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Lewis acid-base interactions in the synthesis of titanium phosphinimide cations.

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Lewis Acid-Base Interactions in the Synthesis of Titanium Phosphinimide Cations

by

Lourdes Isabel Cabrera Lara

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Abstract

The active species $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_4)$ and $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$, generated by the reaction of $Cp(NP^tBu_3)TiMe_2$ with the activators $B(C_6F_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$, are thought to be the active species in olefin polymerization processes. Both species have been stabilized by the coordination of Lewis bases, pyridines (Py, 4-EtPy, 4-^{t}BuPy, and 4-DMAP) and tertiary phosphines (PMe_3, P^nBu_3, $P(C_6H_5)_3$, $P(p\text{-}CH_3C_6H_4)_3$). The use of such Lewis bases allowed for the isolation and characterization of ion pair complexes of the general formula $[Cp(NP^tBu_3)TiMe{\cdot}LB][RB(C_6F_5)_3]$ (LB = Lewis base; R = Me, C_6F_5). These reactions show a dependency on the steric properties of the Lewis base. The use of sterically bulky tertiary phosphines ($P(o\text{-}CH_3C_6H_4)_3$, P^iPr_3, PCy_3 and P^tBu_3) demonstrated this dependency, affording unexpected phosphonium salts as products.

The role of the reaction solvent (dichloromethane and chlorobenzene) is evaluated in these reactions. Dichloromethane reacts with the reagents (active titanium complexes and Lewis bases), promoting the formation of unexpected products (some of these species are characterized). However, chlorobenzene allows a better control of the reactions between the activated complex and Lewis bases.

The dimerization products $[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-}Cl)][RB(C_6F_5)_3]$ (R = Me, C_6F_5) (**2.18**), $[\{Cp(NP^tBu_3)Ti(\mu\text{-}Cl)_2\}][RB(C_6F_5)_3]_2$ (**2.21**) and $[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-}Me)][RB(C_6F_5)_3]$ (**2.23**) of the cationic moiety of the active complexes $[Cp(NP^tBu_3)TiMe]^+$ showed also to be dependent on the reaction conditions and solvent.

Reactions of Lewis acids ($B(C_6F_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$) with Lewis bases (substituted pyridines and tertiary phosphines) are also described. A similarity in reactivity between $B(C_6F_5)_3$ and the trityl carbocation is observed, as the products afforded from these reactions are analogous. Reactions of Lewis acids and Lewis bases were found to be related to the steric bulk associated with the Lewis base in conjunction with the solvent, CH_2Cl_2.

"Love hides in molecular structures." - Jim Morrison (The Doors) 1970

"Some of you may be saying, 'Who cares?'...and that's a good point." - Miss Wentz

"Make it myself? But I'm a physical organic chemist!" - Anonymous

"Anyone who has never made a mistake has never tried anything new."

"Insanity: doing the same thing over and over again and expecting different results."

"If we knew what it was we were doing, it would not be called research, would it?"

"I love to travel, but hate to arrive."

Albert Einstein

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I do not think I could have accomplished such task (as it is obvious from the time that has taken me) without the support and help of a lot of people. Therefore, I would like to thank the ones that in one way or another are part of this work.

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---

[a] The grammar mistakes and misuse of the English language found in this section are due to my ineptitude to express myself correctly, since nobody checked these pages.

I will also like to express my appreciation to everyone that made my life in Windsor an extraordinary adventure, and made this place feel like home (in every sense of the word). I value their advice, support and help, in the academic and non-academic fields. Thanks for **pushing** me and **dragging** me through the path when I was not able to do it by myself. I will always be in debt.

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List of Abbreviations

Å	angstrom
br	broad
Cp	cyclopentadienyl
Cy	Cyclohexyl
d	Doublet
ddd	doublet of doublet of doublets
DEPT	Distortionless Enhancement by Polarization Transfer
d(m)	doublet of multiplets
DMAP	dimethylaminopyridine
Et	ethyl
H	proton
HETCOR	HETeronuclear CORrelation spectroscopy
Hz	Hertz
^{i}Pr	isopropyl
J	coupling constant
LUMO	Lowest Unoccupied Molecular Orbital
M	molar (M L^{-1})
m	multiplet
m	*meta*
Me	methyl
MHz	megahertz
mL	milliliter
μL	microlitre
mmol	millimole
^{n}Bu	normal butyl
NMR	Nuclear Magnetic Resonance
o	*ortho*
p	*para*
PBB	Tris(2,2',2"-perfluorobiphenyl) borane

ppm	parts per million
Py	pyridine
q	quartet
RT	room temperature
s	singlet
t	triplet
t(m)	triplet of multiplets
^{t}Bu	tertiary butyl
δ	chemical shift
ϵ	dielectric constant

1. Introduction

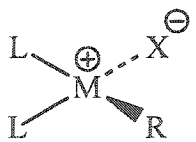
1.1. *Metallocene and Half-Metallocene Cations and Zwitterions of Group 4 Transition Metals*

Almost 50 years have passed since the discovery that ethylene could be polymerized by transition metals using mild conditions.[1] Over the past years, catalysts for the polymerization of α-olefins based on the reactions between metallocene-based systems (pre-catalyst) and Group 13-15 cocatalysts or activators have been developed.[2] A vast amount of research (experimental studies and theoretical calculations)[3,4] has been done targeting increased polymerization activities, greater control over the polymers formed and activity of a variety of different monomers.

1.1.1. Homogeneous Olefin Polymerization Reaction Mechanism

In general, an active olefin polymerization catalyst bearing a Group 4 metal is of the general formula $[L_2MR][X]$ (Figure 1.1)[5] and consists of:

a) an appropriate ancillary ligand framework (L),
b) an electron-deficient and coordinatively unsaturated metal center (M = Ti, Zr or Hf);
c) an effective cocatalyst/weakly coordinating counterion (X^-), which must be chemically robust and resistant to electrophilic attack.



R = alkyl
M = Ti, Zr, Hf
X = counterion

Figure 1.1: General formula of a catalyst for olefin polymerization.

Catalytic olefin polymerization is one of the most commercially important processes for which organometallic compounds are employed. The mechanism of this

process consists of three steps: olefin insertion, chain propagation (Figure 1.2) and chain termination (Figure 1.3).[6] The first step is the coordination of the olefin to the coordinatively unsaturated metal center. Migratory insertion of the complexed α-olefin monomer (or olefin ligand) into the bond between the transition metal atom and the σ-bound carbon then takes place.[7] This insertion generates a new open coordination site, enabling subsequent coordination of another olefin molecule (Figure 1.2)[2] promoting chain propagation.

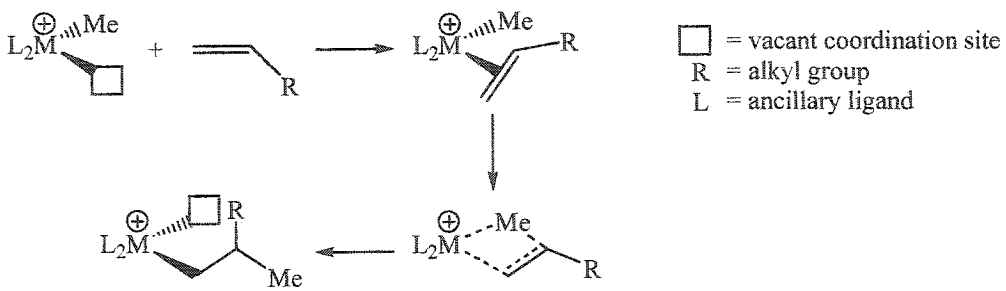


Figure 1.2: Mechanism for Ziegler-Natta olefin polymerization.

One of the main chain termination pathways is β-hydrogen transfer to the monomer. This produces a polymer chain containing a terminal olefin (Figure 1.3a).[7] This long-chain terminal olefin can also participate in the polymerization process by re-incorporating into a growing polymer chain,[8] promoting long-chain branching.[7] From the β-agostic structure, the termination step may also consist of β-hydrogen transfer to the metal center (Figure 1.3b).[9,10] In a similar manner, hydrogen added to the polymerization mixture can compete with the olefin for the free coordination sites. Hydrogen coordinates to the metal center promoting the formation and elimination of a saturated alkane (polymer chain), producing a new empty coordination site. The formation of a metal-hydrogen bond allows for olefin insertion and subsequent chain growth without loss of the active species (Figure 1.3c).[7] In many cases, a transfer agent, such as HCl, is deliberately introduced into the polymerization system to control the molecular weight of the product.[2]

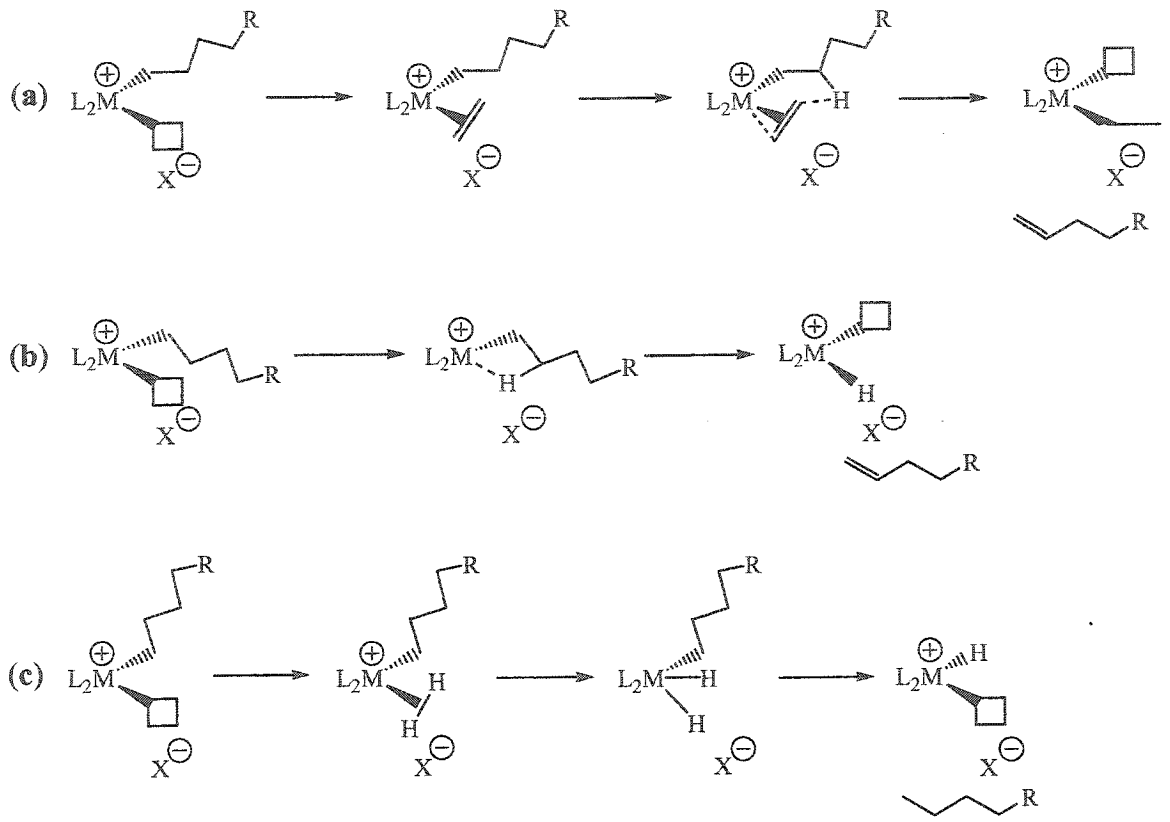
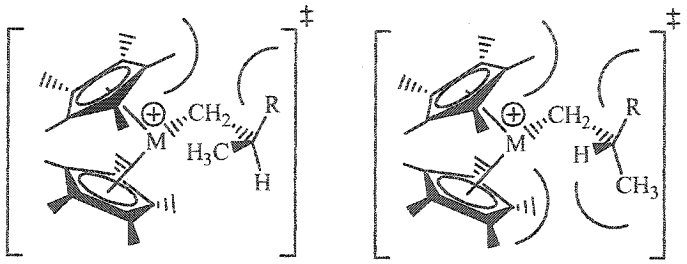


Figure 1.3: Mechanisms of chain termination.

A different chain-transfer mechanism, β-Me transfer, becomes more common when complexes bearing sterically crowded ligands such as $(C_5Me_5)_2MR_2$ (M = Zr, Hf; R = Me, Cl) are used as catalyst precursors for polymerization of α-olefins.[11,12] This process is attributed to the lower steric hindrance present in the transition state **1** *versus* the transition state **2** as shown in Figure 1.4. β-Me transfer involves orientation of the ligand, or of the growing polymer chain, to a conformation in which the migrating methyl group lies between (rather than eclipsing the ring) the sterically demanding C_5Me_5 rings.[13]



1 2

Figure 1.4: Transition states for β-Me (**1**) and β-H (**2**) elimination.

1.1.2. Catalyst Design

Over the years, a variety of compounds have been developed that satisfy the requirements necessary to yield catalysts for olefin polymerization. Some examples of active catalysts are shown in Figure 1.5, including metallocene complexes, *ansa*-metallocene complexes (**3,4**), constrained geometry complexes (**5**), half-metallocene complexes (**6,7**) and even complexes without cyclopentadienyl or other aromatic groups (**8,9**).

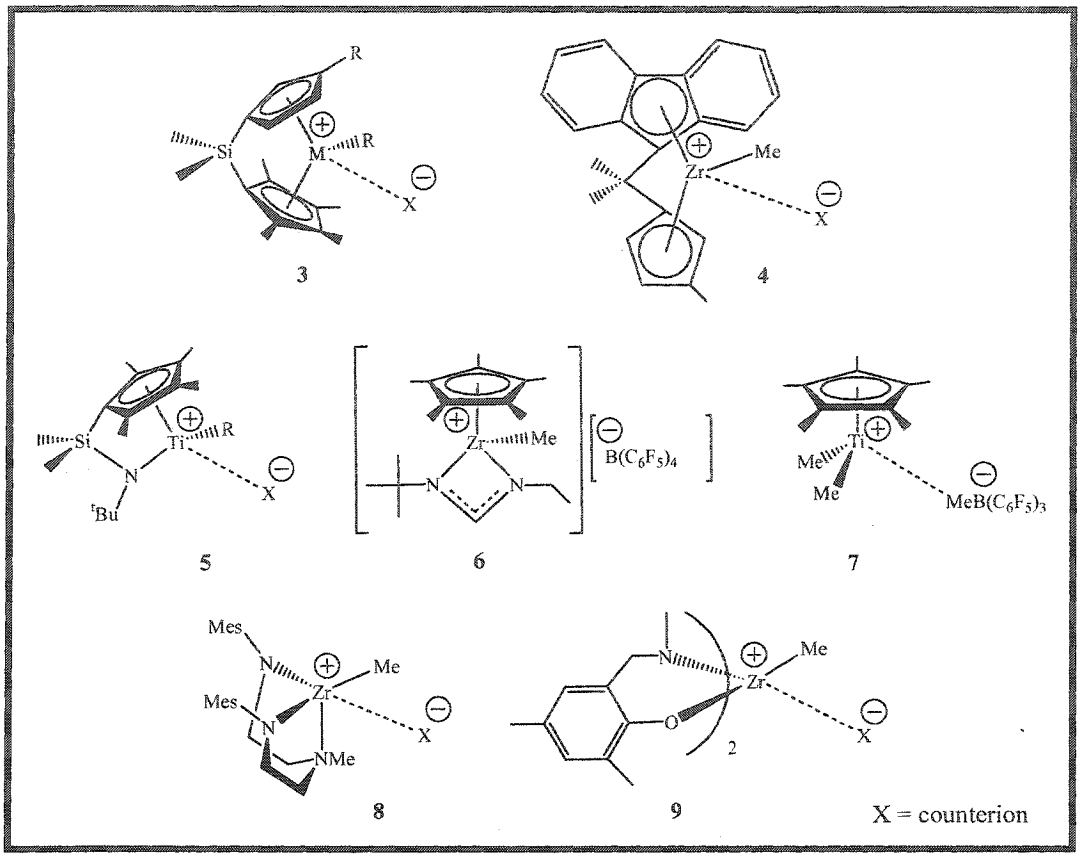


Figure 1.5: Diverse designs of Group 4 Transition Metal Catalyst for Olefin Polymerization.[7,14-23]

The Group 4 catalysts with *ansa*-cyclopentadienyl ligands are used in the polymerization process. With the introduction of a short interannular bridge, wedged metallocene species were obtained. The *ansa*-bridge increases the configurational stability of the metallocene fragment, by stabilizing the Cp ligand acceptor orbital a_1 (a, Figure 1.6). As a result, the back-donation from the metal is enhanced, where the effect is the decrease in energy at the $3a_1$ orbital of the metal (b, Figure 1.6). This provides less d character, minimizing the metal back-bonding with olefins.

