether. The solution was refluxed for 16 hrs, filtered through celite, and volatiles removed *in vacuo* to give a clear liquid. Yield 2.279 g (91.7 %) **^{1}H NMR** (C_6D_6, 300 MHz, 300 K) δ: 5.95 – 6.13 (m, 1H, PCH_2CHCH_2), 4.96 – 5.13 (m, 2H, PCH_2CHCH_2), 2.19 – 2.24 (m, 2H, PCH_2CHCH_2), 1.08 (d, 18H, $^3J_{H\text{-}P}$ = 11 Hz, P^{t}Bu$_2$). **^{13}C{^{1}H} NMR** (C_6D_6, 75 MHz, 300 K) δ: 139.3 (d, $^2J_{C\text{-}P}$ = 18 Hz, PCH_2CHCH_2), 115.3 (d, $^3J_{C\text{-}P}$ = 11 Hz, PCH_2CHCH_2), 32.0 (d, $^1J_{C\text{-}P}$ = 24 Hz, P^{t}Bu$_2$), 30.2 (d, $^2J_{C\text{-}P}$ = 13 Hz, P^{t}Bu$_2$), 27.9 (d, $^1J_{C\text{-}P}$ = 23 Hz, PCH_2CHCH_2). **^{31}P{^{1}H} NMR** (C_6D_6, 121 MHz, 300 K) δ: 27.5 (s).

5.2.3.3 Reactions of $B(C_6F_5)_3$ and Phosphines with Pendant Olefinic Substituents

$^tBu_2PCH(C_3H_6)CH_2B(C_6F_5)_3$ (5.5): To a solution of $B(C_6F_5)_3$ (0.704 g, 1.37 mmol) in CH_2Cl_2 (20 mL), $^tBu_2PCH_2CH_2CH_2CHCH_2$ (0.314 g, 1.47 mmol) was added. The solution was stirred overnight and the solvent removed *in vacuo*. The residue was dissolved in 3 mL of CH_2Cl_2 and pentanes was added to precipitate a white solid. The solid was filtered and washed with pentanes several times and dried *in vacuo*. Yield 0.932 g (93.7%). **^1H NMR** (CD_2Cl_2, 300 MHz, 300 K) δ: 2.78 (br m, 1H, P-CH), 1.95 – 2.30 (br m, 6H, B-CH_2, $PCH_2CH_2CH_2CH$), 1.37 (d, 9H, $^3J_{H-P}$ = 15 Hz, $PtBu_2$), 1.41 – 1.53 (br, m, 2H, $PCH_2CH_2CH_2CH$), 1.22 (d, 18H, $^3J_{H-P}$ = 15 Hz, P^tBu_2). **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2, 96 MHz, 300 K) δ: -13.7 (s). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 75 MHz, 300 K) partial δ:148.8 (dm, $^1J_{C-F}$ = 234 Hz, ortho-C_6F_5), 138.7 (dm, $^1J_{C-F}$ = 245 Hz, para-C_6F_5), 137.4 (dm, $^1J_{C-F}$ = 233 Hz, meta-C_6F_5), 40.2 (d, $^1J_{C-P}$ = 32 Hz, $PCH(C_3H_4)$), 36.2 (d, $^1J_{C-P}$ = 29 Hz, P^tBu_2), 34.8 (d, $^1J_{C-P}$ = 32 Hz, P^tBu_2), 33.2 (s, $PCH_2CH_2CH_2CH$), 28.1 (s, P^tBu_2), 27.3 (s, P^tBu_2), 25.8 (s, $PCH_2CH_2CH_2CH$), 18.7 (d, $^1J_{C-P}$ = 44 Hz, $PCH_2CH_2CH_2CH$). **^{19}F NMR** (CD_2Cl_2, 282 MHz, 300 K) δ: -131.71 (d, 6F, $^3J_{F-F}$ = 23 Hz, ortho-C_6F_5), -163.24 (t, 3F, $^3J_{F-F}$ = 20 Hz, para-C_6F_5), -166.73 (t, 6F, $^3J_{F-F}$ = 20 Hz, meta-C6F5). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 121 MHz, 300 K) δ: 62.3 (s). Anal. Calcd. For $C_{31}H_{27}BF_{15}P$: C, 51.26; H, 3.75; Found: C, 51.26; H, 3.64 %.

$Mes_2PCH(C_3H_4)CH_2B(C_6F_5)_3$ (5.6): To a solution of $B(C_6F_5)_3$ (0.155 g, 0.30 mmol) in CH_2Cl_2 (30 mL), $Mes_2PCH_2CH_2CH_2CHCH_2$ (0.095 g, 0.28 mmol) was added. The solution was refluxed for 72 hours. The solvent was removed *in vacuo*, the residue was dissolved in 3 mL of CH_2Cl_2 and pentanes was added to precipitate a white solid. The

solid was filtered and washed with pentanes several times and dried *in vacuo*. Yield 0.124 g (52.1%). **^{1}H NMR** (CD_2Cl_2, 300 MHz, 300 K) δ: 6.90 – 6.98 (br m, 4H, $C_6H_2Me_3$), 3.50 (m, 1H, $PCH_2CH_2CH_2CH$), 3.32 (br m, 1H, $PCH_2CH_2CH_2CH$), 2.32 – 2.43 (br m, 3H, $PCH_2CH_2CH_2CH$), 2.30 (s, 3H, C_6H_2Me-4), 2.25 (s, 3H, C_6H_2Me-4), 1.85 – 2.22 (br m, 16H, C_6H_2Me-2,6, B-CH_2, $PCH_2CH_2CH_2CH$). **^{11}B{^{1}H} NMR** (CD_2Cl_2, 96 MHz, 300 K) δ:-13.7. **^{13}C{^{1}H} NMR** (CD_2Cl_2, 75 MHz, 300 K) partial δ: 148.6 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *ortho*-C_6F_5), 145.0 (s, *ortho*-$C_6H_2Me_3$), 145.0 (s, *ortho*-$C_6H_2Me_3$), 144.5 (s, *ortho*-$C_6H_2Me_3$), 144.5 (s, *ortho*-$C_6H_2Me_3$), 141.9 (s, *para*-$C_6H_2Me_3$), 141.8 (s, *para*-$C_6H_2Me_3$), 138.6 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *para*-C_6F_5), 137.2 (dm, $^1J_{C\text{-}F}$ = 257 Hz, *meta*-C_6F_5), 133.0 (s, *meta*-$C_6H_2Me_3$), 132.9 (s, *meta*-$C_6H_2Me_3$), 132.4 (s, *meta*-$C_6H_2Me_3$), 132.2 (s, *meta*-$C_6H_2Me_3$), 41.7 (d, $^1J_{C\text{-}P}$ = 33 Hz, $PCH_2CH_2CH_2CH$), 32.1 (d, $^1J_{C\text{-}P}$ = 22 Hz, $PCH_2CH_2CH_2CH$), 30.7 (d, $^2J_{C\text{-}P}$ = 10 Hz, $PCH_2CH_2CH_2CH$), 24.3 (d, $^2J_{C\text{-}P}$ = 10 Hz, $PCH_2CH_2CH_2CH$), 22.9 (s, C_6H_2Me-2,6), 22.8 (s, C_6H_2Me-2,6), 21.3 (s, C_6H_2Me-4), 21.1 (s, C_6H_2Me-4). **^{19}F NMR** (CD_2Cl_2, 282 MHz, 300 K) δ: -132.02 (d, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *ortho*-C_6F_5), -163.47 (t, 3F, $^3J_{F\text{-}F}$ = 25 Hz, *para*-C_6F_5), -166.86 (t, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *meta*-C6F5). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz, 300 K) δ: 52.7(s). Anal. Calcd. For $C_{41}H_{31}BF_{15}P$: C, 57.9; H, 3.67. Found: C, 57.63; H, 3.63 %.