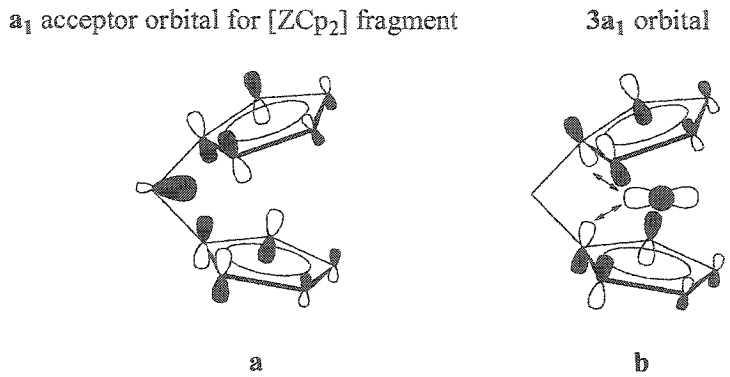


Figure 1.6: (a) Stability of Cp ligand acceptor orbital $\mathbf{a_1}$ (Z = CR'_2, SiR'_2); **(b)** enhanced back-donation lowers the energy of $\mathbf{3a_1}$.

In the polymerization of propylene the tacticity of the polymer can be regulated. Complexes with C_s symmetry[24] (**10**, Figure 1.7) produce syndiotactic polypropylene. This arises from the insertions of propylene from the alternating sides of the metallocene wedge (**11**, Figure 1.7).[25] The methyl group of the propylene moiety avoids the bulky polymer chain and fits into the open region between the substituents of the Cp ligand.

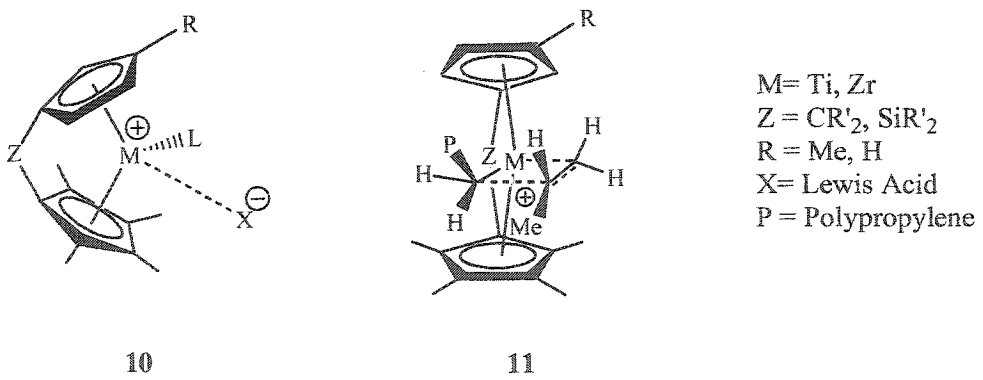
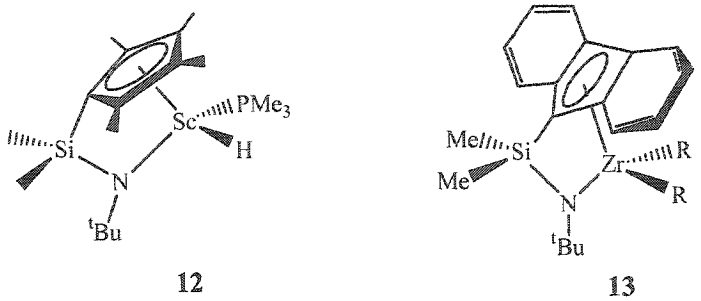


Figure 1.7: General structure of *ansa*-metallocene systems.

Bercaw and Shapiro demonstrated that a cyclopentadienyl moiety linked to a *tert*-butyl amido group by an dialkylsilanyl bond to a metal centre, resulted in an "*ansa*-

metallocene-like" complex (an example is depicted as **12** in Figure 1.8).[26-28] It was found that the reactivity for olefin polymerization was increased for this "*ansa*-metallocene-like" complex or constrained geometry catalyst (CGC). This is likely due to the more accessible metal center that facilitates coordination of the olefin during the propagation step of the polymerization process. Similar designs such as **13** (Figure 1.8)[29] have been developed with the aim to stabilize the highly electophilic metal center without hindering the approach of the unsaturated substrate.[29]



12 **13**

Figure 1.8: Examples of constrained geometry catalysts (CGC).

1.1.3. Lewis Acidic Cocatalysts

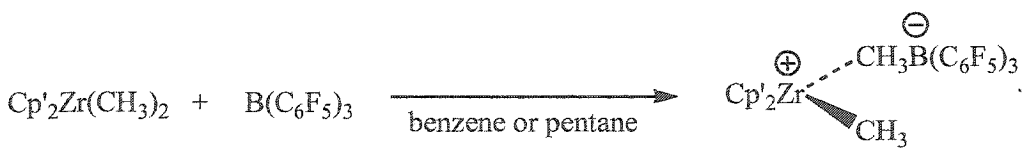
To generate de active catalyst, the Group 4 metallocene complex has to be activated by a Lewis acidic compound. The role of the Lewis acid is to promote the formation of an electron deficient coordinatively unsaturated or "cation-like" metallocene center, (e.g. $[Cp_2MR]^+$, Figure 1.9). The reaction of the cocatalyst (or activator) with the metallocene complex results in the formation of the active species (or active catalyst). After the activation process, the activator becomes an anion, and the Group 4 complex has a cationic nature, both of them forming part of the actual active catalyst. The interaction between the cationic and anionic fragments is of significant importance (discrete anion-cation pair or zwitterions) in the polymerization process and the resulting polymer properties.

Cp = cyclopentadienyl-type ligand; R = alkyl; R' = alkyl; A = cocatalyst

Figure 1.9: Generation of the active catalyst.

In 1980 Sinn *et al.*[30,31] reported that Group 4 metallocene compounds, in the presence of an excess of methylalumoxane, generated highly active catalysts for olefin polymerization. This prompted the explorations and use of methylalumoxane (MAO), alkylaluminum halides, dehydroxylated alumina (DA) and related oxides.[32]

Perfluoroaryl boranes and trityl borates are also activators and have been studied in great detail.[32] It was later reported that when *tris*(pentafluorophenyl)borane $B(C_6F_5)_3$ (developed by Massey and Park in 1964)[33] was combined with Group 4 metallocene dialkyls, it facilitated the olefin polymerization process.[34] Marks *et al.*[35-37] have shown that the reaction of $B(C_6F_5)_3$ with a variety of zirconocene dimethyl complexes proceeds rapidly and quantitatively at room temperature in non-coordinating solvents by inducing a high degree of cationic polarization at the metal center *via* methide "abstraction" to yield zwitterionic complexes akin to $Cp_2ZrMe(\mu\text{-}MeB(C_6F_5)_3)$ (**14**) (Figure 1.10).



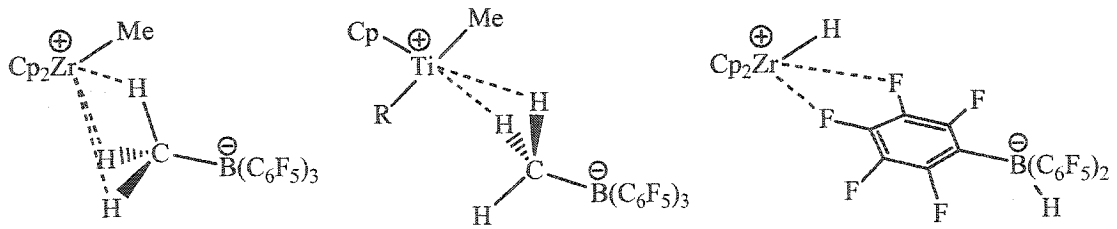
14

Cp': η^5-C_5H_5; η^5-1,2-$Me_2C_5H_3$; η^5-C_5Me_5; η^5-1,3$(SiMe_3)_2C_5H_3$

Figure 1.10: Generation of the zwitterion $Cp_2ZrCH_3(\mu\text{-}CH_3B(C_6F_5)_3)$.

The interaction M←(H–C) (M = Ti, Zr, Hf) in a zwitterion such as $Cp_2M(CH_3)(\mu\text{-}CH_3B(C_6F_5)_3)$ is described as an "intermolecular agostic" interaction. This is observed when an electron deficient metal center (M) receives electron density from a

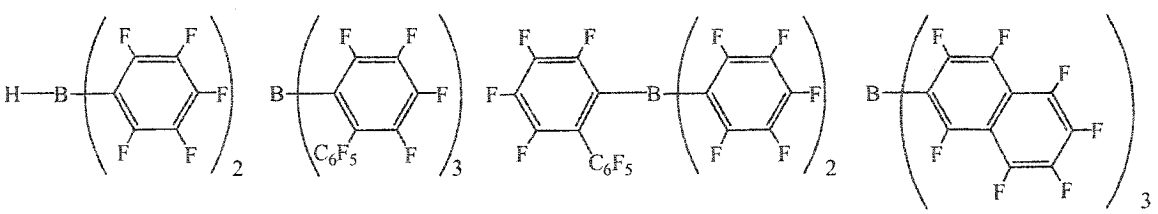
C–H σ-bond.[38] For example, in the complex $[Cp_2ZrCH_3(\mu\text{-}CH_3)B(C_6F_5)_3]$ (**14**), the moiety $[(CH_3)B(C_6F_5)_3]^-$, provides electron density to the metal center *via* an agostic interaction from the B–bound methyl group.[38,39] There have also been reports of two or even three agostic interactions from the anion[39] (Figure 1.11). The weak donation of electron density and steric crowding results in relatively long bond distances between donor and acceptor centers, and therefore this weak interaction is easily displaced in the presence of a stronger donor.



15 **16** **17**

Figure 1.11: Examples of 3 agostic interactions **15** and 2 agostic interactions **16** and **17**.

More recently, a number of new perfluoroaryl borane activators have been designed and synthesized.[34,40] Piers *et al.* developed the *bis*(pentafluorophenyl) borane $[HB(C_6F_5)_2]_2$ (**18**).[41] Marks *et al.* has introduced the sterically encumbered *tris*(2,2',2''-perfluorobiphenyl) borane **19**, *bis*(pentafluorophenyl)(2-perfluorobiphenyl) borane **20**, and *tris*(β-perfluoronaphthyl) borane **21** (Figure 1.12).[32,42-44]



18 **19** **20** **21**

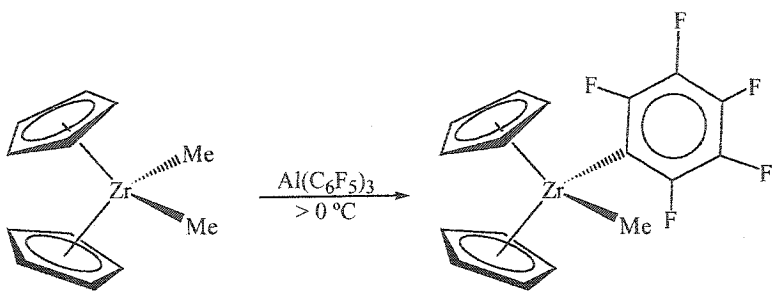
Figure 1.12: Boranes developed by Piers and Marks group.

1.1.4. Catalyst Deactivation Pathways

Catalyst degradation has been studied for a great number of systems, and a variety of different deactivation pathways have been identified, such as ligand redistribution, intramolecular C-H activation, intermolecular C-H activation and β-H transfer, all of which will be discussed further.

1.1.4.1 Ligand redistribution

An example of ligand redistribution involves the decomposition of $[((Me_3Si)_2C_5H_3)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$ to give the non-catalytic products $((Me_3Si)_2C_5H_3)_2ZrMe(C_6F_5)$ and $MeB(C_6F_5)_2$.[37] Analogous reactions have been reported to occur with $Al(C_6F_5)_3$, where the observed product is $Cp_2ZrMe(C_6F_5)$ (**22**, Figure 1.13).[32,45]



22

Figure 1.13: Example of deactivation of the catalyst by ligand redistribution.

1.1.4.2 Intramolecular C-H activation.

An example of intramolecular C–H bond activation is the reaction of the highly crowded activated metallocene complex $[(C_5Me_5)_2ZrMe]^+$ **23** (Figure 1.14) with dienes such as 1,3-butadiene. The initial product, an η^3-allyl complex **24** (Figure 1.14), undergoes C–H activation to afford the product **25** (Figure 1.14).[46]

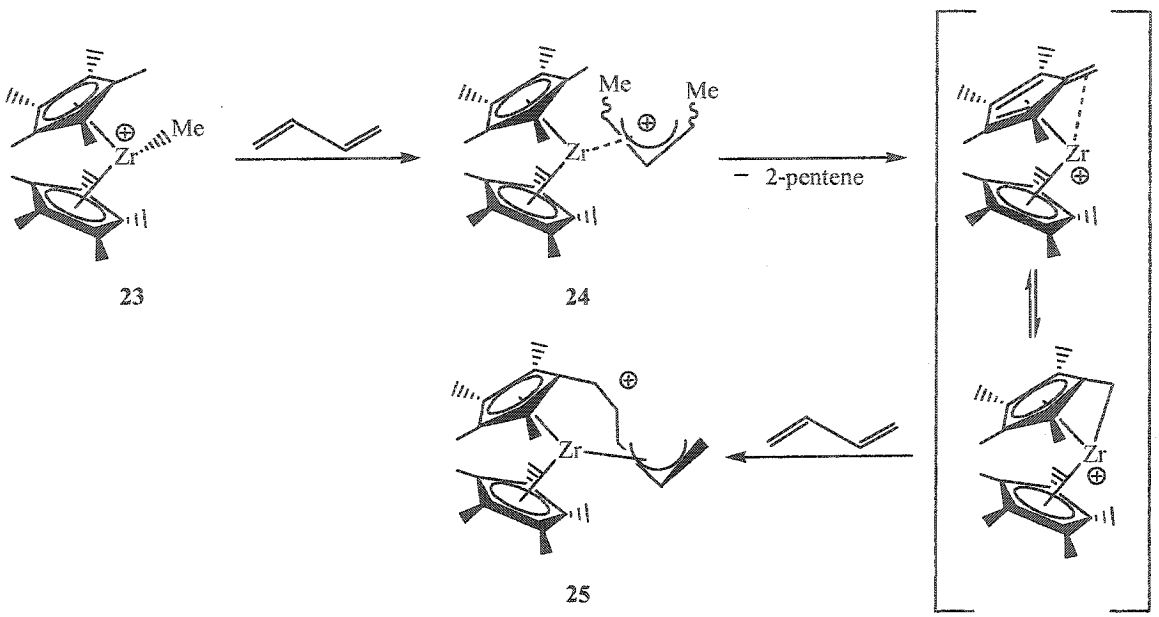


Figure 1.14: Reaction mechanism of $[(C_5Me_5)_2ZrMe]^+$ **(23)** with 1,3-butadiene.

Intramolecular C–H activation can also occur at the σ-bound methyl ligand in a cationic metallocene complex as shown in Figure 1.15.[35,37,47,48] The open coordination environment of Zr(IV), the high Lewis acidity at the metal center, and the accessibility of the unactivated methyl group **26** are factors that promote C–H activation **27** and ultimately lead to the deactivation of the catalyst **28**.

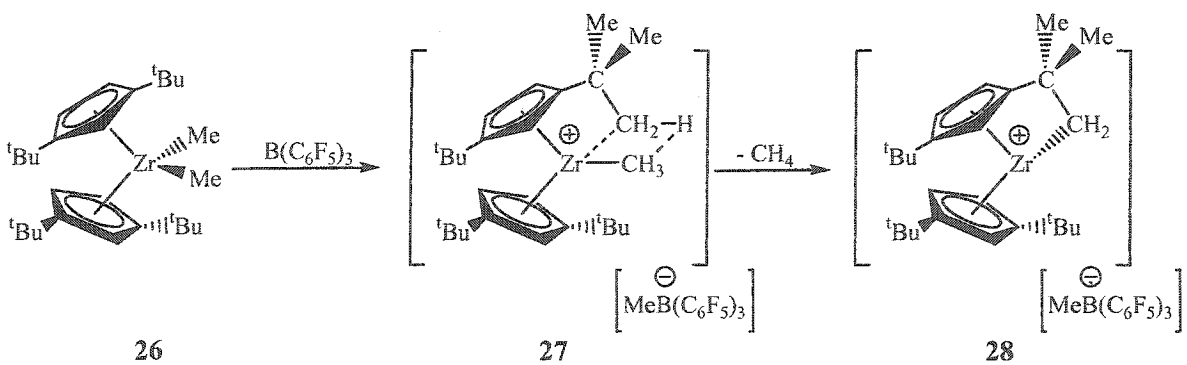


Figure 1.15: Intramolecular C–H activation at the Zr σ–bound methyl ligand.

1.1.4.3 β-H transfer

Elimination of the β-hydrogen atom from the growing chain of an agostic precursor **30** (Figure 1.16) results in the formation of a metal hydride olefin species **31** (Figure 1.16), which can then follow two different pathways, (**a**) and (**b**). Pathway (**a**) is a polymerization termination pathway by β-hydrogen transfer, where catalyst **31a** (Figure 1.16) is still active. Pathway (**b**) results in the formation of an allyl functionality in the long polymer chain at the metal complex **32** (Figure 1.16), which is inactive to further insertions of monomer.[49-53]

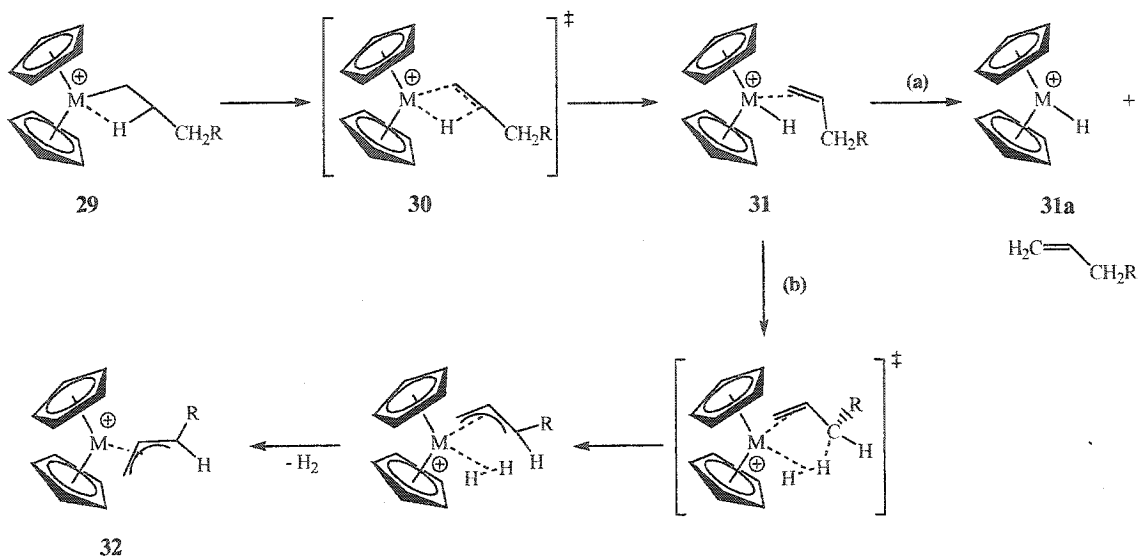
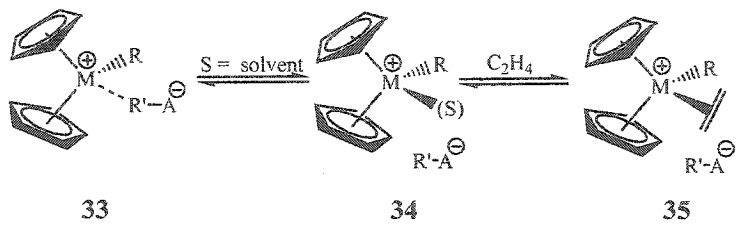


Figure 1.16: β-hydride elimination, formation of a terminal allyl **30**.

1.1.5. Stabilization of the Alkyl Cation

Coordinatively unsaturated species such as cationic metallocenes $[Cp_2MR]^+$ are very reactive and may undergo a number of reactions in solution. Since the cation is a strong electrophile, it can interact with any available nucleophile in the media, such as an anion **33**, solvent **34**, or the olefin substrate **35** (Figure 1.17).[54]



33 34 35

Figure 1.17: $[Cp_2M(R)]^+$ complexes establish a series of equilibriums in solution with available nucleophiles.

However, if the counterion is very weakly coordinated, (e.g. *tetrakis*(pentafluorophenyl)borate) the ion pair stability is relatively poor[55] and tends to form μ-Me dimers in the presence of excess neutral dimethylmetallocene, $Cp_2M(CH_3)_2$. This is due to the neutral dimethylmetallocene being a better Lewis base than the borate counterion. The μ-Me dimers generated in the presence of the $[MeB(C_6F_5)_3]^-$ counterion exist as part of an equilibrium between a solvent-separated ion pair and a contact ion pair (Figure 1.18). Most of the μ-Me dimers are thermally stable, where high temperatures shift the equilibrium toward the monomeric components of the dimer.[56] It has not been determined if the presence of such dinuclear species or dimers present during the polymerization can be unfavorable. Experimental data suggest that the dimers do not affect the process directly, but instead may stabilize the more active monomeric alkyl cations responsible for the olefin polymerization.[56]

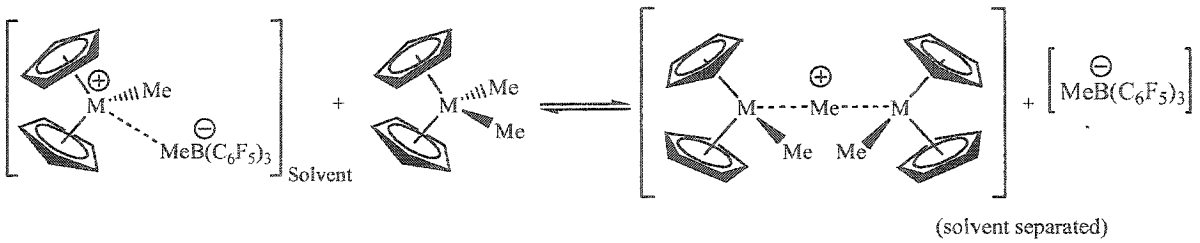


Figure 1.18: Equilibrium between the solvent-separated ion pair and the cationic μ-Me dimer.

Lewis bases coordinated with metallocene cations $[Cp_2TiR]^+$ (R = alkyl) permit the isolation and characterization of such cationic complexes. Jordan *et al.* reported the synthesis of complexes of the type $[Cp_2Zr(R)(L)]^+$ (L = THF, CH_3CN, 4,4'-dimethylbipyridine and 4-(dimethylamino)-pyridine), Figure 1.19), by reacting $Cp_2Zr(CH_3)I$ with $AgPF_6$ or with $TlPF_6$ (Figure 1.20) followed by the addition of the Lewis base.[57,58]

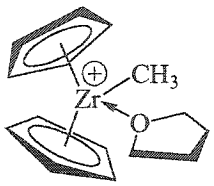


Figure 1.19: Coordination of THF as a Lewis base to the zirconocene cation, allowing its isolation and characterization.

$$Cp_2Zr(CH_3)X \quad (X = Cl, I) \quad + \quad M[PF_6] \quad (M = Ag, Tl) \xrightarrow{CH_3CN} [Cp_2Zr(CH_3)(CH_3CN)][PF_6] \quad + \quad MX$$

Figure 1.20: Generation of $[Cp_2ZrMe(L)]^+$ complexes.[57]

Similar studies showed [59] that $Ag[BPh_4]$ provided access to $[Cp_2Zr(R)]^+$ complexes, where the cation may be trapped with electron donating groups (often nitriles, amines, ketones, aldimines, carbonyls, phosphines, and cyclic ethers).[59] $[BPh_4]^-$ as a counterion provided a more stable compound for studying than the corresponding $[PF_6]^-$ salts. Complexes with $[PF_6]^-$ as the counterion were stable in the solid state, but decomposed in solution with THF, CH_2Cl_2 or CH_3CN as solvents. What was generated was $Cp_2Zr(CH_3)F$ and Cp_2ZrF_2 as a secondary product *via* F^- abstraction from $[PF_6]^-$.[57] Ligand exchange with $[BPh_4]^-$ is less favorable, providing a more stable ion pair complex. A variety of these complexes are used to study catalytic reactions that take place during the polymerization process (as well as the deactivation pathways of the catalyst).[34,60-75] .

The stabilized dicationic organometallic complexes have also been prepared.[76-78] Examples include the ((diarylphosphino)methyl)cyclopentadienyl-derived zirconocenes **36** (Figure 1.21). These complexes are internally phosphine-stabilized zirconocene cationic systems, leading to mono- **37** and dicationic **38** phosphine-stabilized zirconocene systems.[79,80] In these cases, the adducts obtain from the reaction of the phosphine and the activator ($B(C_6F_5)_3$) would be reversible, allowing then the abstraction of the methyl group bound to the transition metal. This promotes the formation of the phosphine-stabilized systems. Analogous systems that have (dimethylamino)methyl substituents on their Cp rings have also been prepared, having as the counterion $[B(C_6F_5)_4]^-$. [47, 81]

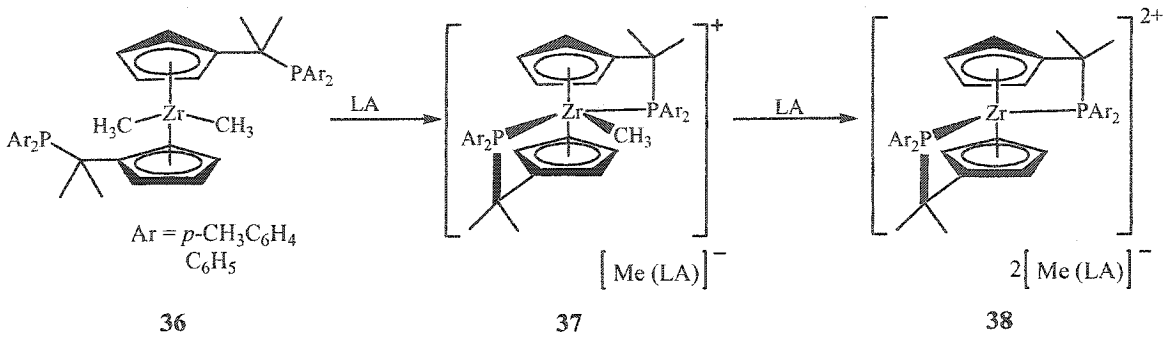


Figure 1.21: Generation of internally phosphine-stabilized zirconocene systems.

1.2. Cyclopentadienyl-Titanium Phosphinimide Complexes

Stephan *et al.* reported a family of complexes of the general formula $Cp(NPR_3)TiCl_2$ that are effective catalyst precursors for ethylene polymerization.[63,82,83] The metal complexes that contain both the Cp and the phosphinimide ligands structurally imitate the *bis*(cyclopentadienyl) complexes.[82] The phosphinimide ligand ($^tBu_3PN$) shows steric similarity to the cyclopentadienyl ring. The cone angle of Ti–Cp is 83°, while for Ti–NP^tBu_3, the value is about 87° (Figure 1.22).[84] Furthermore, the distance between Ti–P is longer than the Ti–Cp –centroid. As a result, steric bulk supplied by the phosphinimide ligand is removed from the metal center. This factor plays a significant role in the effectiveness of the catalyst.[84]

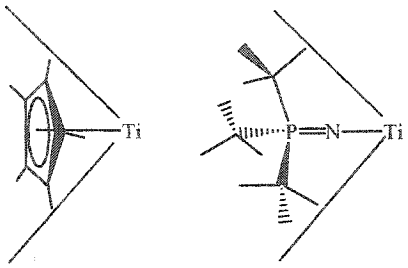


Figure 1.22: Steric similarity between the Cp ring and the phosphinimide ligand.

Additional studies on these systems suggested that reduced steric congestion could trigger deactivation pathways, including the interaction with Lewis acids leading to C–H activation.[85-87] Observations also suggested that if the phosphinimide ligand possesses electron-withdrawing substituents, it would result in highly Lewis acidic titanium species. Presumably, this acidity can also prompt the deactivation of the activated catalyst.[87] The electronic character of phosphinimide ligands has been previously studied by Dehnicke *et al.*.[88,89] Studies showed that the σ–2π nature of the interaction of the phosphinimide ligand with a metal center is also analogous to a cyclopentadienyl ring (Figure 1.23). In case **a** both, the cyclopentadienyl (a_1 orbital) and phosphinimide (p_z orbital) ligands can interact with the metal to form a σ bond. For **b** and **c**, the cyclopentadienyl degenerated e_1 orbitals are isolobal with the also degenerated phosphinimide p_x and p_y orbitals, where they can form a set of π–bonds with the metal.

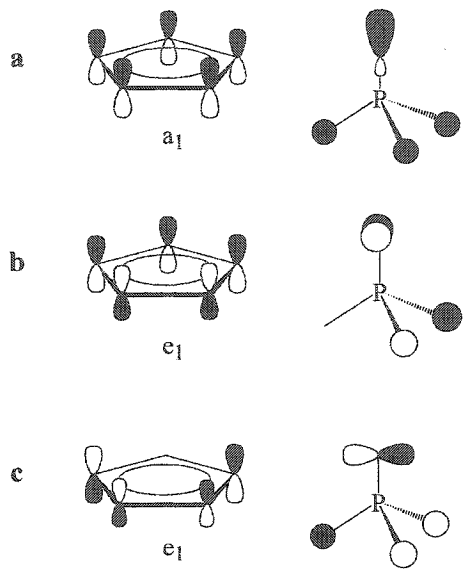
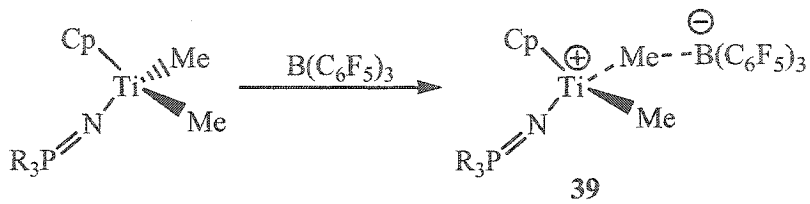


Figure 1.23: Analogy between the cyclopentadienyl ligand orbitals and the phosphinimide orbital ligands.