^{t}Bu$_2$P(CH$_2$CHCH$_2$)C$_6$F$_4$BF(C$_6$F$_5$)$_2$ (5.7): To a solution of $B(C_6F_5)_3$ (0.253 g, 0.49 mmol) in CH_2Cl_2 (10 mL), ^{t}Bu$_2$PCH$_2$CHCH$_2$ (0.094 g, 0.50 mmol) was added. The solution was stirred overnight and the solvent removed *in vacuo*. The residue was dissolved in 3 mL of CH_2Cl_2 and hexanes was added to precipitate a white solid. The solid was filtered and washed with pentanes several times to give a white solid which was dried *in vacuo*. Yield 0.176 g (51.4 %). **^{1}H NMR** (CD_2Cl_2, 300 MHz, 300 K) δ: 5.75 –

5.83 (br m, 1H, $Bu_2PCH_2CHCH_2$), 5.58 – 5.66 (m, 2H, $Bu_2PCH_2CHCH_2$), 3.58 – 3.61 (br m, 2H, $Bu_2PCH_2CHCH_2$), 1.56 (d, 18H, $^3J_{H-P}$ = 15 Hz, P^tBu_2). **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2, 96 MHz, 300 K) δ: -0.5 (d, $^1J_{B-F}$ = 62 Hz). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 75 MHz, 300 K) partial δ: 148.4 (dm, $^1J_{C-F}$ = 237 Hz, *C*F), 139.6 (dm, $^1J_{C-F}$ = 245 Hz, *C*F), 137.3 (dm, $^1J_{C-F}$ = 257 Hz, *C*F), 125.5 – 125.7 (m, PCH_2CHCH_2), 38.9 (d, $^1J_{C-P}$ = 30 Hz, P^tBu_2), 27.8 (s, P^tBu_2), 24.9 (dd, $^1J_{C-P}$ = 33 Hz, $^3J_{C-F}$ = 13 Hz, PCH_2CHCH_2). **^{19}F NMR** (CD_2Cl_2, 282 MHz, 300 K) δ: -123.14 - -122.94 (m, 1F, C_6F_4), -128.43 (s, 1F, C_6F_4), -128.98 (s, 1F, C_6F_4), -131.63 - -131.51 (m, 1F, C_6F_4), -135.90 (t, 4F, $^3J_{F-F}$ = 14 Hz, *ortho*-C_6F_5), -161.85 (t, 2F, $^3J_{F-F}$ = 20 Hz , *para*-C_6F_5), -166.90 - -166.72 (m, 4F, *meta*-C_6F_5), -193.13 (br d, 1F, $^1J_{F-B}$ = 76 Hz, B*F*). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 121 MHz, 300 K) δ: 51.7 (s).

$^tBu_2P((CH_2)_9CHCH_2)C_6F_4BF(C_6F_5)_2$ (5.8): To a solution of $B(C_6F_5)_3$ (0.254 g, 0.50 mmol) in CH_2Cl_2 (10 mL), $^tBu_2P(CH_2)_9CHCH_2$ (0.156 g, 0.52 mmol) was added. The solution was stirred overnight and the solvent removed *in vacuo*. The residue was dissolved in 3 mL of CH_2Cl_2 and hexanes was added to precipitate an off-white solid. The solid was filtered and washed with pentanes several times to give a white solid which was dried *in vacuo*. Yield 0.198 g (50.0 %). **^1H NMR** (CD_2Cl_2, 300 MHz, 300 K) δ: 5.74 – 5.88 (m, 1H, $^tBu_2P(CH_2)_9CHCH_2$), 4.89 – 5.01 (m, 2H, $^tBu_2P(CH_2)_9CHCH_2$), 2.51 -2.63 (br m, 2H, $^tBu_2P(CH_2)_9CHCH_2$), 1.99 – 2.08 (br m, 2H, $^tBu_2P(CH_2)_9CHCH_2$), 1.62 -1.79 (br, m, 2H, $^tBu_2P(CH_2)_9CHCH_2$), 1.51 (d, 18H, $^3J_{H-P}$ = 13 Hz, $^tBu_2$), 1.25 – 1.36 (br, 12H, $^tBu_2P(CH_2)_9CHCH_2$). **$^{11}B\{^1H\}$ NMR** (CD_2Cl_2, 96 MHz, 300 K) δ: -0.1 (br). **$^{13}C\{^1H\}$ NMR** (CD_2Cl_2, 75 MHz, 300 K) partial δ: 148.4 (dm, $^1J_{C-F}$ = 238 Hz, *C*F), 139.7 (s, $^tBu_2P(CH_2)_9CHCH_2$), 139.5 (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 137.1 (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 114.3 (s, $^tBu_2P(CH_2)_9CHCH_2$), 38.3 (d, $^1J_{C-P}$ = 32 Hz, $^tBu_2$), 34.2 (s,

$^{t}Bu_2P(CH_2)_9CHCH_2$), 32.1 (s, $^{t}Bu_2P(CH_2)_9CHCH_2$), 31.9 (s, $^{t}Bu_2P(CH_2)_9CHCH_2$), 29.9 (s, $^{t}Bu_2P(CH_2)_9CHCH_2$), 29.5 (s, $^{t}Bu_2P(CH_2)_9CHCH_2$), 29.4 (s, $^{t}Bu_2P(CH_2)_9CHCH_2$), 29.2 (s, $^{t}Bu_2P(CH_2)_9CHCH_2$), 27.9 (s, $^{t}Bu_2$), 20.0 (dd, $^{1}J_{C\text{-}P}$ = 40 Hz, $^{3}J_{C\text{-}F}$ = 13 Hz, $^{t}Bu_2P(CH_2)_9CHCH_2$). **^{19}F NMR** (CD_2Cl_2, 282 MHz, 300 K) δ: -119.93 – -119.73 (m, 1F, C_6F_4), -125.24 (s, 1F, C_6F_4), -125.82 (s, 1F, C_6F_4), -130.28 – -130.06 (m, 1F, C_6F_4), -132.54 (t, 4F, $^{3}J_{F\text{-}F}$ = 12 Hz, *ortho*-C_6F_5), -158.28 (t, 2F, $^{3}J_{F\text{-}F}$ = 20 Hz , *para*-C_6F_5), -163.78 – -163.22 (m, 4F, *meta*-C_6F_5), -190.87 (br s). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121 MHz, 300 K) δ: 54.9 (s).

Table 5.1 Selected NMR Data

	δ ^{31}P	δ ^{11}B	^{19}F $\Delta_{p\text{-}m}$*	δ ^{19}F (*o*-F, *p*-F, *m*-F)
Starting Materials				
$B(C_6F_5)_3$[167]		59	18.2	-128.5, -143.1, -161.3
P^tBu_3[a]	62.1			
$HPMes_2$[b]	-92.7			
$^tBu_2P(CH_2)_3CHCH_2$[b]	27.8			
$Mes_2PCH_2CH_2CH_2CHCH_2$[b]	-22.1			
$^tBu_2PCH_2CHCH_2$[b]	27.5			
$^tBu_2P(CH_2)_9CHCH_2$[b]	27.8			
Reaction of $B(C_6F_5)_3$ and phosphines with olefins				
$^tBu_3P(C_2H_4)B(C_6F_5)_3$ (**5.1**)[c]	50.0	-13.3	3.2	-132.6, -164.1, -167.3
$^tBu_3P(CH(CH_3)CH_2)B(C_6F_5)_3$ (**5.2**)[c]	56.9	-11.6	3.1	-129.1, -162.4, -165.5
$^tBu_3P(CH(C_4H_9)CH_2)B(C_6F_5)_3$ (**5.3**)[c]	58.3	-13.0	3.2	-129.3, -130.6, -164.2, -167.4
$Mes_2PH(CH(C_4H_9)CH_2)B(C_6F_5)_3$ (**5.4**)[c]	5.4	-13.7	3.7	-131.9, -163.2, -166.9
Reaction of $B(C_6F_5)_3$ and phosphines with pendant olefinic substituents				
$^tBu_2PCH(C_3H_6)CH_2B(C_6F_5)_3$ (**5.5**)[d]	62.4	-13.8	3.5	-131.7, -163.2, -166.7
$Mes_2PCH(C_3H_4)CH_2B(C_6F_5)_3$ (**5.6**)[d]	52.8	-13.7	3.4	-132.0, -163.5, -166.9
$^tBu_2P(CH_2CHCH_2)C_6F_4BF(C_6F_5)_2$ (**5.7**)[d]	51.8	-0.5	5.0	-123.0, -128.4, -129.0, -131.6, -135.9, -161.9, -166.8, -193.1
$^tBu_2P((CH_2)_9CHCH_2)C_6F_4BF(C_6F_5)_2$ (**5.8**)[d]	55.0	-0.2	5.2	-119.8, -125.2, -125.8, -130.1, -132.5, -158.3, -163.5, -190.9

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

5.2.4 X-ray Data

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[168] on a Siemens SMART System CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). 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[169] and absorption corrections were applied using SADABS.[170] 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.[171] 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 compound **5.3** disordered CH_2Cl_2 solvent molecules were removed using the 'squeeze' command in PLATON.[172,173] All ORTEP figures are shown with ellipsoids at 30%.