The reaction of the system $Cp(NPR_3)TiMe_2$ with the Lewis acid $B(C_6F_5)_3$ in hexanes yielded the zwitterionic species, $CpTiMe(NPR_3)(\mu\text{-}MeB(C_6F_5)_3)$ (**39**) (Figure 1.24).[83] For the system $Cp(NPPh_2(NP^tBu_3))TiMe_2$ with the borane $B(C_6F_5)_3$, the product $[CpTi(\mu\text{-}Cl)(NPPh_2(NP^tBu_3))]_2[B(C_6F_5)_4]_2$ was isolated,[87] suggesting solvent activation and borate substituent redistribution occurred. The explanation offered for this phenomenon was that the electron-withdrawing phosphinimide substituent on the metal bound phosphinimide ligand yields a highly Lewis acidic Ti species which initiates deactivation of the catalyst. For the case of $Cp(NP^tBu_3)TiMe_2$, when the reaction is carried out in the presence of a donor, the stable cation $[Cp(NP^tBu_3)TiMe{\cdot}LB][MeB(C_6F_5)_3]$ ($Cp = \eta^5\text{-}C_5H_5$; $LB = PMe_3$) is obtained.[90]



39

Figure 1.24: Generation of the zwitterion $CpTiMe(NP^tBu_3)(\mu\text{-}MeB(C_6F_5)_3)$ (**39**).

1.3. Tris(pentafluorophenyl)borane Lewis Acid/Base Adducts with Group 15

Because of a vacant 2p-orbital, triorganoboranes (R_3B), in general, can accept electrons from a nucleophile, which can be neutral (L) or charged (R'^-) to form an $R_3B{\cdot}L$ adduct or an $[R_3BR']^-$ anion.[91] The nature of the bond formed between tertiary boranes, and tertiary derivatives of Group 15, particularly those of nitrogen and phosphorus, has been the object of continued interest and investigation.[92-96]

Recently, there has been a growing interest in *tris*(fluoroaryl)boranes, because of their high Lewis acidity and chemical and thermal stability.[97] The reactivity of *tris*(pentafluorophenyl)borane towards donor molecules (ammonia, trimethylamine, triphenylphosphine and pyridine) has been studied.[33,98] Through the course of these studies, it was found that stable, crystalline adducts with *N,N*-di*iso*propylbenzamide and a variety of carbonyl-containing compounds, such as, benzaldehyde, acetophenone, and ethyl benzoate were formed.[73] Two equivalents of $B(C_6F_5)_3$ coordinate to imidazole to further react with aminonium chlorides to give the delocalized stable *bis*$[B(C_6F_5)_3]$–imidazolate salts **40** (Figure 1.25).[99] In this same area, Piers *et al.* published the synthesis and structural features of imine–$B(C_6F_5)_3$ complexes.[97, 100]

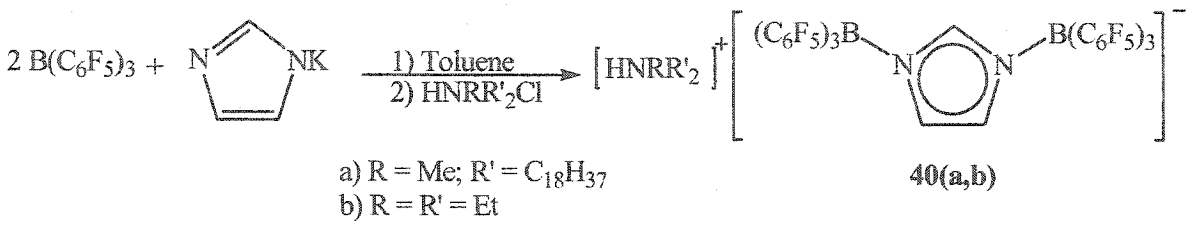


Figure 1.25: Generation of $B(C_6F_5)_3$ adducts with imidazole as a Lewis bases.

New borane systems with coordination of Group 15 compounds can be obtained by formation of Lewis acid/base adducts. For example, the nitrogen donor adduct $[CPh_3][(C_6F_5)_3B{-}CN{-}B(C_6F_5)_3]$ was designed for the purpose of affording a better activator by reducing the nucleophilicity of the anion. The strategy was to distribute the negative charge over two boron atoms. The coordination of nitriles (**41**), as well as isonitriles (**42**) (sp-N), to $B(C_6F_5)_3$ has led to the formation of neutral Lewis acid/base adducts (Figure 1.26), which result in an increase in the C≡N bond strength. Overall, electrostatic interactions are of importance in the bonding of $(C_6F_5)_3B{\cdot}L$ complexes, since they have been shown to be responsible for bond-strengthening effects in these neutral adduct systems.[101] The adducts generated with the nitrogen donors, $C_3N_3H_3$ (sp^2-N) (**43, 44**), and NH_2CN (sp- and sp^3-N), where the coordination is *via* the -CN nitrogen atom, have also been reported (Figure 1.27).[102] In the case of substituted pyridines (RC_5H_4N) where the R group contains an amine or other Lewis basic groups, $B(C_6F_5)_3$ reacts readily with the pyridine moiety. Marder *et al.* reported this observation in the syntheses of the adducts 4-Me_2N-$C_5H_4N{\cdot}B(C_6F_5)_3$, *trans*-4-$Me_2N$-$C_6H_4$-C(H)=C(H)-$C_5H_4N{\cdot}B(C_6F_5)_3$, 4-$Me_2N$-$C_6H_4$-C≡C-$C_5H_4N{\cdot}B(C_6F_5)_3$, and *trans*-4-MeO-$C_6H_4$-C(H)=C(H)-$C_5H_4N{\cdot}B(C_6F_5)_3$.[103]

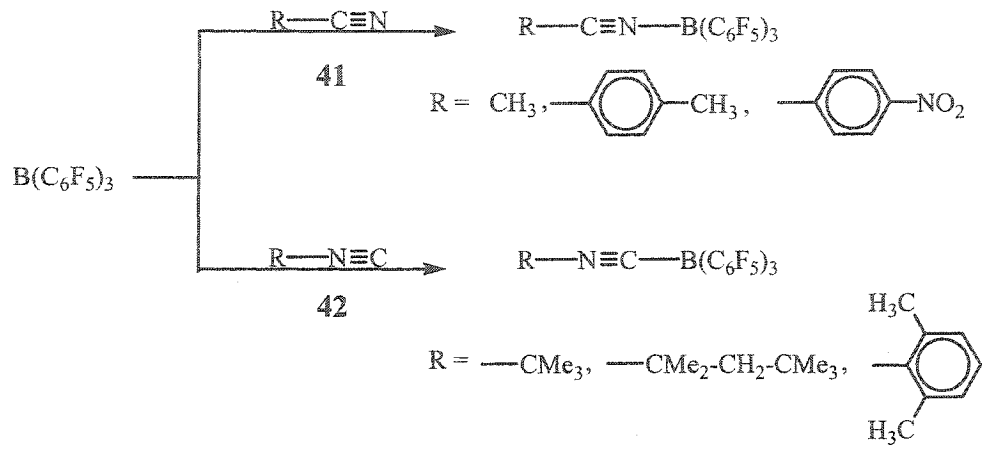
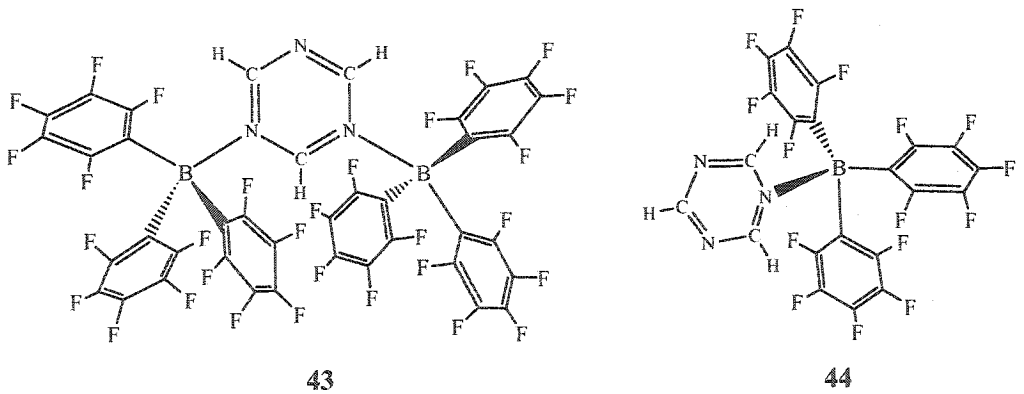


Figure 1.26: Coordination of nitriles **41** and isonitriles **42** to the Lewis acid $B(C_6F_5)_3$.

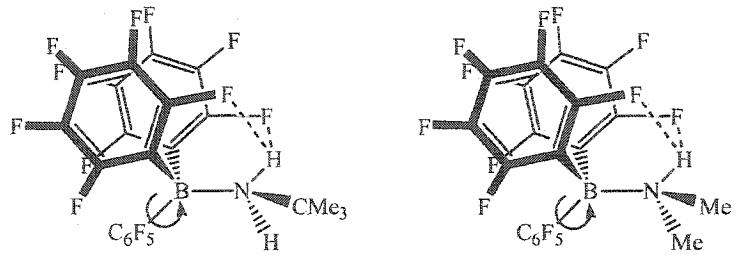


43 **44**

Figure 1.27: The $B(C_6F_5)_3$ adducts generated with the nitrogen donors in aromatic systems of the general formula $C_3N_3H_3$ (sp^2-N) (**43**, **44**).

A common feature observed in amine adducts of $B(C_6F_5)_3$ is hydrogen-bonding interactions between N–H and *ortho*-F atoms of C_6F_5 groups.[100,104] In some cases, these intramolecular interactions are strong enough to persist in solution even at room temperature and may allow H···F coupling to be observed. Hydrogen-bonding has an influence on molecular geometry and dynamics, and is very strong where two fluorines connect to a single N–H functionality to give a C–F···H···F–C arrangement (**45**, **46**; Figure 1.28), resulting in a strong hindered aryl rotation. In the case of tertiary amine

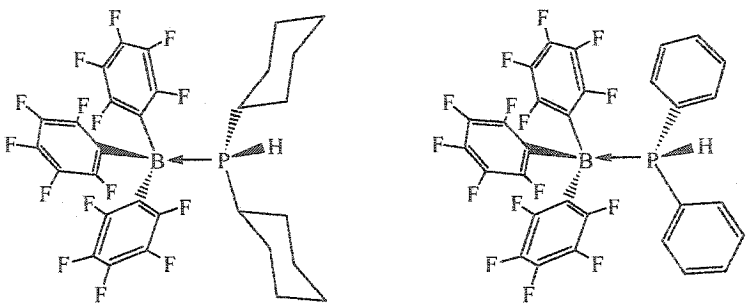
adducts (such as $[(C_6F_5)_3B(MeNEt_2)]$), free rotation around the B–N is observed, implying the lack of hydrogen bonding with *ortho*-fluorine atoms.[104]



45 46

Figure 1.28: H-bonding with two *ortho*-F present in the adducts $^tBuH_2N{\cdot}B(C_6F_5)_3$ (**45**) and $Me_2HN{\cdot}B(C_6F_5)_3$ (**46**).

In the case where the electron donating molecules (L) are phosphines, the reaction with $B(C_6F_5)_3$ also affords the adduct $B(C_6F_5)_3{\cdot}L$. As in the case with amine-adducts, hydrogen-bonding interactions between P–H and *ortho*-F atoms (rather than *meta*- or *para*-F) of C_6F_5 groups of the kind P–H···F–C are also observed, but only for primary phosphines.[105] The P–H···F interaction in secondary phosphine-$B(C_6F_5)_3$ adducts such as, $(C_6F_5)_3B(PHCy_2)$ (**47**) and $(C_6F_5)_3B(PHPh_2)$ (**48**) is not significant (Figure 1.29).[104] Crystallographic studies showed that the distance between the phosphorus atom and the boron atom are further apart than nitrogen and boron, not allowing an interaction between the *o*-F atoms and the P-H hydrogen.



47 48

Figure 1.29: Secondary phosphine adducts **47** and **48** of *tris*(pentafluorophenyl)borane

Steric repulsion from the phosphine substituents also plays a significant role. For example, in the case of *tert*-butyl phosphine, the *tert*-butyl substituent and the perfluorinated aryl group repel each other, resulting in the distortion of the angles between the adduct bond and the perfluorinated aryl groups.[105] The tilting produced by an attractive interaction between the hydrogens in the phosphine and the *ortho*-F will also distort the molecule. Distortions of the perfluoroaryl groups around the adduct bond can therefore be attributed to steric repulsions from the subtituents present in the phosphine and attractive intermolecular F···H interactions.[105]

For the case of phosphine (PH_3) there are no expected distortions due to steric repulsions, thus it should retain its three-fold symmetry around the adduct bond.[105,106] Upon coordination of PH_3 to $B(C_6F_5)_3$, the H–P–H angle widens. This is an indication of the quasi tetrahedral coordination at the P–center. The same effect, although less pronounced, is observed in $(C_6F_5)_3B{\cdot}PPh_3$. A larger phosphine ligand influences the cone angle, and leads to a lengthening of the B–P bond. The reason is that the potential energy surface around the B–L equilibrium distance is shallow, allowing for a large variation in the bond length.[101] This may be the explanation for why secondary phosphines do not present the P–H···F interactions observed in PH_3 and primary phosphines as the distances between the hydrogen and the *ortho*-F may be too great.

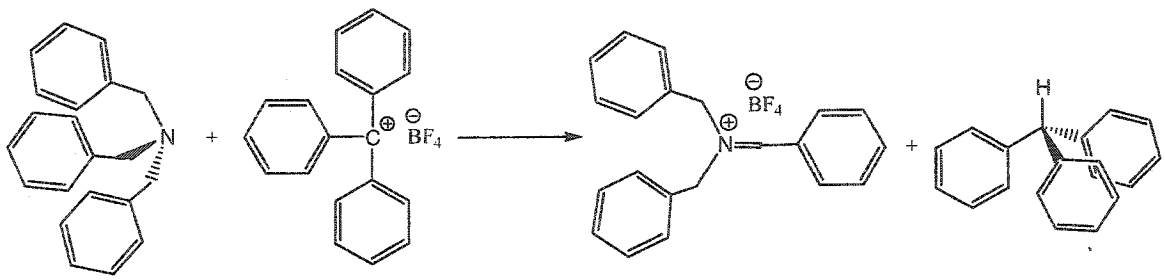
1.4. Trityl Tetrakis(pentafluorophenyl)borate Lewis Acid/Base Adducts with Group 15.

Trityl *tetrakis*(pentafluorophenyl)borate has not been used as extensively in the study of Lewis acid/base adducts with Group 15 reagents. However, there are studies with the trityl cation bearing hexafluorophosphate or tetrafluoroborate as anions, and even with trityl chloride.