Table 5.2 Selected Crystallographic Data for Compounds 5.1, 5.2, 5.3

Crystal	5.1	5.2	5.3
Formula	$C_{32}H_{31}BF_{15}P$	$C_{33}H_{33}BF_{15}P$	$C_{36}H_{38}BF_{15}P$
Formula weight	742.35	756.37	797.44
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	P-1
a(Å)	11.9532(14)	9.6037(15)	11.352(4)
b(Å)	15.3319(18)	11.2601(18)	11.609(4)
c(Å)	18.729(2)	15.519(3)	15.623(5)
α(°)	90	100.501(2)	111.445(4)
β(°)	107.436(2)	91.834(2)	99.753(4)
γ(°)	90	95.109(2)	93.350(4)
V (Å^3)	3274.7(7)	16.41.5(5)	18.72.4(11)
Z	4	2	2
d(calc) g cm^{-1}	1.506	1.530	1.414
Abs coeff, ε, cm^{-1}	0.193	0.194	0.174
Data collected	31010	4867	17977
Data $F_o^2>3\sigma(F_o^2)$	5758	1319	6576
Variables	546	451	486
R^a	0.0452	0.0638	0.0483
R_w^b	0.1045	0.1746	0.1357
Goodness of Fit	1.017	1.054	1.066

This data was collected at 25°C with Mo Kα radiation (λ = 0.71073 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 5.3 Selected Crystallographic Data for Compounds 5.4 and 5.5

Crystal	**5.4-CH_2Cl_2**	**5.5**
Formula	$C_{43}H_{37}BF_{15}PCl_2$	$C_{31}H_{27}BF_{15}P$
Formula weight	916.77	726.31
Crystal system	P-1	$P2_1$
Space group	Triclinic	Monoclinic
a(Å)	11.987(20)	14.994(3)
b(Å)	12.74(2)	12.770(2)
c(Å)	17.13(3)	16.538(3)
α(°)	106.12(2)	90
β(°)	101.06(2)	94.449(3)
γ(°)	109.00(2)	90
V ($Å^3$)	2259(6)	3157.1(9)
Z	2	4
d(calc) g cm^{-1}	1.399	1.528
Abs coeff, ε, cm^{-1}	0.271	0.198
Data collected	19859	29773
Data $F_o^2>3\sigma(F_o^2)$	7871	11111
Variables	571	865
R^a	0.0701	0.0838
R_w^b	0.1788	0.1934
Goodness of Fit	1.036	1.006

This data was collected at 25°C with Mo Kα radiation (λ = 0.71073 Å).
$^aR=\Sigma(F_o-F_c)/\Sigma F_o$ $^bR_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{½}$

5.3 Results and Discussion

5.3.1 Reaction of $B(C_6F_5)_3$ and Tertiary Phosphines with Olefins

A bromobenzene solution containing the "frustrated" Lewis pair combination of P^tBu_3 and $B(C_6F_5)_3$ was purged with ethylene and sealed under 1 atm of ethylene at 25 °C. Over the course of several hours, a colorless precipitate **5.1** formed, which was isolated by filtration in 63% yield. The $^{31}P\{^1H\}$ NMR spectrum of **5.1** showed a singlet resonance at 50.1 ppm while the corresponding $^{11}B\{^1H\}$ NMR signal was observed at -13.3 ppm. The ^1H NMR spectrum of **5.1** showed broad multiplets at 1.69-1.94 ppm. These data strongly suggest the presence of phosphonium and borate fragments linked by C_2H_4 and is consistent with the formulation of **5.1** as $^tBu_3P(C_2H_4)B(C_6F_5)_3$ as shown in Figure 5.2.

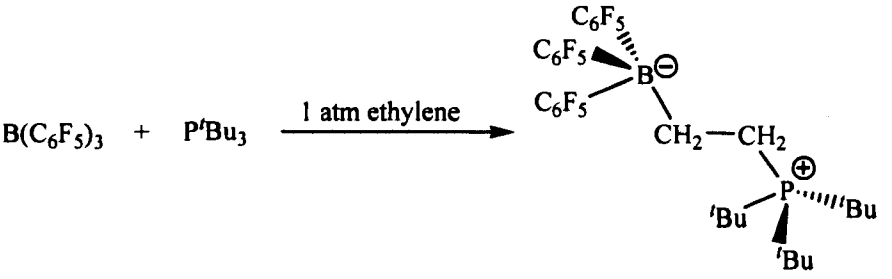


Figure 5.2 Reaction of P^tBu_3 and $B(C_6F_5)_3$ with Ethylene

An X-ray crystallographic study (Figure 5.3, Table 5.1) confirmed the proposed zwitter-ionic formulation, establishing unambiguously that the phosphine and borane add to opposite ends of ethylene. Both the P and B centers are found in pseudo-tetrahedral environments with the B-C and P-C distances of 1.653(4) Å and 1.831(3) Å, respectively. These metric parameters are expected for alkyl phosphonium and alkyl borate species.

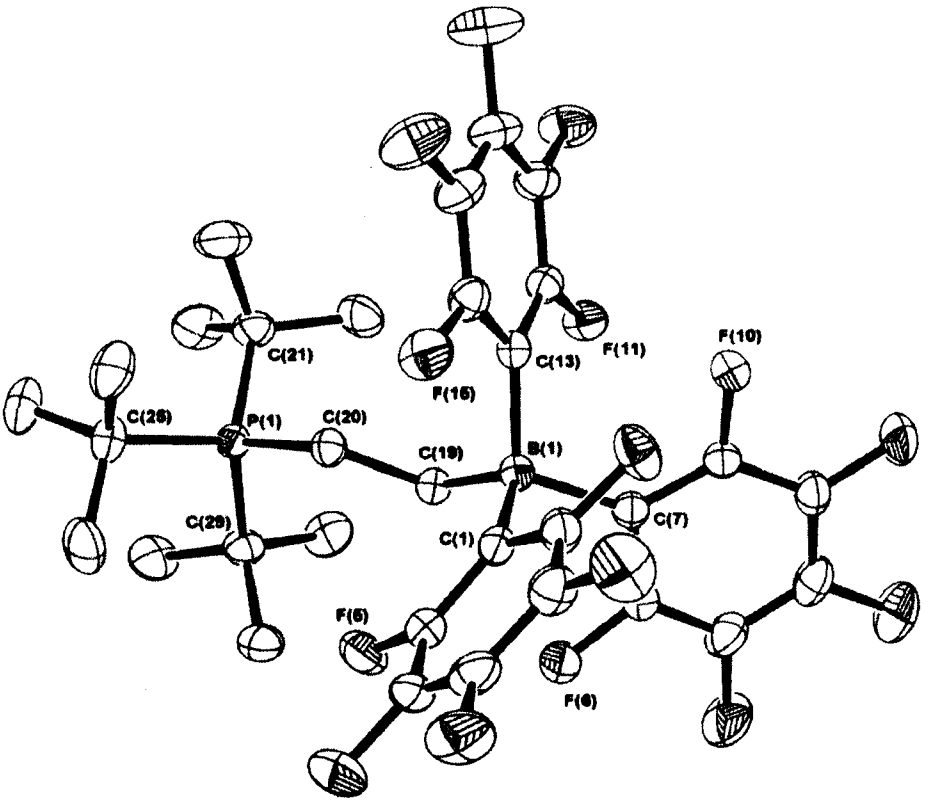


Figure 5.3 ORTEP of 5.1

30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected metrical parameters {Distances (Å) angles (°)}: P(1)-C(20) 1.831(3), P(1)-C(29) 1.883(3), P(1)-C(21) 1.884(3), P(1)-C(25) 1.891(3), C(13)-B(1) 1.658(4), C(7)-B(1) 1.665(4), C(1)-B(1) 1.667(4), C(19)-B(1) 1.653(4), C(19)-C(20) 1.532(4), C(20)-P(1)-C(29) 110.29(13), C(20)-P(1)-C(21) 107.71(13), C(29)-P(1)-C(21) 111.84(13), C(20)-P(1)-C(25) 103.68(12), C(29)-P(1)-C(25) 111.46(13), C(21)-P(1)-C(25) 111.48(13), C(19)-C(20)-P(1) 122.61(19), C(20)-C(19)-B(1) 113.7(2), C(19)-B(1)-C(13) 103.9(2), C(19)-B(1)-C(7) 109.0(2), C(13)-B(1)-C(7) 112.7(2), C(19)-B(1)-C(1) 115.5(2), C(13)-B(1)-C(1) 112.0(2), C(7)-B(1)-C(1) 103.98(19), B(1)-C(19)-C(20)-P(1) 172.63(19).

Similar intermolecular reactions of propylene and 1-hexene with P^tBu_3 and $B(C_6F_5)_3$, afforded the new species **5.2** and **5.3**,respectively, which are illustrated in Figure 5.4. These white solids were subsequently isolated in 63 and 55% yield, respectively. The products exhibited $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR signals at 56.9, and 58.3 and -11.6 and -13.0 ppm, respectively, consistent with the presence of phosphonium and borate fragments similar to **5.1**. The ^1H and ^{19}F NMR spectra reveal the expected resonances for propyl and hexyl groups and inequivalent C_6F_5 groups consistent with the generation of a chiral center from the prochiral olefins. Two dimensional ^{13}C-^1H NMR correlation spectra were used to establish resonance assignments. These data supported a regiochemistry of addition in which P-atom adds to the secondary olefinic carbon while the B-atom adds to the terminal methylene group, indicating that **5.2** and **5.3** can be formulated as $^tBu_3P(CH(R)CH_2B(C_6F_5)_3$ (R = CH_3, C_4H_9), respectively.

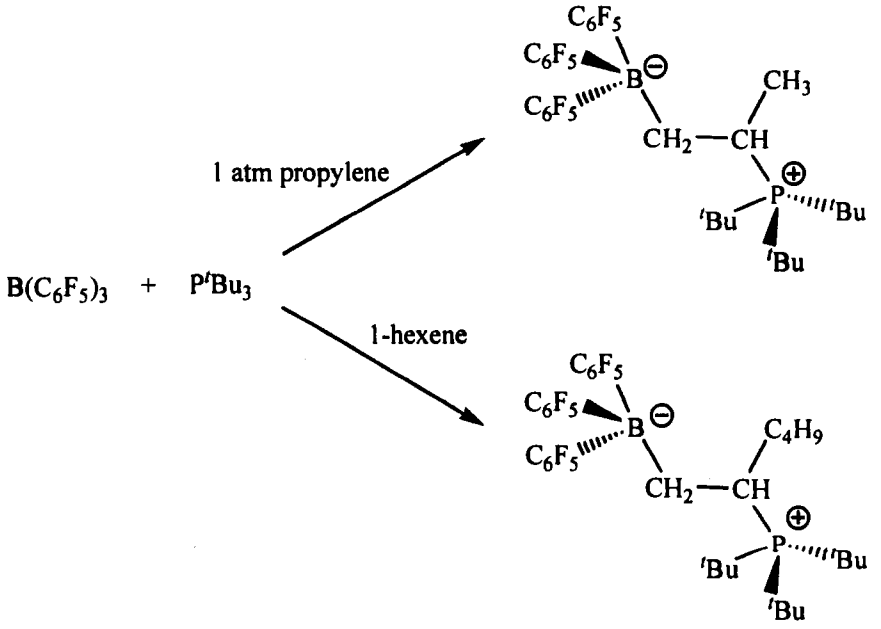


Figure 5.4 Reaction of P^tBu_3 and $B(C_6F_5)_3$ with α-olefins

X-ray crystallographic study of **5.2** and **5.3** confirmed this regiochemistry of addition (Figure 5.5, Table 5.1). The B-C bond lengths of **5.2** and **5.3** are 1.678(18) and 1.670(3), and the P-C bond lengths 1.903(14) and 1.890(2) respectively. These bond lengths are similar to those observed for **5.1**. The remaining metrical parameters are also quite similar to **5.1** and remain unexceptional. It should be noted in the X-ray crystal structures of **5.1 – 5.3** exhibit weak intermolecular C-H···F-C interactions of approximately 2.5 Å between the ^{t}Bu groups on P and the fluoroaryl groups on B. These interactions, as well as the zwitter-ionic charge structure, likely contribute to the low solubility of **5.1 – 5.3** in most organic solvents.

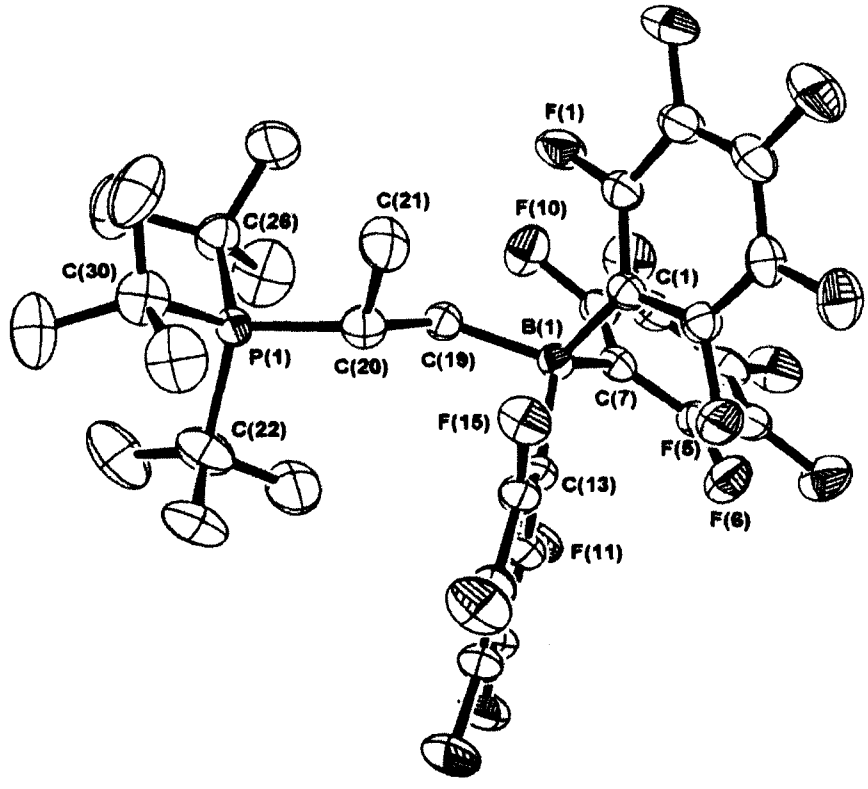


Figure 5.5 ORTEP of 5.2

30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected metrical parameters {Distances (Å) angles (°)}: P(1)-C(26) 1.867(12), P(1)-C(22) 1.873(13), P(1)-C(20) 1.903(14), P(1)-C(30) 1.936(16), B(1)-C(13) 1.62(3), B(1)-C(1) 1.64(3), B(1)-C(19) 1.678(18), B(1)-C(7) 1.68(3), C(19)-C(20) 1.472(15), C(20)-C(21) 1.640(18), C(26)-P(1)-C(22) 113.8(7), C(26)-P(1)-C(20) 112.7(7), C(22)-P(1)-C(20) 109.9(7), C(26)-P(1)-C(30) 110.1(7), C(22)-P(1)-C(30) 105.6(7), C(20)-P(1)-C(30) 104.0(8), C(19)-C(20)-P(1) 116.7(11), C(21)-C(20)-P(1) 114.2(10), C(20)-C(19)-B(1) 121.1(12), C(13)-B(1)-C(1) 110(2), C(13)-B(1)-C(19) 104.6(15), C(1)-B(1)-C(19) 117.1(16), C(13)-B(1)-C(7) 112(2), C(1)-B(1)-C(7) 101.2(15), C(19)-B(1)-C(7) 111.5(16), B(1)-C(19)-C(20)-P(1) -154.9(14), C(30)-P(1)-C(20)-C(19) -164.2(10), C(26)-P(1)-C(20)-C(21) 79.7(12), C(30)-P(1)-C(20)-C(21) -39.5(12), B(1)-C(19)-C(20)-C(21) 76.5(17)