The interaction of trityl salts with Lewis bases such as aliphatic and aromatic amines forms ammonium products. These processes are reversible equilibria that are concentration and solvent dependent. Aromatic amines reactions with trityl salts exhibit electron donor-acceptor interactions only when the amine is present at higher

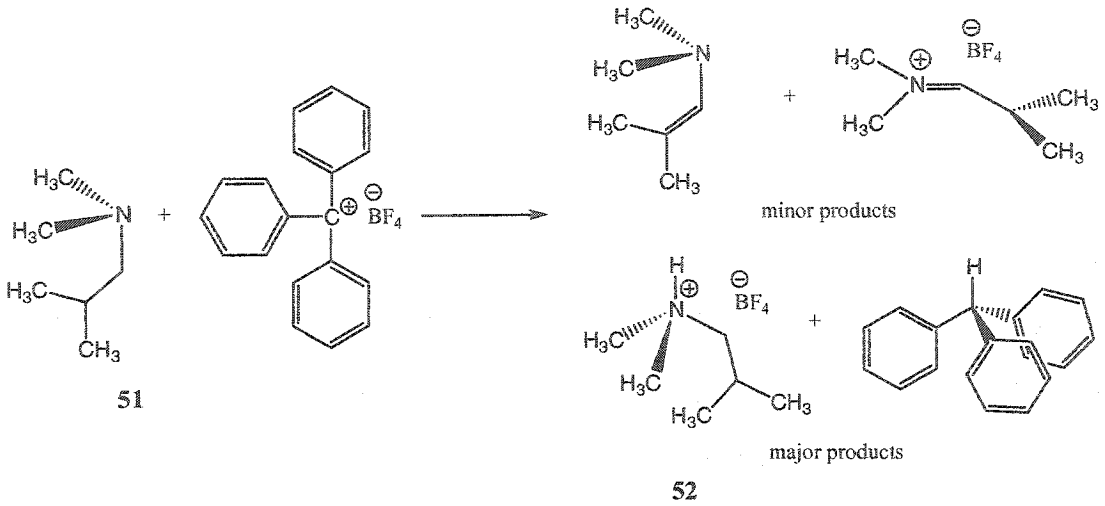
concentrations than the salt. On the other hand, aliphatic amines reactions (*n*-butylamine, ethanolamine, piperidine, triethylamine) will tend to equilibrium when the dielectric constant of the solvent is higher, shifting towards the free cations and free amine.[107]

On the other hand, trityl salts can promote extraction of a hydride ion from tertiary amines. This process is assisted by the formation of the stable tertiary iminium salts. An example is the oxidation of tribenzylamine upon reacting with trityl fluoroborate, yielding the corresponding iminium salt.[108] Tertiary amines containing at least one α-aliphatic hydrogen atom appear to be the only amines capable of undergoing hydride transfer reactions with trityl salts. Tertiary amines containing only α-hydrogen atoms **49** produce the corresponding tertiary iminium salt **50** (Figure 1.30). Tertiary amines containing both α- and β-hydrogens **51** react further to build up ammonium salts **52** (Figure 1.31). Secondary aliphatic amines **53** give little or no hydride transfer with trityl ion. Instead the corresponding trityldialkylamine **54** and dialkylammonium salts **55** are obtained (Figure 1.32).[108]



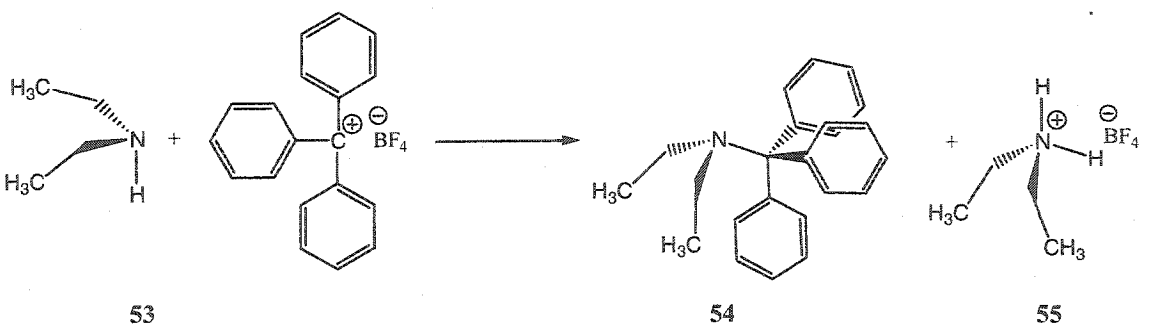
49 **50**

Figure 1.30: Reaction of tertiary amines **49** with trityl salts.



51 52

Figure 1.31: Reaction of tertiary amines bearing α- and β-hydrogens **51** with trityl salts.



53 54 55

Figure 1.32: Reaction of secondary aliphatic amines **53** with trityl salts.

The reaction of the trityl cation with the relatively electron-donating pyridine, affords the N-tritylpyridinium salt. The nitrogen in the pyridine has a lone pair that can form a new bond with the trityl cation. The new coordinative bond between the carbon and nitrogen is elongated to minimize the steric strain between the phenyl groups and pyridine. Electron density flows from the pyridine to the trityl fragment; the nitrogen becomes positively charged, thus decreasing the electron charge density in the aromatic ring.[109]

Various trivalent phosphorus compounds (R_3P where R = H or various alkyl, alkoxy, or aryl groups) have been treated with trityl hexafluorophosphate, while using

dichloromethane as the solvent. In these reactions, the trityl-substituted phosphonium salts $[R_3PCPh_3][PF_6]$ were obtained as the major products, along with trace amounts of the less sterically hindered product $[(p\text{-}R_3P\text{-}C_6H_4)(C_6H_5)_2CH][PF_6]$.[110] An example is presented by the reaction of triphenylphosphine with the trityl cation, which gives both $(C_6H_5)_3C{-}P^+(C_6H_5)_3$ (**56**) and $(p\text{-}(C_6H_5)_3P^+\text{-}C_6H_4)(C_6H_5)_2CH$ (**57**) as products (Figure 1.33).[111] Similarly, in the reaction of methyl-*tert*-butylphenylphosphine $(CH_3)(^tBu)(Ph)P$ with tritylchloride, the product was the [*p*-benzhydryl-phenyl]-phosphonium salt instead of the expected trityl-phosphonium salt.[112] It is evident that the reactivity depends on the R-groups present in the phosphine and reaction conditions.

A deeper investigation into the matter showed that the tetrafluoroborate salt **56**, when dissolved in acetonitrile or dichloromethane isomerizes to **57** in the presence of a Lewis base such as piperidine, tribenzylamine, pyridine, *tert*-butyl*iso*propylamine and even chloride ions. To explain this isomerization, the mechanism showed in Figure 1.33 has been proposed on the basis of experimental observations.[111]

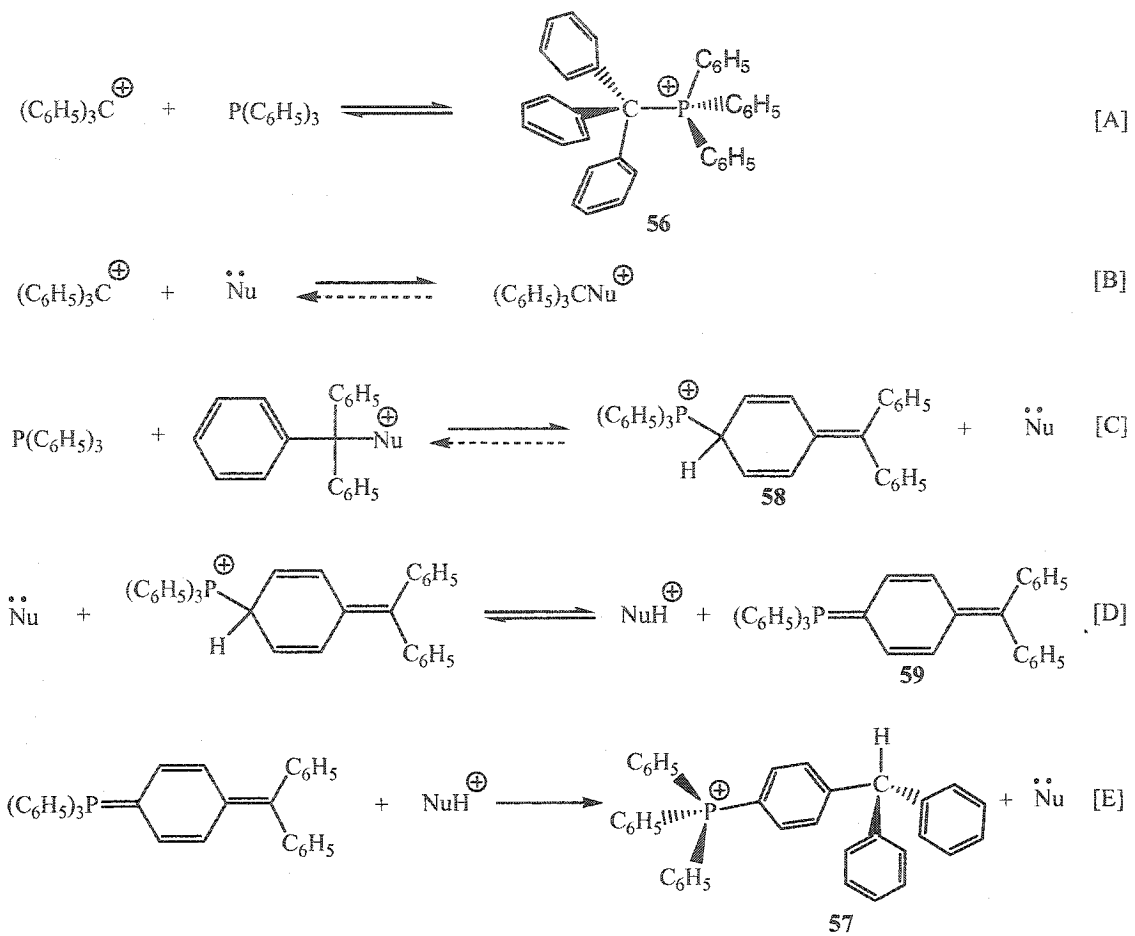
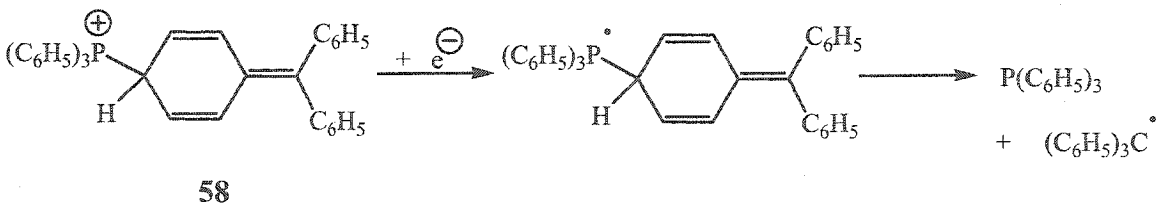


Figure 1.33: Mechanism for interconversion of the isomers $(C_6H_5)_3C{-}P^+(C_6H_5)_3$ **(56)** and $(C_6H_5)_2CHC_6H_4{-}P^+(C_6H_5)_3$ **(57)**.[111]

Reaction [**C**] is a nucleophilic substitution step (S_N2). Reactions [**D**] and [**E**] represent the detail of the reaction that converts the 4-benzhydrylidene-(cyclohexadienyl)phosphonium **58** into the phosphonium cation **57**. Therefore, in order for the addition at the *para-* position of one of the phenyl groups of the trityl cation to take place, it is necessary that the tertiary carbon is covalently bound to a non-ionizable nucleophile (as shown in reaction [**B**] Figure 1.33) such as the chloride ion, or an aliphatic amine. For attacks of a triphenylphosphine molecule to occur, the nucleophile must be liberated according to the S_N2 mechanism. In addition, in [**D**] the formation of an ylide **59** provides a more stable compound than **58**. Kinetic studies of ylide **59** formation

indicated it is independent of the nature and concentration of the nucleophile, and is only a function of temperature. This means that the rate determining kinetic reaction in the proposed mechanism is reaction [**A**].[111]

Parallel to the isomerization process, the ylide can undergo another reaction. The ylide is a good reducing agent, capable of reducing the phosphonium cation **58**, promoting phosphorus-carbon cleavage with formation of an aromatic ring.[111] Therefore, a trityl radical species will be present in the reaction (Figure 1.34).



58

Figure 1.34: Generation of trityl radical species and free phosphine from phosphonium cation **58**.

The reaction [**E**] shown in Figure 1.33 is irreversible, since the ylide **59** is consumed as it is produced. The neutral trityl radicals present in the reaction media are susceptible to dismutation in the presence of NuH^+ (Figure 1.35) forming triphenylmethane, which consumes the available protons that could protonate the ylide.[111]

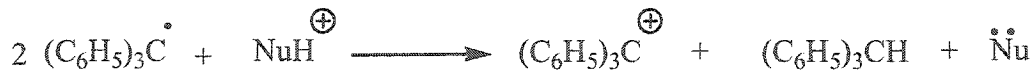


Figure 1.35: Nucleophilic attack to neutral trityl radicals.

1.5. Relevance of the Thesis

This introduction provided a brief synopsis about the studies accomplished with respect to the nature of the reactivity of Group 4 Transition Metal Catalysts. All these studies have contributed to the understanding of how a catalytic system behaves during

the polymerization process. It has also been observed that even when it is possible to make general statements about certain systems, the design of the complex plays a very important role in the catalytic system. To isolate zwitterionic compounds, the use of Lewis bases has been instrumental. The stabilized cations obtained as a result have been the center of attention of most of the research focused in this area. Nevertheless, the performance of the cation in olefin polymerization will not only depend on the design; the counter anion, as well as with the Lewis base employed, also affect the reactivity. These are the variables that define a catalytic system, and when they are manipulated, the efficiency of the system can be enhanced.

This thesis describes the stabilization of the cationic species $[Cp(NP^tBu_3)TiMe]^+$ with a variety of Lewis bases, namely tertiary phosphines and pyridines. The generated stable cationic species $[Cp(NP^tBu_3)TiMe{\cdot}LB]^+$ (LB = Lewis base), where the counterion is a borate $[BR_4]^-$, exhibit interesting features dependent on the Lewis base used. A probe in the ability of Lewis bases as electron donors and their steric properties when they interact with the $[Cp(NP^tBu_3)TiMe]^+$ system is described.

There is considerable ongoing interest in the chemistry and reactions of boron reagents with phosphines and pyridines. Of particular significance has been the role of the solvent on the reactions of these Lewis acids (borane reagents) and bases (phosphines and pyridines). The results reported illustrate the novel chemistry that these reactions generate.

2. Stabilization of the Cyclopentadienyl Titanium Phosphinimide Active Species with Lewis Bases

2.1. *Introduction*

Group 4 metallocene "cationic" complexes are regarded as the active species in homogeneous olefin polymerization. Some of these systems can very easily be prepared using standard inert-atmosphere techniques.[113] Typical examples include the species $[Cp_2ZrCH_3][B(C_6F_5)_4]$, obtained by methyl abstraction from the precursor complex $Cp_2Zr(CH_3)_2$ using $[C(C_6H_5)_3][B(C_6F_5)_4]$. Similarly the zwitterion $Cp_2ZrCH_3(\mu\text{-}MeB(C_6F_5)_3)$ can be obtained from the reaction between $Cp_2Zr(CH_3)_2$ and $B(C_6F_5)_3$.[113] Due to their strong electrophilic nature, complexes of the type $[Cp_2ZrCH_3][X]$ (X = counterion) coordinate with any available nucleophile.[114] Most cationic species are stabilized in solution by formation of a tight ion pair with their respective counterion or neutral donor ligands such as THF, amines or phosphines (Figure 2.1).[115,116]

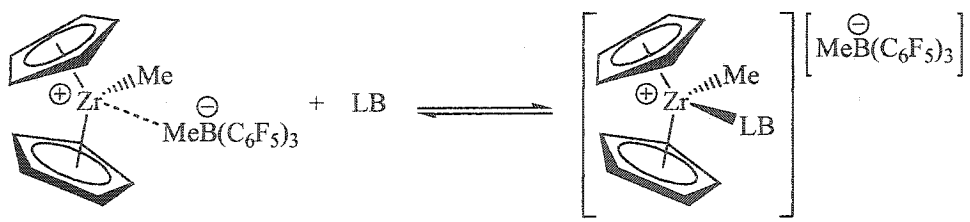


Figure 2.1: Reversible stabilization of the ion pair by addition of a Lewis base (LB).

The reactions of $Cp(NP^tBu_3)TiMe_2$ with $B(C_6F_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$ in hexanes gave the titanium zwitterion $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ and ion-pair $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ respectively.[82,83] Prior successful attempts to obtain the solvent-separated ion pair complex include the coordination of THF[b] or PMe_3[90] (Figure 2.2).

[b] E. Hollink and J.C. Stewart unpublished results.

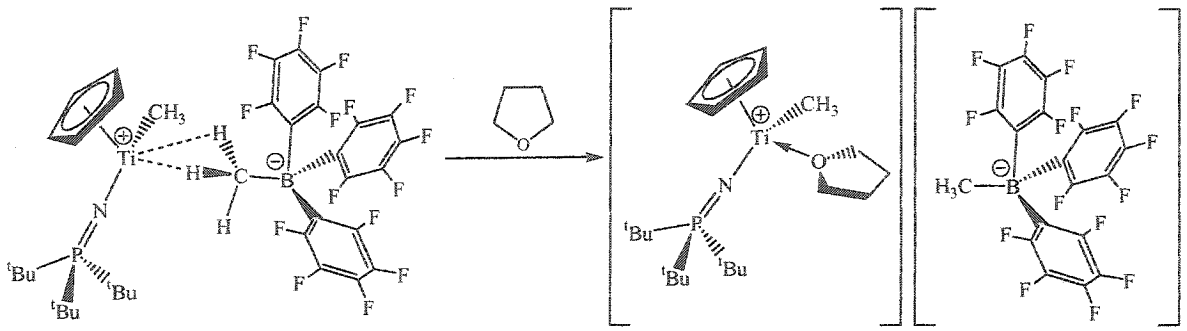


Figure 2.2: Coordination of THF to the metal center of the zwitterionic species $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$, generating an ionic pair complex.

In this chapter, the generation of ion pairs from the precursor $Cp(NP^tBu_3)TiMe_2$ is described. The complex $Cp(NP^tBu_3)TiMe_2$ is activated by either $B(C_6F_5)_3$ or $[C(C_6H_5)_3][B(C_6F_5)_4]$ to achieve the complexes $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ and $[Cp(NP^tBu_3)Ti\text{-}Me][B(C_6F_5)_4]$ respectively. Pyridines (Py, 4-^{t}BuPy, 4-EtPy, 4-DMAP) and tertiary phosphines (PMe_3, P^nBu_3, $P(C_6H_5)_3$, $P(p\text{-}CH_3C_6H_4)_3$, $P(o\text{-}CH_3C_6H_4)_3$, P^iPr_3, PCy_3, P^tBu_3), are used to form the complexes of the general formula $[Cp(NP^tBu_3)TiMe{\cdot}LB][RB(C_6F_5)_3]$, (LB = Lewis base; R = Me, C_6F_5). The effects of the electron donating ability and steric properties of the Lewis bases on the cationic fragment of the active species are discussed.

2.2. *Experimental*

2.2.1. General Comments

All experiments were performed with the exclusion of oxygen and moisture in oven-dried (140°C) Schlenk-type glassware on a Schlenk line or in a nitrogen-filled Vacuum Atmospheres glovebox.

NMR spectra were recorded on Bruker Avance 500 MHz and Bruker Avance 300 MHz spectrometers. The ^{1}H NMR spectra were referenced to resonances of residual protons in the deuterated solvents (δ 7.28 ppm for downfield signal of C_6D_5Br, δ 5.32

ppm for CD_2Cl_2, δ 7.16 ppm for C_6D_6). The $^{13}C\{^1H\}$ NMR spectra were referenced to the carbon resonances of the deuterated solvent (δ 122.4 ppm for C_{ipso} of C_6D_5Br, δ 54 ppm for CD_2Cl_2, δ 128.4 ppm for C_6D_6). Chemical shifts (δ) are reported relative to tetramethylsilane (downfield shifts are positive). The $^{31}P\{^1H\}$ NMR spectra were referenced using 85% $H_3PO_{4(aq)}$ as an external standard. The ^{19}F NMR spectra were referenced using 80% $CFCl_3$ in $CDCl_3$ as an external standard. The $^{11}B\{^1H\}$ NMR spectra were referenced using $BF_3{\cdot}Et_2O$ as an external standard. $|J|$ values are given in Hertz.

2.2.2. Solvents

Dichloromethane-d_2 (CD_2Cl_2), bromobenzene-d_5 (C_6D_5Br) and benzene-d_6 (C_6D_6) (Cambridge Isotopes Laboratories) were degassed and dried over CaH_2, P_2O_5 and Na; and then were vacuum-transferred and stored over 4 Å molecular sieves under a nitrogen atmosphere, respectively.

The reagent grade solvents dichloromethane, chlorobenzene, toluene and pentane were purchased from Aldrich Chemical Co., and were pre-dried using Grubbs' column systems, manufactured by Innovative Technologies, Inc.[117] Dichloromethane was further distilled from CaH_2, C_6H_5Cl was distilled from P_2O_5, and toluene and pentane were distilled from Na prior to use.

2.2.3. Materials

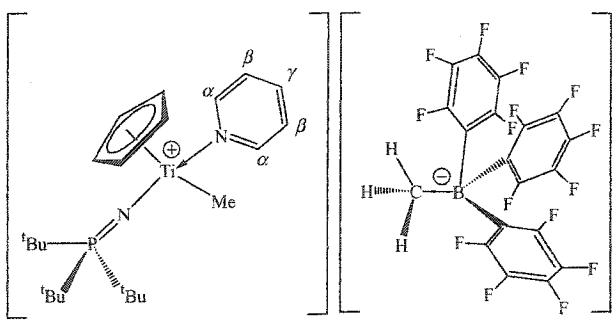
4 Å molecular sieves were purchased from Aldrich Chemical Co. and were dried at 100°C *in vacuo* for 24 h prior to use.

2.2.4. Reagents

The starting materials $Cp(NP^tBu_3)TiCl_2$, $B(C_6F_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$ were generously donated by Nova Chemicals Co. and were used as received. $Cp(NP^tBu_3)TiMe_2$ was prepared according to published procedure.[90]

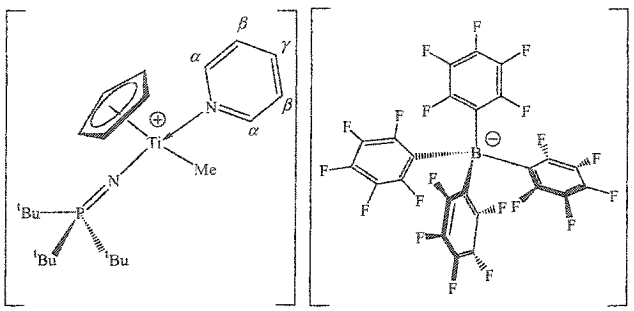
The reagents ^{i}PrMgCl (2.0 M in THF), Py, 4-EtPy, 4-^{t}BuPy, 4-DMAP, PMe_3 (1.0 M in toluene), PCy_3 and $P^{t}Bu_3$ were purchased from Aldrich Chemical Co.. ^{i}PrMgCl, PMe_3, PCy_3 and $P^{t}Bu_3$ were used as received. Py, 4-EtPy and 4-^{t}BuPy were dried over CaH_2, fractionally distilled, and then stored in contact with 4 Å molecular sieves. 4-DMAP was recrystallized from toluene prior to use. $P^{i}Pr_3$, $P^{n}Bu_3$, $P(p\text{-}CH_3C_6H_4)_3$, and $P(o\text{-}CH_3C_6H_4)_3$ were obtained from Strem Chemicals and were used as received. $P(C_6H_5)_3$ was obtained from Strem Chemicals and recrystallized from pentanes prior to use.

2.2.5. Syntheses

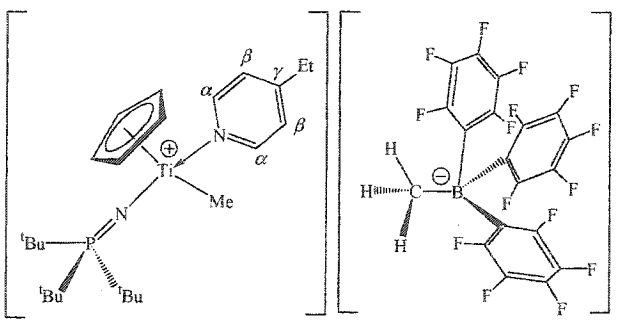


[Cp(NP^{t}Bu$_3$)TiMe·Py][MeB(C$_6$F$_5$)$_3$] (2.1): Pyridine (12 μL, 0.14 mmol) was added at RT to a solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (50 mg, 0.14 mmol) in CH_2Cl_2 (3 mL), followed by the addition of a solution of $B(C_6F_5)_3$ (72 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) at RT to the reaction mixture. The resulting solution was left to stir for 30 minutes. The solvent was removed *in vacuo*, and the oily residue was washed with pentane (3 x 5 mL) before drying to afford a bright yellow solid (110 mg, 83 %). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.20 (s, br, 2H, $C_5\mathbf{H}_5N$ (α-H)), 8.02 (t, 1H, $^{3}J_{H-H}$ = 8 Hz, $C_5\mathbf{H}_5N$ (γ-H)), 7.56 (t, 2H, $^{3}J_{H-H}$ = 7 Hz, $C_5\mathbf{H}_5N$ (β-H)), 6.46 (s, 5H, $C_5\mathbf{H}_5$), 1.45 (d, 27H, $^{3}J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.28 (s, 3H, Ti-$C\mathbf{H}_3$), 0.50 (s, br, 3H, $\mathbf{H}_3CB(C_6F_5)_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^{1}J_{C-F}$ = 240 Hz, C_6F_5 (o-C)), 148.3 (s, C_5H_5N (α-C)), 143.5 (s, C_5H_5N (γ-C)), 138.0 (d(m), $^{1}J_{C-F}$ = 237 Hz, C_6F_5 (p-C)), 137.0 (ddd, $^{1}J_{C-F}$ = 247 Hz, $^{2}J_{C-F}$ = 24 Hz, $^{3}J_{C-F}$ = 11 Hz, C_6F_5 (m-C)), 129.31 (s, br, C_6F_5 (*ipso*-C)), 126.7 (s, C_5H_5N (β-C)), 115.6 (s, C_5H_5), 54.9 (s, Ti-CH_3), 42.2 (d, $^{1}J_{P-C}$ = 43 Hz, $C(CH_3)_3$), 29.8 (s, $C(CH_3)_3$), 10.6 (q, br, $^{1}J_{B-C}$ = 54 Hz, $H_3CB(C_6F_5)_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −15.2 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.35 (d, 6F, $^{3}J_{F-F}$ = 23 Hz,

C_6F_5 (*o*-F)), −165.54 (t, 3F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −168.10 (t, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 51.7 (s).

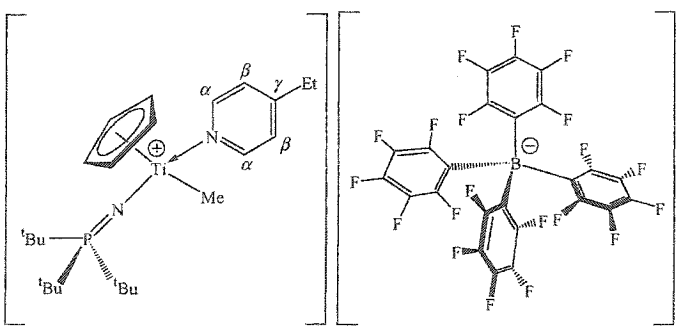


[Cp(NP^{t}Bu$_3$)TiMe·Py][B(C_6F_5)$_4$] (2.2): Pyridine (12 μL, 0.14 mmol) was added to a solution of [C(C_6H_5)$_3$][B(C_6F_5)$_4$] (128 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) at RT and left to stir for 30 minutes. A solution of Cp(NP^{t}Bu$_3$)$TiMe_2$ (50 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) was added to the reaction mixture. The resulting amber solution was left to stir for another 30 minutes. After removing the solvent *in vacuo*, the oily residue was washed with pentane (3 x 5 mL) before drying to afford a yellow solid (147 mg, 93 %). ^1H NMR (300 MHz, CD_2Cl_2) δ: 8.20 (s, br, 2H, C_5H_5N (α-H)), 8.05 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_5H_5N (γ-H)), 7.61 (t, 2H, $^3J_{H-H}$ = 7 Hz, C_5H_5N (β-H)), 6.46 (s, 5H, C_5H_5), 1.46 (d, 27H, $^3J_{P-H}$ = 14 Hz, C(CH_3)$_3$), 1.29 (s, 3H, Ti-CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*o*-C)), 148.0 (s, C_5H_5N (α-C)), 142.4 (s, C_5H_5N (γ-C)), 138.9 (d(m), $^1J_{C-F}$ = 243 Hz, C_6F_5 (*p*-C)), 136.9 (d(m), $^1J_{C-F}$ = 247 Hz, C_6F_5 (*m*-C)), 127.0 (s, C_5H_5N (β-C)), 124.8 (s, br, C_6F_5 (*ipso*-C)), 115.5 (s, C_5H_5), 54.9 (s, Ti-CH_3), 42.2 (d, $^1J_{P-C}$ = 43 Hz, C(CH_3)$_3$), 29.7 (s, C(CH_3)$_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.24 (s, 8F, C_6F_5 (*o*-F)), −163.85 (t, 4F, $^3J_{F-F}$ = 21 Hz, C_6F_5 (*p*-F)), −167.70 (t, 8F, $^3J_{F-F}$ = 17 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 51.7 (s).