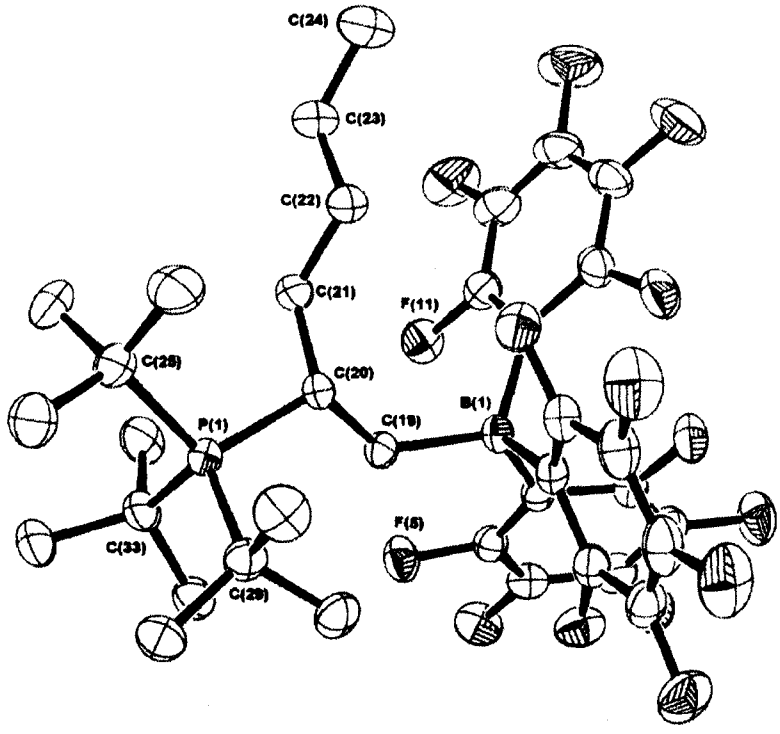


Figure 5.6 ORTEP of 5.3

30% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Selected metrical parameters {Distances (Å) angles (°)}: P(1)-C(20) 1.890(2), P(1)-C(33) 1.896(2), P(1)-C(29) 1.906(2), P(1)-C(25) 1.921(3), B(1)-C(13) 1.664(3), B(1)-C(6) 1.669(3), B(1)-C(19) 1.670(3), B(1)-C(7) 1.672(3), C(19)-C(20) 1.556(3), C(20)-C(21) 1.552(3), C(21)-C(22) 1.522(3), C(22)-C(23) 1.518(4), C(23)-C(24) 1.493(4), C(20)-P(1)-C(33) 111.11(10), C(20), P(1)-C(29) 107.18(10), C(33)-P(1)-C(29) 110.73(11), C(20)-P(1)-C(25) 109.37(11), C(33)-P(1)-C(25) 109.94(12), C(29)-P(1)-C(25) 108.42(12), C(21)-C(20)-P(1) 112.49(14), C(19)-C(20)-P(1) 114.15(14), C(20)-C(19)-B(1) 121.45(17), C(13)-B(1)-C(6) 100.89(16), C(13)-B(1)-C(19) 114.19(17), C(6)-B(1)-C(19) 111.09(17), C(13)-B(1)-C(7) 114.36(17), C(6)-B(1)-C(7) 108.93(16), C(19)-B(1)-C(7) 107.23(17), B(1)-C(19)-C(20)-P(1) -150.55(16), C(25)-P(1)-C(20)-C(21) -43.22(19), C(33)-P(1)-C(20)-C(21) 78.33(17), C(33)-P(1)-C(20)-C(19) -48.46(17), C(25)-P(1)-C(20)-C(19) -170.01(16), B(1)-C(19)-C(20)-C(21) 81.6(2)

In an effort to probe the limits of the observed reactivity the frustrated Lewis pair combination of $PMes_3$ and $B(C_6F_5)_3$ was also investigated towards activation of olefins. A bromobenzene solution of equi-molar amounts of $PMes_3$ and $B(C_6F_5)_3$ was purged with ethylene and stored under 1 atm of ethylene at 25 °C for 12 hours and, surprisingly, no reactivity was observed. This result stands in stark contrast to the related H_2 activation chemistry, where the "frustrated" Lewis pair of $PMes_3$ and $B(C_6F_5)_3$ readily cleaves H_2.[119] Additionally, combinations of $PMes_3$ or P(*o*-tolyl)$_3$ and $B(C_6F_5)_3$ were stable in neat 1-hexene. These results demonstrate that not only are the sterics of the phosphine important, but the electronic attributes are essential as well. Here the considerably less basic phosphines, $PMes_3$ and P(*o*-tolyl)$_3$, do not activate olefins in the presence of $B(C_6F_5)_3$, where as the more basic P^tBu_3 does. Additionally, attempts to activate 1-hexene with perfluoroaryl-linked phosphino-borane, $R_2P(C_6F_4)B(C_6F_5)_2$ (R = ^{t}Bu or Mes),[108] at room temperature were also unsuccessful. As the phosphine in the perfluoroaryl-linked phosphine-borane compound is bonded to a strongly electron withdrawing fluoroaryl group, similar arguments based on lack of base strength can rationalize this lack of reactivity.

It has recently been reported by the Stephan Group that phosphine-$B(C_6F_5)_3$ adducts will undergo thermal rearrangement to give zwitter-ionic phosphonium borates of the form, $[R_3P(C_6F_4)BF(C_6F_5)_2]$.[114] Additionally, bulky phosphines such as PCy_3 rapidly react with $B(C_6F_5)_3$ to generate $[Cy_3P(C_6F_4)BF(C_6F_5)_2]$.[108] We envisioned that carrying out these reactions in the presence of olefins may prevent *para*-nucleophilic aromatic substitution. Heating the $HPCp_2B(C_6F_5)_3$ adduct to reflux in neat 1-hexene resulted in formation of only the perfluoroaryl linked phosphonium-borate, $[HPCp_2(C_6F_4)BF(C_6F_5)_2]$. Similarly, addition of PCy_3 to a solution of $B(C_6F_5)_3$ in neat 1-

hexene, showed only formation of the zwitter-ion, $[Cy_3P(C_6F_4)BF(C_6F_5)_2]$. These results indicate that the nucleophilic aromatic substitution reaction is more rapid than olefin addition.

5.3.2 Reaction of $B(C_6F_5)_3$ and Secondary Phosphines with Olefins

Sterically encumbered secondary phosphines HPR_2 (R = ^{t}Bu, Mes), form very weak adducts with $B(C_6F_5)_3$, and the subsequent zwitter-ion formation is relatively slow. Therefore, there exists the possibility that such phosphine and $B(C_6F_5)_3$ combinations could effect the activation of olefins. The secondary phosphine, HP^tBu_2, was added to a solution of $B(C_6F_5)_3$ in 1-hexene. Formation of a white precipitate was observed almost immediately. The product was isolated and solution NMR spectroscopy indicated the formation of both the previously reported perfluoroaryl linked phosphonium-borate, $[^tBu_2PH(C_6F_4)BF(C_6F_5)_2]$, and a new alkyl linked phosphonium-borate product $[^tBu_2PH(CH(C_4H_9)CH_2B(C_6F_5)_3]$, as illustrated in Figure 5.7. Unfortunately, due to their similar solubilities the products could not be separated and the new alkyl linked complex was not fully characterized.

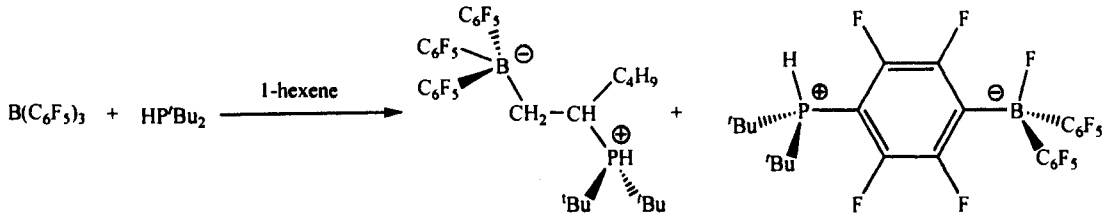


Figure 5.7 Reaction of HP^tBu_2 and $B(C_6F_5)_3$ with 1-hexene

In contrast to the reactivity with HP^tBu_3, addition of $HPMes_2$ to a solution of $B(C_6F_5)_3$ in 1-hexene at 25 °C, afforded the new species **5.4,** which was isolated in 67 % yield. This product exhibited $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR signals at 5.4, and -13.7 ppm, respectively, consistent with the presence of phosphonium and borate fragments similar to **5.3**. No evidence of the perfluoroaryl linked phosphonium-borate product was observed by NMR spectroscopy. This difference in reactivity can be attributed to the relative rates of nucleophilic aromatic substitution where the HP^tBu_2 reaction proceeds at room temperature while complete $HPMes_2$ reaction is only achieved after refluxing in toluene for 16 hours.[108] Similar to **5.2** and **5.3** the data supported a regiochemistry of addition in which P-atom adds to the secondary olefinic carbon while the B-atom adds to the terminal methylene group, prompting the formulation of **5.4** as $Mes_2PH(CH(C_4H_9)CH_2B(C_6F_5)_3$ as shown in Figure 5.8. The reaction of $HPMes_2$ is in contrast to that of $PMes_3$ which showed no reactivity toward 1-hexene. Clearly the reduced steric bulk of $HPMes_2$ allows for closer approach to the olefin and favours further pyrimidalization at P.

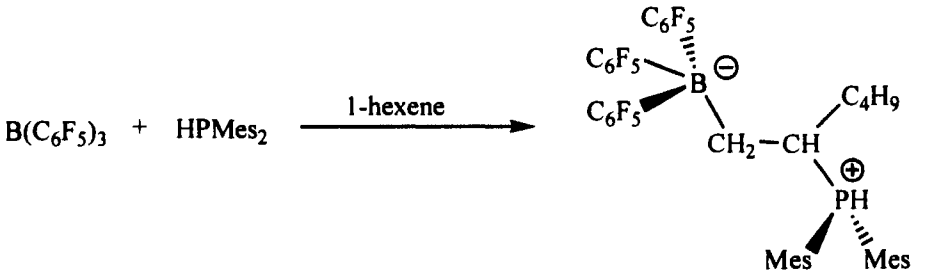


Figure 5.8 Reaction of $HPMes_2$ and $B(C_6F_5)_3$ with 1-hexene

X-ray crystallographic study of **5.4** confirmed this regiochemistry of addition (Figure 5.9, Table 5.2), metrical parameters are similar to those reported for **5.1** – **5.3**, with the newly formed B-C and P-C bond distances of 1.693(7) and 1.858(5), respectively and remain unexceptional.

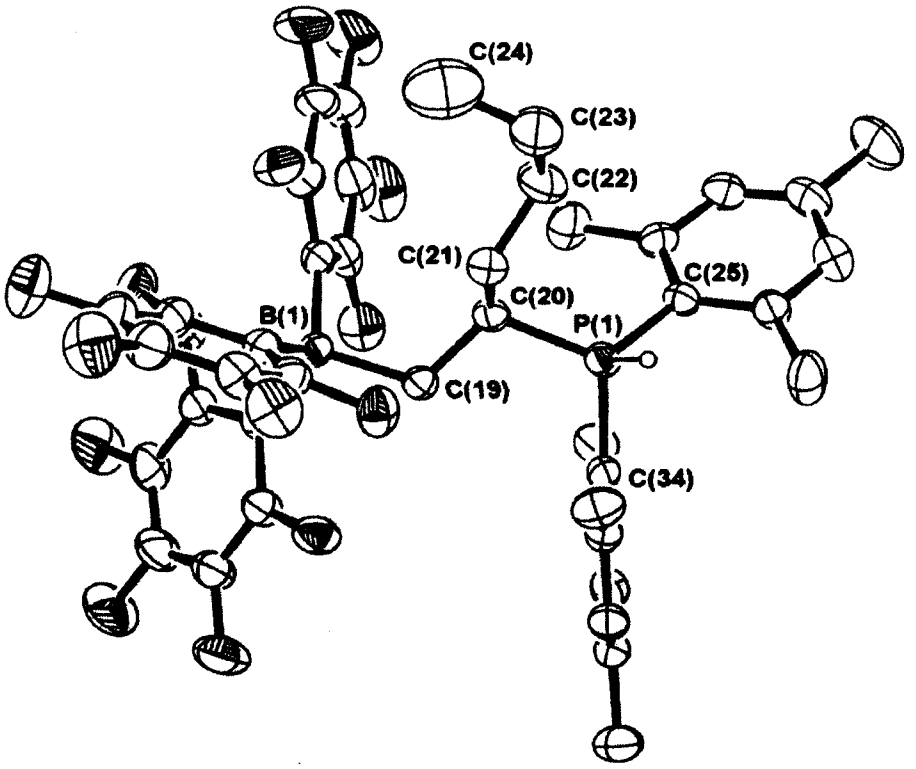


Figure 5.9 ORTEP of 5.4

30% thermal ellipsoids are shown. Hydrogen atoms on carrbon are omitted for clarity. Selected metrical parameters {Distances (Å) angles (°)}: P(1)-H(1) 1.34(4), P(1)-C(34) 1.812(4), P(1)-C(25) 1.827(5), P(1)-C(20) 1.858(5), C(1)-B(1) 1.665(7), C(7)-B(1) 1.673(7), C(13)-B(1) 1.662(7) , C(19)-C(20) 1.546(6), C(21)-C(22) 1.523(7), C(22)-C(23) 1.550(9), C(23)-C(24) 1.520(11), C(34)-P(1)-C(25) 114.0(2), C(34)-P(1)-C(20) 113.4(2), C(25)-P(1)-C(20) 118.5(2), C(19)-C(20)-P(1) 112.0(3), C(21)-C(20)-P(1) 107.9(3), C(20)-C(19)-B(1) 117.7(4), C(13)-B(1)-C(1) 113.9(4), C(13)-B(1)-C(7) 111.7(4), C(1)-B(1)-C(7) 102.3(4), C(13)-B(1)-C(19) 104.1(4), C(1)-B(1)-C(19) 116.7(4), C(7)-B(1)-C(19) 108.3(4), B(1)-C(19)-C(20)-P(1) -175.1(3), B(1)-C(19)-C(20)-C(21) 61.1(5), P(1)-C(20)-C(21)-C(22) 69.2(5), C(25)-P(1)-C(20)-C(21) -96.0(3)

5.3.3 Reaction of $B(C_6F_5)_3$ and phosphines with pendant olefinic substituents

"Frustrated" Lewis pairs can also react with olefins in an intramolecular fashion. The olefinic derivatives of sterically demanding phosphines of the form $CH_2CH(CH_2)_3PR_2$ (R = ^{t}Bu, Mes) were prepared via conventional methods outlined in Chapter 4. Stoichiometric reactions with $B(C_6F_5)_3$ were monitored by ^{31}P NMR spectroscopy. These data reveal no evidence of phosphine-borane adduct formation. The phosphine, $CH_2CH(CH_2)_3P^tBu_2$ was added to a solution of $B(C_6F_5)_3$ in CH_2Cl_2 at 25°C to give species **5.5** in 94 % isolated yield. A Solution of $CH_2CH(CH_2)_3PMes_2$ and $B(C_6F_5)_3$ in CH_2Cl_2 was heated to reflux (45°C) to form **5.6** in a 52 % isolated yield. The $^{31}P\{^1H\}$ NMR spectrum of **5.5** and **5.6** showed singlet resonances at 62.4 and 52.8 ppm, respectively, while the corresponding $^{11}B\{^1H\}$ NMR signals were observed at -13.8 and -13.7 ppm, respectively. ^{19}F NMR spectra for **5.5** and **5.6** confirmed the presence of C_6F_5 groups. These data together with the ^1H and ^{13}C NMR data support the loss of the olefinic substituents and the formulation of **5.5** and **5.6** as the cyclized phosphonium-borate $R_2PCH(C_3H_6)CH_2B(C_6F_5)_3$ (R = ^{t}Bu **5.5**, $C_6H_2Me_3$ **5.6**). In both cases no formation of the perfluoroaryl linked phosphonium-borate was observed nor were the products due to the intermolecular activation of the olefin detected.

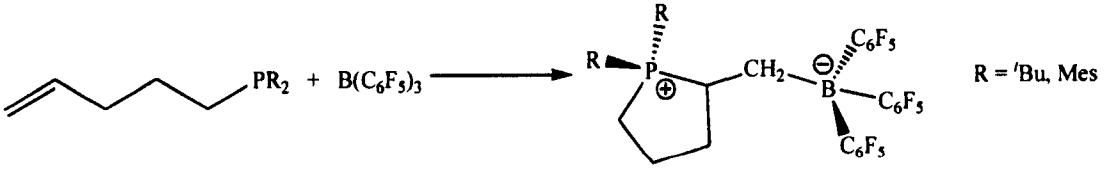


Figure 5.10 Intramolecular Cyclization

An X-ray crystallographic study of **5.5** (Figure 5.11, Table 5.2) confirmed the proposed connectivity, although rotational disorder of *t*-butyl groups dictated a constrained refinement. Related cyclic products have been generated by addition of PH bonds to a pendant olefinic group mediated by a lanthanide species. These have been proposed as catalytic hydrophosphination intermediates en route to the secondary phospholes $HPCH(Me)(C_3H_6)$.[174,175]