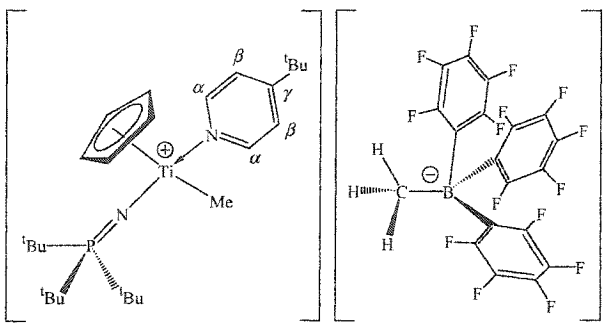
[Cp(NP^{t}Bu$_3$)TiMe·(4-EtPy)][MeB(C_6F_5)$_3$] (2.3): 4-EtPy (8 μL, 0.07 mmol) was added at RT to a solution of Cp(NP^{t}Bu$_3$)$TiMe_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (3 mL). A solution of B(C_6F_5)$_3$ (36 mg, 0.07

mmol) in CH_2Cl_2 (3 mL) was added and the reaction mixture was left to stir for 30 minutes. The solvent was removed *in vacuo*, and the oily residue was washed with pentane (3 x 5 mL) before drying to afford a light yellow solid (60 mg, 88 %). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.00 (d, 2H, $^3J_{H-H}$ = 6 Hz, 4-$(CH_3CH_2)C_5\mathbf{H}_4N$ (β-H)), 7.42 (d, 2H, $^3J_{H-H}$ = 6 Hz, 4-$(CH_3CH_2)C_5\mathbf{H}_4N$ (α-H)), 6.43 (s, 5H, $C_5\mathbf{H}_5$), 1.76 (q, 2H, $^3J_{H-H}$ = 8 Hz, 4-$(CH_3C\mathbf{H}_2)C_5H_4N$), 1.45 (d, 27H, $^3J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.27 (t, 3H, $^3J_{H-H}$ = 8 Hz, 4-$(C\mathbf{H}_3CH_2)C_5H_4N$), 1.24 (s, 3H, Ti-$C\mathbf{H}_3$), 0.48 (s, br, 3H, $\mathbf{H}_3CB(C_6F_5)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 161.3 (s, 4-$(CH_3CH_2)C_5H_4N$ (γ-C)), 148.9 (d(m), $^1J_{C-F}$ = 240 Hz, $\mathbf{C}_6F_5$ (*o* -C)), 147.4 (s, 4-$(CH_3CH_2)C_5H_4N$ (α -C)), 138.0 (d(m), $^1J_{C-F}$ = 240 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 137.0 (ddd, $^1J_{C-F}$ = 244 Hz, $^2J_{C-F}$ = 24 Hz, $^3J_{C-F}$ = 11 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 129.0 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 126.4 (s, 4-$(CH_3CH_2)\mathbf{C}_5H_4N$ (α-C)), 115.4 (s, $\mathbf{C}_5H_5$), 54.5 (s, Ti-$\mathbf{C}H_3$), 42.1 (d, $^1J_{P-C}$ = 43 Hz, $\mathbf{C}(CH_3)_3$), 29.8 (s, $C(\mathbf{C}H_3)_3$), 29.1 (s, 4-$(CH_3\mathbf{C}H_2)C_5H_4N$), 13.8 (s, 4-$(\mathbf{C}H_3CH_2)C_5H_4N$), 10.6 (q, br, $^1J_{B-C}$ = 54 Hz, $H_3\mathbf{C}B(C_6F_5)_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −15.1 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.41 (d, 6F, $^3J_{F-F}$ = 22 Hz, $C_6\mathbf{F}_5$ (*o*-F)), −165.54 (t, 3F, $^3J_{F-F}$ = 21 Hz, $C_6\mathbf{F}_5$ (*p*-F)), −168.09 (t, 6F, $^3J_{F-F}$ = 20 Hz, $C_6\mathbf{F}_5$ (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 51.1 (s).

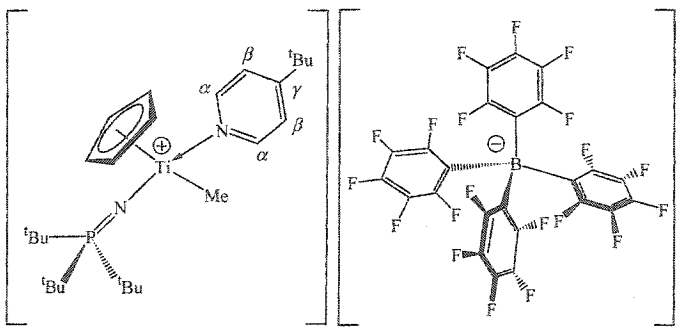


[Cp(NP^{t}Bu$_3$)TiMe·(4-EtPy)][B(C_6F_5)$_4$] (2.4): To a solution of $[C(C_6H_5)_3][B(C_6F_5)_4]$ (64 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) was added 4-EtPy (8 μL, 0.07 mmol) at RT and after stirring for 30 minutes, a solution of Cp(NP^{t}Bu$_3$)$TiMe_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) was added to the reaction mixture and allowed to stir for another 30 minutes. The solvent was removed *in vacuo*, and the oily residue was washed with pentane (3 x 5 ml) before drying to afford a light yellow solid (72 mg, 91 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.16 (d, 2H, $^3J_{H-H}$ = 6 Hz, 4-$(CH_3CH_2)C_5\mathbf{H}_4N$ (β-H)), 7.23 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-$(CH_3CH_2)C_5\mathbf{H}_4N$ (α-H)), 6.44 (d, 5H, $C_5\mathbf{H}_5$), 2.78 (q, 2H, $^3J_{H-H}$ = 8 Hz, 4-$(CH_3C\mathbf{H}_2)C_5H_4N$), 1.45 (d, 27H, $^3J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.27 (t, 3H, $^3J_{H-H}$ = 8 Hz, 4-$(C\mathbf{H}_3CH_2)C_5H_4N$), 1.24 (s, 3H, Ti-

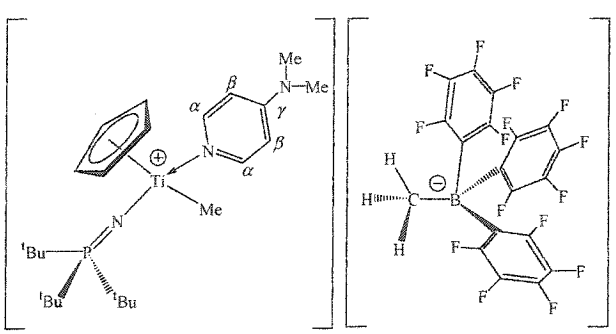
CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 160.0 (s, 4-$(CH_3CH_2)C_5H_4N$ (γ-C)), 148.8 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*o*-C)), 148.0 (s, 4-$(CH_3CH_2)C_5H_4N$ (α-C)), 138.9 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*p*-C)), 137.0 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*m*-C)), 126.2 (s, 4-(CH_3CH_2)-C_5H_4N (β-C), 124.6 (s, br, C_6F_5 (*ipso*-C)), 115.5 (s, C_5H_5), 54.6 (s, Ti-CH_3), 42.2 (d, $^1J_{P-C}$ = 43 Hz, $C(CH_3)_3$), 29.9 (s, $C(CH_3)_3$), 29.1 (s, 4-$(CH_3CH_2)C_5H_4N$), 13.9 (s, 4-$(CH_3CH_2)C_5H_4N$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.30 (s, 6F, C_6F_5 (*o*-F)), −163.91 (t, 3F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.72 (m, 6F, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 51.2 (s).



[Cp(NP^{t}Bu$_3$)TiMe·(4-^{t}BuPy)][MeB(C_6F_5)$_3$] (2.5): 4-^{t}BuPy (10 μL, 0.07 mmol) was added at RT to a solution of Cp(NP^{t}Bu$_3$)$TiMe_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (3 mL). Subsequently a solution of $B(C_6F_5)_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) was added at RT and the reaction mixture was left to stir for 30 minutes. The solvent was removed *in vacuo*. The remaining oil was washed with pentane (3 x 5 mL) before drying to afford a yellow powder (62 mg, 88 %). ^1H NMR (500 MHz, CD_2Cl_2) δ: 8.17 (d, 2H, $^3J_{H-H}$ = 6 Hz, 4-$(CH_3)_3C$-C_5H_4N, (α-H)), 7.49 (d, 2H, $^3J_{H-H}$ = 6 Hz, 4-$(CH_3)_3C$-C_5H_4N, (β-H)), 6.44 (s, 5H, C_5H_5), 1.45 (d, 27H, $^3J_{P-H}$ = 14 Hz, $C(CH_3)_3$), 1.31 (s, 9H, 4-$(CH_3)_3C$-C_5H_4N), 1.27 (s, 3H, Ti-CH_3), 0.48 (s, br, 3H, $H_3CB(C_6F_5)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^1J_{C-F}$ = 230 Hz, C_6F_5 (*o*-C)), 147.2 (s, 4-$(CH_3)_3C$-C_5H_4N (α-C)), 137.9 (d(m), $^1J_{C-F}$ = 250 Hz, C_6F_5 (*p*-C)), 137.0 (d(m), $^1J_{C-F}$ = 253 Hz, C_6F_5 (*m*-C)), 128.6 (s, br, C_6F_5 (*ipso*-C)), 123.4 (s, 4-$(CH_3)_3C$-C_5H_4N (β-C)), 115.4 (s, C_5H_5), 54.4 (s, Ti-CH_3), 42.1 (d, $^1J_{P-C}$ = 43 Hz, NP$C(CH_3)_3$), 35.4 (s, 4-$(CH_3)_3C$-C_5H_4N), 30.3 (s, 4-$(CH_3)_3C$-C_5H_4N), 29.8 (s, NPC$(CH_3)_3$), 10.7 (q, br, $^1J_{B-C}$ = 54 Hz, $H_3CB(C_6F_5)_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −15.1 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.39 (d, 6F, $^3J_{F-F}$ = 22 Hz, C_6F_5 (*o*-F)), −165.56 (t, 3F, $^3J_{F-F}$ = 21 Hz, C_6F_5 (*p*-F)), −168.09 (t, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 51.1 (s).

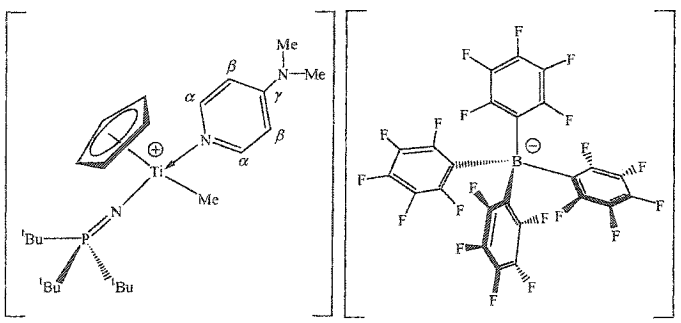


[Cp(NP^{t}Bu$_3$)TiMe·(4-^{t}BuPy)][B(C$_6$F$_5$)$_4$] (2.6): 4-^{t}BuPy (10 μL, 0.07 mmol) was added to a solution of [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) at RT and was stirred for 30 minutes. A solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) was added to the reaction mixture and the resulting solution was stirred for another 30 minutes. The solvent was removed *in vacuo*, and the oily residue was washed with pentane (3 x 5 mL) before drying to afford a yellow solid (70 mg, 86 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.06 (s, br, 2H, 4-(CH$_3$)$_3$C-C$_5$**H**$_4$N, (α-H)), 7.56 (s, br, 2H, 4-(CH$_3$)$_3$C-C$_5$**H**$_4$N, (β-H)), 6.44 (s, 5H, C$_5$**H**$_5$), 1.44 (d, 27H, $^3J_{P-H}$ = 14 Hz, C(C**H**$_3$)$_3$), 1.32 (s, 9H, 4-(C**H**$_3$)$_3$C-C$_5$H$_4$N), 1.27 (s, 3H, Ti-C**H**$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 160.0 (s, 4-(CH)$_3$C)**C**$_5$H$_4$N (γ-C)), 148.8 (d(m), $^1J_{C-F}$ = 235 Hz, **C**$_6$F$_5$ (o-C)), 147.7 (s, 4-(CH$_3$)$_3$C-**C**$_5$H$_4$N (α-C)), 138.8 (d(m), $^1J_{C-F}$ = 246 Hz, **C**$_6$F$_5$ (p-C)), 136.9 (d(m), $^1J_{C-F}$ = 250 Hz, **C**$_6$F$_5$ (m-C)), 125.2 (s, br, **C**$_6$F$_5$ (*ipso*-C)), 123.8 (s, 4-(CH$_3$)$_3$C-**C**$_5$H$_4$N (β-C)), 115.4 (s, **C**$_5$H$_5$), 54.5 (s, Ti-**C**H$_3$), 42.2 (d, $^1J_{P-C}$ = 43 Hz, NP**C**(CH$_3$)$_3$), 34.7 (s, 4-(CH$_3$)$_3$**C**-C$_5$H$_4$N), 30.2 (s, 4-(**C**H$_3$)$_3$C-C$_5$H$_4$N), 29.8 (s, NPC(**C**H$_3$)$_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.22 (s, 8F, C$_6$**F**$_5$ (o-F)), −163.91 (t, 4F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (p-F)), −167.71 (s, br, 8F, C$_6$**F**$_5$ (m-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 51.1 (s).



[Cp(NP^{t}Bu$_3$)TiMe·(4-DMAP)][MeB(C$_6$F$_5$)$_3$] (2.7): 4-DMAP (9 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT to a solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). A solution of B(C$_6$F$_5$)$_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT and the yellow reaction mixture was left to stir for 30

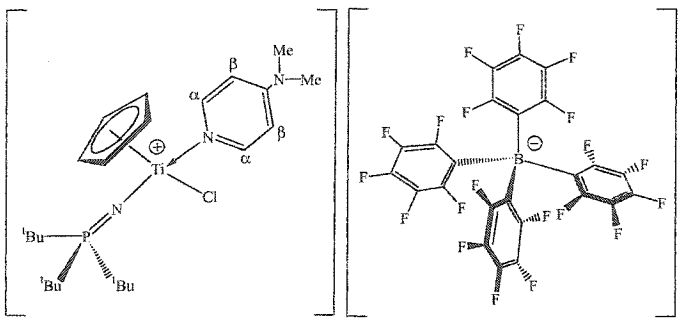
minutes. The solvent was removed *in vacuo*, and the oily residue was washed with pentane (3 x 5 mL) before drying to afford a yellow solid (65 mg, 93 %). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.62 (d, 2H, $^{3}J_{H-H}$ = 7 Hz, 4-$(CH_3)_2NC_5H_4N$, (α-H)), 6.52 (d, 2H, $^{3}J_{H-H}$ = 7 Hz, 4-$(CH_3)_2NC_5H_4N$, (β-H)), 6.37 (s, 5H, C_5H_5), 3.07 (s, 6H, 4-$(CH_3)_2NC_5H_4N$), 1.46 (d, 27H, $^{3}J_{P-H}$ = 14 Hz, $C(CH_3)_3$), 1.10 (s, 3H, Ti-CH_3), 0.48 (s, br, 3H, $H_3CB(C_6F_5)_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 155.9 (s, 4-$(CH_3)_2NC_5H_4N$, (γ-C)), 148.7 (d(m), $^{1}J_{C-F}$ = 255 Hz, C_6F_5 (*o*-C)), 146.9 (s, 4-$(CH_3)_2NC_5H_4N$, (α-C)), 138.0 (d(m), $^{1}J_{C-F}$ = 233 Hz, C_6F_5 (*p*-C)), 136.9 (d(m), $^{1}J_{C-F}$ = 234 Hz, C_6F_5 (*m*-C)), 128.6 (s, br, C_6F_5 (*ipso*-C)), 114.7 (s, C_5H_5), 107.3 (s, 4-$(CH_3)_2NC_5H_4N$, (β-C)), 52.1 (s, Ti-CH_3), 42.1 (d, $^{1}J_{P-C}$ = 43 Hz, $C(CH_3)_3$), 39.8 (s, $(CH_3)_2N$), 29.8 (s, $C(CH_3)_3$), 10.7 (q, br, $^{1}J_{B-C}$ = 54 Hz, $H_3CB(C_6F_5)_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −15.2 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.42 (d, 6F, $^{3}J_{F-F}$ = 22 Hz, C_6F_5 (*o*-F)), −165.52 (t, 3F, $^{3}J_{F-F}$ = 21 Hz, C_6F_5 (*p*-F)), −168.15 (t, 6F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 49.1 (s).