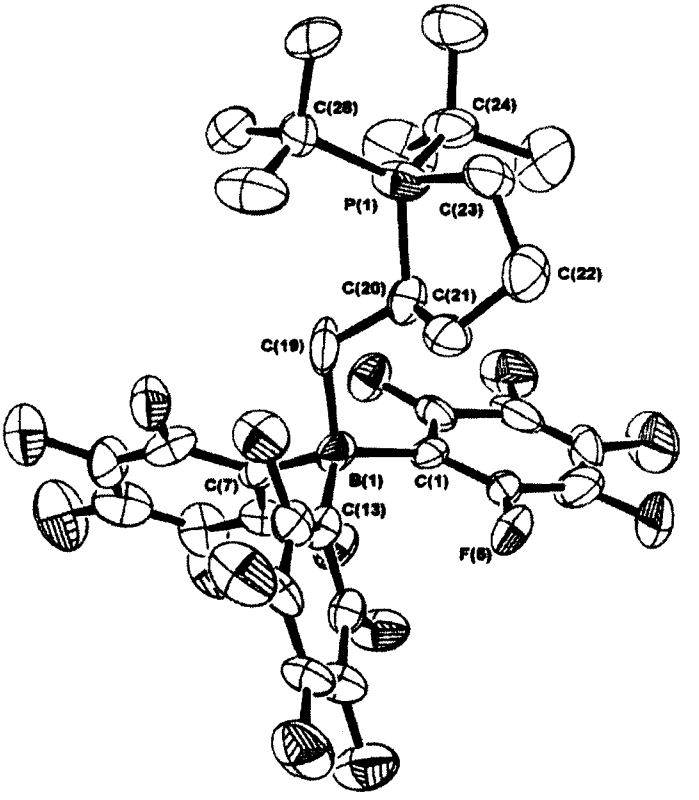


Figure 5.11 ORTEP of 5.5

30% thermal ellipsoids are shown. Hydrogen atoms on carrbon are omitted for clarity. Selected metrical parameters {Distances (Å) angles (°)}: P(1)-C(28) 1.791(12), P(1)-C(24) 1.843(13), P(1)-C(20) 1.857(11), P(1)-C(23) 1.894(11), B(1)-C(7) 1.644(11), B(1)-C(13) 1.651(11), B(1)-C(1) 1.656(11), B(1)-C(19) 1.691(13), C(19)-C(20) 1.500(9), C(20), C(21) 1.539(15), C(21)-C(22) 1.513(16), C(22)-C(23) 1.526(16), C(28)-P(1)-C(24) 120.1(5), C(28)-P(1)-C(20) 117.7(5), C(24)-P(1)-C(20) 109.2(5), C(28)-P(1)-C(23) 105.3(6), C(24)-P(1)-C(23) 106.3(6), C(20)-P(1)-C(23) 94.2(5), C(19)-C(20)-P(1) 117.9(8), C(21)-C(20)-P(1) 103.3(7), C(22)-C(23)-P(1) 105.1(8), C(20)-C(19)-B(1) 116.7(9), C(7)-B(1)-C(13) 102.6(8), C(7)-B(1)-C(1) 111.6(9), C(13)-B(1)-C(1) 116.3(8), C(7)-B(1)-C(19) 106.7(8), C(13)-B(1)-C(19) 115.8(10), C(1)-B(1)-C(19) 103.7(8), B(1)-C(19)-C(20)-P(1) 172.4(9), C(28)-P(1)-C(20)-C(19) 36.9(12), C(24)-P(1)-C(20)-C(19) -104.5(11)

The impact of the chain length was investigated in attempt to vary the size of the phosphine ring generated by this reaction. Reaction of $^{t}Bu_2PCH_2CHCH_2$ and $^{t}Bu_2P(CH_2)_9CHCH_2$ with $B(C_6F_5)_3$ in CH_2Cl_2 resulted in the formation of the products 5.7 and 5.8 in 51.4 and 50.0 % yield respectively. The $^{31}P\{^{1}H\}$ NMR spectrum shows peaks at 51.8 and 55.0 indicating the formation of a four coordinate phosphonium cation. The $^{11}B\{^{1}H\}$ and ^{19}F NMR spectra indicates formation of the perfluoroaryl linked phosphonium-borates , 5.7 and 5.8 as illustrated in Figure 5.12. This was also supported by ^{1}H and ^{13}C NMR spectra, most tellingly by presence of remaining olefinic peaks between 4.89 – 5.88 ppm.

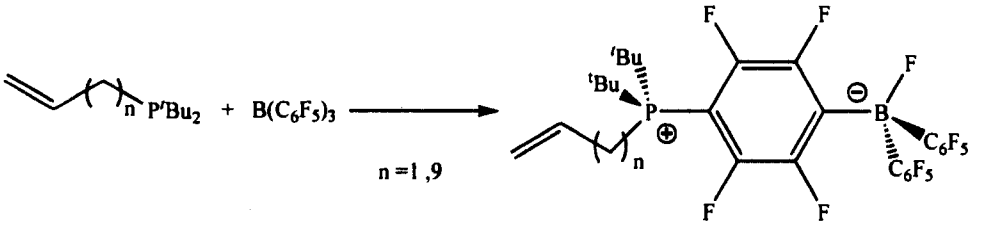


Figure 5.12 Perfluoroaryl-Linked Phosphonium-Borates

The formation of the perfluoroaryl linked phosphonium-borate via nucleophilic aromatic substitution is favoured over the intramolecular olefin activation due to the ability of the phosphine to intramolecularly add to the olefin. In the case of the phosphine with a 3 carbon linker between the phosphine and olefin, $^{t}Bu_2P(CH_2)_3CHCH_2$, a stable five-member ring is formed. However for the chain shortened species $^{t}Bu_2PCH_2CHCH_2$ the expected intramolecular addition product would generate an unstable three member ring. Upon increasing the chain length to the phosphine $^{t}Bu_2P(CH_2)_9CHCH_2$ the ability of

the phosphine to "bite back" and add to the olefin is reduced the nucleophilic aromatic substitution is more rapid.

5.3.4 Mechanistic Insights

The mechanism of the present reactions is intriguing given that neither phosphines or boranes of this type are not known to react individually with olefins. It is tempting to suggest that these reactions are initiated by Lewis acid activation of the olefin, which prompts attack by the phosphine. This view is supported to some degree by the observations of Herrebout and van der Veken[176] who reported IR data for the van der Waals BF_3-ethylene and BF_3-propylene complexes generated in an Argon matrix at 93-125 K. We attempted to observe an analogous borane-olefin interaction by variable temperature NMR methods using solutions of $B(C_6F_5)_3$ in neat 1-hexene. At temperatures to -90°C no evidence of interaction was observed by ^{19}F, ^{11}B or ^{1}H NMR spectroscopy. It is noteworthy that DFT calculations for ethylene-alane[177] and borane adducts[178] suggested weak π-donation complexes are formed. In the case of the olefin-BF_3 adduct, only small deviations to the geometry of the olefin and the borane were computed upon complexation[178] suggesting that in the present cases, the phosphine nucleophile may play a significant role in driving the addition reaction. It is noteworthy that the conventional hydroboration reaction is postulated to proceed via a π-olefin-borane complex.[179] As well, these additions of B and P across olefins are reminiscent of Br_2 addition to olefins, as the latter is proposed to proceed via electrophilic bromonium ion (Br^+, Lewis acid) attack followed by nucleophilic attack of bromide ion (Br^-, Lewis base).[179]

Very recent calculations by Papai and co-workers have suggested that in solution the 'frustrated' Lewis pair combination $P^tBu_3/B(C_6F_5)_3$ can exist as an encounter complex, held together by dispersion forces and weak intermolecular CH FC interactions with phosphorus / boron distances of approximately 4.2 Å.[180] (Figure 5.13)

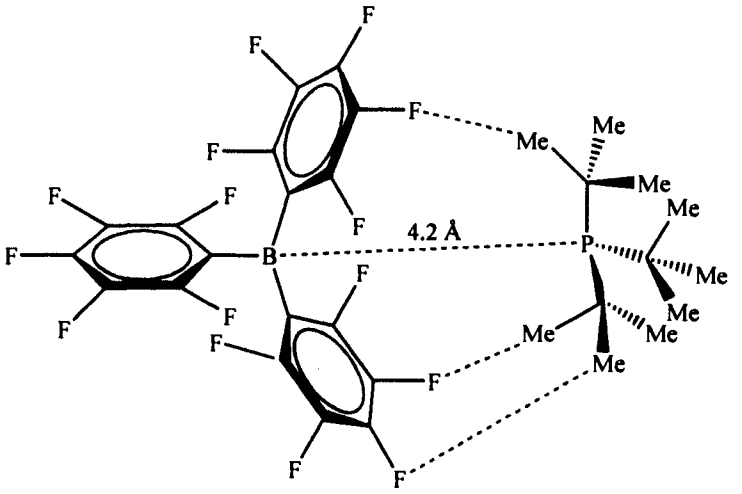


Figure 5.13 $P^tBu_3/B(C_6F_5)_3$ Encounter Complex

It is proposed that the addition of P^tBu_3 and $B(C_6F_5)_3$ to olefin occurs via a synergistic phosphine-olefin and borane-olefin interaction, and the addition process has a slight asynchronous character with the development of the B-C bond occurring before the formation of the P-C bond. This would develop an increased positive charge on the beta carbon of the olefin, which, in the cases of propylene and 1-hexene, would be stabilized by the electron donating pendant alkyl chain. Their results also support the regioselectivity of the addition to alkyl-substituted olefins, as the terminal CH_2 group acts as a Lewis base due to the excess electron density on the primary carbon of the double bond.[181] In a similar theoretical study, Guo and Li also suggest the intramolecular

cyclization of the phosphines with the olefinic substituent and $B(C_6F_5)_3$ occurs through a similar concerted transition state.[182]

5.4 Summary and Conclusions

In summary, sterically frustrated Lewis pairs of bulky phosphines and the borane, $B(C_6F_5)_3$ exhibit unprecedented reactivity with olefins, affording both intermolecular additions as well as intramolecular cyclizations. These reactions are all the more remarkable given that any pair of these reagents do not react but combination of the three reagents results in product formation. The expansion of the reactivity of the olefin activation is hindered by the nucleophilic aromatic substitution reactions. The utility of such remarkably selective three component reactions and the further reactivity of "frustrated" Lewis pairs are the subject of ongoing study. Currently, the development of novel boranes which prohibit *para*-nucleophilic substitution are being developed and the application to olefin activation being studied. Additionally, the investigation of three component reactions of phosphines, boranes and internal olefins, dienes and alkynes is being pursued.

Chapter 6: Summary

The application of the concept of "frustrated" Lewis Pairs in the polymerization and activation of olefins has been investigated.

Phosphonium-borates, phosphonium-alkoxyl borates, and phosphino-boranes, are all novel compounds derived from "frustrated" Lewis pairs and have been demonstrated to be effective co-catalysts for the polymerization of ethylene. The incorporation of a bulky phosphine moiety in a borane framework has been demonstrated to have an increase in the observed ethylene polymerization activity, due to the proposed increasing the ion-pair separation of the cation-anion systems through interactions of the Lewis basic phosphine with the cationic metal center.

The use of sterically bulky phosphine additives to the polymerization of ethylene using the $CpTiMe_2(NP^tBu_3)/B(C_6F_5)_3$ catalyst systems results in observed polymerization activities greater than those observed for the parent catalyst system. The increase is observed activity is postulated to be a result of increasing the ion-pair separation of the cation-anion systems through interactions of the Lewis basic phosphine with the cationic metal center.

The design and synthesis of sterically bulky phosphine-functionalized monomers was conducted and attempts to polymerize these monomers investigated. Although homo-polymerizations attempts were unsuccessful, the phosphine functionalized monomer was co-polymerized with 1-hexene, albeit in low percent yield and low incorporation of the functionality. Investigations of the potential inhibition pathways indicated the co-polymerizations and homo-polymerizations of the phosphine-functionalized monomers

are inhibited by reactivity with the co-catalyst, intermolecular coordination of the phosphine functionality, and intramolecular coordination of the phosphine.

Sterically "frustrated" Lewis pairs of phosphines and the borane, $B(C_6F_5)_3$ exhibit unprecedented reactivity with olefins, affording both intermolecular additions as well as intramolecular cyclizations.

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Appendix A: Standard Ethylene Polymerization Results

A.1 Overview

There are numerous factors that may affect polymerization results obtained using the Buchi reactor system. To ensure results obtained were comparable routine standards were run to evaluate reproducibility of the system. These polymerization results and analysis are outlined

.

A.1.1 Polymerization Protocol

A.1.1.1 Description of Polymerization Reactor Set-up

Polymerizations were performed in a 1 L Buchi reactor system. Following assembly, the reactor vessel and solvent storage unit were refilled with nitrogen via 4 refill/evacuation cycles over at least 90 minutes. Approximately 600 mL of toluene was transferred to the solvent storage container from the purification column. The solvent was then purged with dry nitrogen for 20 minutes and transferred to the reactor vessel by differential pressure. In the reactor vessel, the solvent was stirred at 1500 ± 5 RPM and the temperature was kept constant at 30 ± 2 °C. Ethylene was introduced into the reactor vessel via five vent/refill cycles

A.1.1.2 Description of Catalyst and Co-catalyst Preparation

The pre-catalyst, co-catalyst and scrubber stock solutions were freshly prepared, loaded into syringes in a glovebox, and then transferred to the reactor immediately before injection to limit possibility of catalyst decomposition. An example polymerization experiment using $CpTiMe_2(NP^tBu_3)$ as the catalyst, 1 equivalent of $B(C_6F_5)_3$ as co-catalyst, and 20 equivalents of T*i*BAl as the scrubber will be used to describe how the stock solutions were prepared.

Catalyst Solution: $CpTiMe_2(NP^tBu_3)$ (0.012 g, 0.032 mmol) was weighed into a vial. Toluene (15.570 g, 18.0 mL) was then added to form a clear, light yellow solution. 1.0 mL (0.0018 mmol $CpTiMe_2(NP^tBu_3)$) of the solution was transferred to a syringe for injection into the reactor.

Co-Catalyst Solution: $B(C_6F_5)_3$ (0.011 g, 0.022 mmol) was weighed into a vial. Toluene (15.570 g, 18.0 mL) was added to form a clear, colourless solution. 1.5 mL (0.0018 mmol $B(C_6F_5)_3$, 1 equivalent) of the solution was transferred to a syringe for injection into the reactor.

Scrubber Solution: 0.2 mL of a 25.2 weight % solution of T*i*BAl in heptanes (0.18 mmol Al*i*-Bu_3) was added to toluene (12.836 g, 14.84 mL) to produce a clear, colourless solution. 3.0 mL (0.036 mmol T*i*BAl, 20 equivalents) of the solution was transferred to a syringe for injection into the reactor.

A.1.1.3 Description of Polymerization Experiments

The prepared solution of T*i*BAl (3.0 mL) was injected into the reaction vessel through the catalyst injection inlet and allowed to stir for 5 min. The prepared $CpTiMe_2(NP^tBu_3)$ solution (1.0 mL) was then injected into the reaction vessel followed immediately by

injection of the $B(C_6F_5)_3$ solution (1.5 mL). The mixture was stirred at 1500 ± 5 RPM at 30 °C under 2 atm of dynamic ethylene flow for 10 minutes. Temperature and ethylene flow rate were recorded manually at regular intervals. After 10 minutes, polymerization was stopped by closing the ethylene inlet valve and venting the reactor. Stirring was stopped, and the reactor disassembled.

A.1.1.4 Description of Polymer Recovery and Work-up

The contents of the reactor were emptied into a 4 L beaker that contained approximately 100 mL of 10% HCl (v/v) in MeOH. The polymer that precipitated was then collected by filtration, washed with toluene and acetone, and dried overnight. Resulting polymer was weighed and polymerization activity calculated according to Equation 2.1:

Equation 2.1: Polymerization Activity

$$Activity\ (g\ mmol^{-1}\ hr^{-1}\ atm^{-1}) = \frac{mass\ of\ polymer\ (g)}{amount\ of\ catalyst\ (mmol)\ x\ time\ (hr)\ x\ pressure\ of\ ethylene\ (atm)}$$

A.2 Polymerization Results

A catalyst, $CpTiMe_2(NP^tBu_3)$, concentration of 3 μmol/L was used, and 1 equivalents of the co-catalyst. The polymerizations were conducted at 30°C for 10 minutes in toluene, under an atmosphere of 2 atm of ethylene. The results are shown in Table A.1.

Table A. 1 Polymerization Results

Run	Activity[b]	Run	Activity[b]
1	15550	8	16817
2	13272	9	13700
3	15462	10	15647
4	13347	11	13810
5	12468	12	14165
6	13432	13	15753
7	14560		

[a] Polymerization Conditions: Catalyst – $CpTiMe_2[NP^tBu_3]$ (3 μmol/L), 1 equiv. co-catalyst, 20 equiv. T*i*BAL, ethylene pressure – 2 atm, polymerization time – 10 min, polymerization temperature – 30 °C
[b] Activity reported in g $mmol^{-1}$ hr^{-1} atm^{-1}

A.2.1 Average Activity

To calculate the average activity for the 13 trials Equation A.1 was employed.

Equation A.1

$$Activity\ (g\ mmol^{-1}hr^{-1}atm^{-1}) = \frac{\sum Activity\ (g\ mmol^{-1}hr^{-1}atm^{-1})}{Number\ of\ Trials}$$

A.2.2 Percent Difference

To calculate the % difference between the highest activity and lowest activity observed equation A.2 was employed.

Equation A.2

$$\%\ Difference = \frac{|highest\ activity - lowest\ activity|\ (g)}{average\ activity\ (g)}\ x\ 100$$

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Articles Published or Accepted in Refereed Journals

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Scholarships and Awards

Doctoral Tuition Scholarship, Sept. 2007-present
Ontario Graduate Scholarship, Sept. 2006-Aug. 2007
Ontario Graduate Scholarship – Science and Technology, May 2006-Sept. 2006
Doctoral Tuition Scholarship , Sept. 2005-April 2006
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