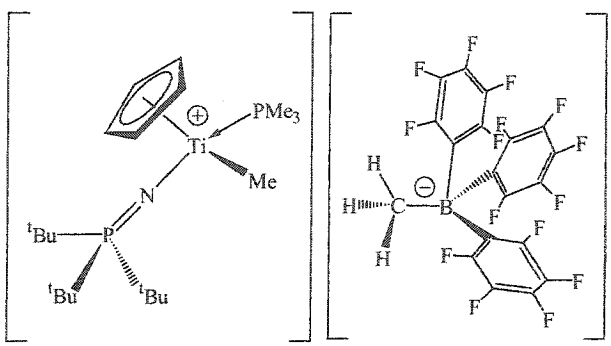
[Cp(NP^{t}Bu$_3$)TiMe·(4-DMAP)][B(C_6F_5)$_4$] (2.8):

Cp(NP^{t}Bu$_3$)$TiMe_2$ (25 mg, 0.07 mmol), $[C(C_6H_5)_3][B(C_6F_5)_4]$ (64 mg, 0.07 mmol) and 4-DMAP (9 mg, 0.07 mmol) were each dissolved separately in CH_2Cl_2 (2 mL). The $[C(C_6H_5)_3][B(C_6F_5)_4]$ and 4-DMAP solutions were combined at RT. The titanium solution was then added, and the resulting yellow mixture was stirred for 30 minutes. The solvent was removed *in vacuo*, and the oily residue was washed with pentane (3 x 5 mL) before drying to afford a yellow solid (66 mg, 82%). Compound **[Cp(NP^{t}Bu$_3$)TiCl·(4-DMAP)] (2.22)** was obtained from a solution of **2.8** in CH_2Cl_2 for two months. Characterization of **[Cp(NP^{t}Bu$_3$)TiMe·(4-DMAP)][B(C_6F_5)$_4$] 2.8**: ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.65 (d, 2H, $^{3}J_{H-H}$= 7 Hz, 4-$(CH_3)_2NC_5H_4N$, (α-H)), 6.53 (d, 2H, $^{3}J_{H-H}$ = 7 Hz, 4-$(CH_3)_2NC_5H_4N$), (β-H)), 6.38 (s, 5H, C_5H_5), 3.08 (s, 6H, 4-$(CH_3)_2NC_5H_4N$), 1.48 (d, 27H, $^{3}J_{P-H}$ = 14 Hz, $C(CH_3)_3$), 1.12

(s, 3H, Ti-C**H**$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 155.9 (s, 4-$(CH_3)_2$N**C**$_5$H$_4$N, (γ-C)), 148.8 (d(m), $^1J_{C-F}$ = 253 **C**$_6$F$_5$ (o-C)), 147.0 (s, 4-$(CH_3)_2$N**C**$_5$H$_4$N, (α-C)), 138.9 (d(m), $^1J_{C-F}$ = 245 Hz, **C**$_6$F$_5$ (p-C)), 137.0 (d(m), $^1J_{C-F}$ = 238 Hz, **C**$_6$F$_5$ (m-C)), 125.1 (s, br, **C**$_6$F$_5$ (*ipso*-C)), 114.6 (s, **C**$_5$H$_5$), 107.4 (s, 4-$(CH_3)_2$N**C**$_5$H$_4$N, (β-C)), 52.3 (s, Ti-**C**H$_3$), 42.2 (d, $^1J_{P-C}$ = 43 Hz, **C**$(CH_3)_3$), 39.7 (s, $(CH_3)_2$N), 29.9 (s, C$(CH_3)_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.34 (s, 8F, C$_6$**F**$_5$ (o-F)), −163.89 (t, 4F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (p-F)), −167.72 (s, br, 8F, C$_6$**F**$_5$ (m-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 48.9 (s).

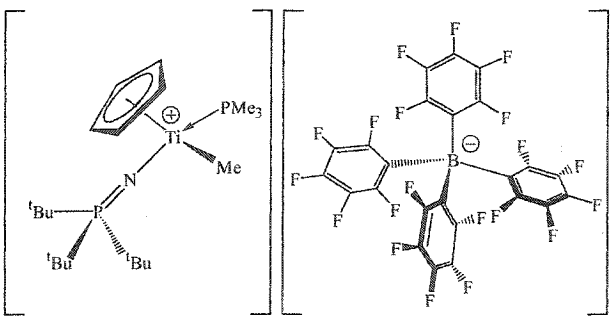


Characterization of compound **[Cp(NP^{t}Bu$_3$)TiCl·(4-DMAP)][B(C$_6$F$_5$)$_4$] (2.22):** ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.64 (d, 2H, $^3J_{H-H}$= 7 Hz, 4-$(CH_3)_2$NC$_5$**H**$_4$N, (α-H)), 6.51 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-$(CH_3)_2$NC$_5$**H**$_4$N), (β-H)), 6.35 (s, 5H, C$_5$**H**$_5$), 3.06 (s, 6H, 4-$(CH_3)_2$NC$_5$H$_4$N), 1.46 (d, 27H, $^3J_{P-H}$ = 14 Hz, C$(CH_3)_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 155.6 (s, 4-$(CH_3)_2$N**C**$_5$H$_4$N, (γ-C)), 148.8 (d(m), $^1J_{C-F}$ = 252 **C**$_6$F$_5$ (o-C)), 146.7 (s, 4-$(CH_3)_2$N**C**$_5$H$_4$N, (α-C)), 138.9 (d(m), $^1J_{C-F}$ = 245 Hz, **C**$_6$F$_5$ (p-C)), 136.9 (d(m), $^1J_{C-F}$ = 240 Hz, **C**$_6$F$_5$ (m-C)), 125.0 (s, br, **C**$_6$F$_5$ (*ipso*-C)), 115.0 (s, **C**$_5$H$_5$), 107.0 (s, 4-$(CH_3)_2$N**C**$_5$H$_4$N, (β-C)), 42.1 (d, $^1J_{P-C}$ = 43 Hz, **C**$(CH_3)_3$), 39.7 (s, $(CH_3)_2$N), 29.9 (s, C$(CH_3)_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.32 (s, 8F, C$_6$**F**$_5$ (o-F)), −163.87 (t, 4F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (p-F)), −167.70 (s, br, 8F, C$_6$**F**$_5$ (m-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 49.0 (s).

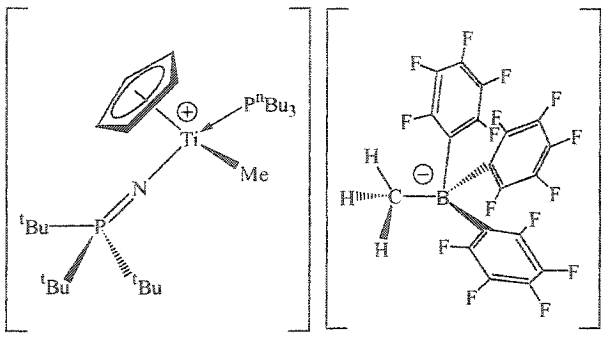


[Cp(NP^{t}Bu$_3$)TiMe·PMe$_3$][MeB(C$_6$F$_5$)$_3$] (2.9): To a solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added a solution of PMe_3 (1.0 M in toluene; 280 μL, 0.28 mmol). B(C$_6$F$_5$)$_3$ (36 mg, 0.07

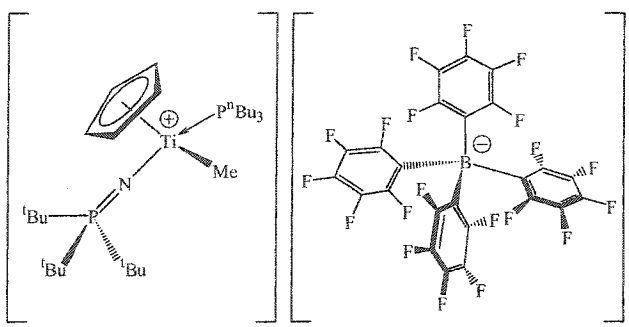
mmol) in CH_2Cl_2 (2 mL) was added to the resulting mixture. The solution was left to stir at RT for 30 minutes. The solvent was removed *in vacuo*, and the amber oil was washed with pentanes (3 x 5 mL) to afford a yellow solid (50 mg, 75%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 6.45 (s, 5H, $C_5\mathbf{H}_5$), 1.54 (d, 27H, $^3J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.37 (d, 9H, $^2J_{P-H}$ = 8 Hz, $PC\mathbf{H}_3$), 0.80 (s, 3H, Ti-$C\mathbf{H}_3$), 0.48 (s, br, 3H, $\mathbf{H}_3CB(C_6F_5)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.7 (d(m), $^1J_{C-F}$ = 238, $\mathbf{C}_6F_5$ (*o*-C)), 138.1 (d(m), $^1J_{C-F}$ = 243 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 136.9 (ddd, $^1J_{C-F}$ = 245 Hz, $^2J_{C-F}$ = 24 Hz, $^3J_{C-F}$ = 12 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 129.2 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 114.9 (s, $\mathbf{C}_5H_5$), 63.9 (d, $^2J_{P-C}$ = 5 Hz, Ti-$\mathbf{C}H_3$), 42.0 (d, $^1J_{P-C}$ = 43 Hz, $\mathbf{C}(CH_3)_3$), 30.0 (s, $C(\mathbf{C}H_3)_3$), 26.4 (d, $^1J_{P-C}$ = 23 Hz, $P\mathbf{C}H_3$), 10.6 (q, br, $^1J_{B-C}$ = 54 Hz, $H_3\mathbf{C}B(C_6F_5)_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −15.2 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.70 (d, 6F, $^3J_{F-F}$ = 20 Hz, $\mathbf{C}_6F_5$ (*o*-F)), −165.64 (t, 3F, $^3J_{F-F}$ = 20 Hz, $\mathbf{C}_6F_5$ (*p*-F)), −168.14 (7, 6F, $^3J_{F-F}$ = 20 Hz, $\mathbf{C}_6F_5$ (*m*-F)). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2) δ: 52.1 (s, $N\mathbf{P}^tBu_3$), −18.6 (s, $\mathbf{P}Me_3$).



[Cp(NP^{t}Bu$_3$)TiMe·PMe$_3$][B(C$_6$F$_5$)$_4$] (2.10): $[C(C_6H_5)_3][B(C_6F_5)_4]$ (64 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) was added to a solution of $Cp(NP^tBu_3)TiMe_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) at RT. To the resulting mixture PMe_3 (1.0 M in toluene; 280 μL, 0.28 mmol) was added at RT and stirred for 30 minutes. The solvent was removed *in vacuo*, and the amber oil was washed with pentanes (3 x 5 mL) before drying to afford a bright yellow solid (58 mg, 75 %).^{1}H NMR (300 MHz, CD_2Cl_2) δ: 6.45 (s, 5H, $C_5\mathbf{H}_5$), 1.55 (d, 27H, $^3J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.37 (d, 9H, $^2J_{P-H}$ = 8 Hz, $PC\mathbf{H}_3$), 0.80 (s, 3H, Ti-$C\mathbf{H}_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.3 (d(m), $^1J_{C-F}$ = 244 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 138.5 (d(m), $^1J_{C-F}$ = 234 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 136.5 (ddd, $^1J_{C-F}$ = 240 Hz, $^2J_{C-F}$ = 24 Hz, $^3J_{C-F}$ = 11 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 124.0 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 114.8 (s, $\mathbf{C}_5H_5$), 63.9 (s, Ti-$\mathbf{C}H_3$), 41.9 (d, $^1J_{P-C}$ = 43 Hz, $\mathbf{C}(CH_3)_3$), 30.0 (s, $C(\mathbf{C}H_3)_3$), 14.8 (d, $^1J_{P-C}$ = 23 Hz, $P\mathbf{C}H_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.26 (s, 8F, $\mathbf{C}_6F_5$ (*o*-F)), −163.87 (t, 4F, $^3J_{F-F}$ = 20 Hz, $\mathbf{C}_6F_5$ (*p*-F)), −167.69 (t, 8F, $^3J_{F-F}$ = 20 Hz, $\mathbf{C}_6F_5$ (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 52.2 (s, $N\mathbf{P}^tBu_3$), −18.9 (s, $\mathbf{P}Me_3$).

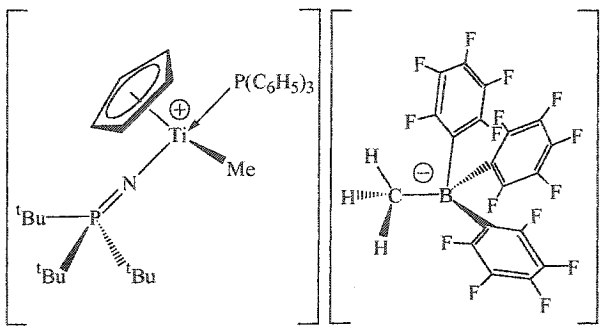


[Cp(NP^{t}Bu$_3$)TiMe·P^{n}Bu$_3$][MeB(C$_6$F$_5$)$_3$] (2.11): To a solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) was added P^{n}Bu$_3$ (18 μL, 0.07 mmol), followed by the addition of a solution of B(C$_6$F$_5$)$_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) to the resulting mixture. The bright yellow solution was left to stir at RT for 30 minutes. The solvent was removed *in vacuo*, and the oily residue was washed with pentanes (3 x 5 mL) before drying to afford a bright yellow solid (97 mg, 84%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 6.44 (d, 5H, $^3J_{P-H}$ = 1 Hz, $C_5\mathbf{H}_5$), 1.76 (m, 6H, $PC\mathbf{H}_2CH_2CH_2CH_3$), 1.56 (d, 27H, $^3J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.38 (m, 6H, $PCH_2C\mathbf{H}_2CH_2CH_3$), 1.29 (m, 6H, $PCH_2CH_2C\mathbf{H}_2CH_3$), 0.94 (t, 9H, $^3J_{H-H}$ = 7 Hz, $PCH_2CH_2CH_2C\mathbf{H}_3$), 0.83 (s, 3H, Ti-$C\mathbf{H}_3$), 0.50 (s, br, 3H, $\mathbf{H}_3CB(C_6F_5)_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 148.9 (d(m), $^1J_{C-F}$ = 240 Hz, $^2J_{C-F}$ = 14 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 138.1 (d(m), $^1J_{C-F}$ = 240 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 137.0 (ddd, $^1J_{C-F}$ = 250 Hz, $^2J_{C-F}$ = 24 Hz, $^3J_{C-F}$ = 11 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 129.2 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 114.6 (s, $\mathbf{C}_5H_5$), 64.1 (d, $^2J_{P-C}$ = 5 Hz, Ti-$\mathbf{C}H_3$), 42.1 (d, $^1J_{P-C}$ = 43 Hz, $\mathbf{C}(CH_3)_3$), 30.1 (s, $C(\mathbf{C}H_3)_3$), 26.4 (s, $P\mathbf{C}H_2CH_2CH_2CH_3$), 25.0 (d, $^2J_{P-C}$ = 13 Hz, $CH_2\mathbf{C}H_2CH_2CH_3$), 24.3 (d, $^3J_{P-C}$ = 18 Hz, $PCH_2CH_2\mathbf{C}H_2CH_3$), 13.7 (s, $PCH_2CH_2CH_2\mathbf{C}H_3$), 10.6 (q, br, $^1J_{B-C}$ = 54 Hz, $H_3\mathbf{C}B(C_6F_5)_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −15.2 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.34 (d, 6F, $^3J_{F-F}$ = 20 Hz, $C_6\mathbf{F}_5$ (*o*-F)), −165.64 (t, 3F, $^3J_{F-F}$ = 20 Hz, $C_6\mathbf{F}_5$ (*p*-F)), −168.15 (m, 6F, $C_6\mathbf{F}_5$ (*m*-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 52.1 (s, N$\mathbf{P}^t$Bu$_3$), 3.0 (s, $\mathbf{P}^n$Bu$_3$).



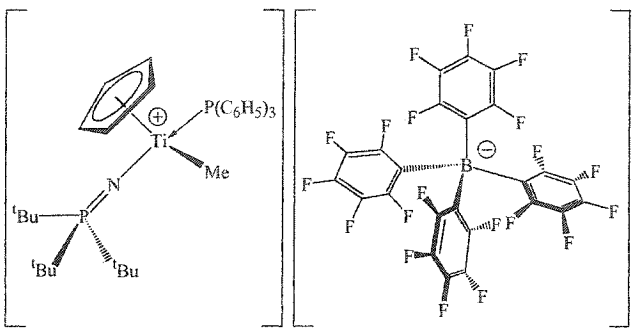
[Cp(NP^{t}Bu$_3$)TiMe·P^{n}Bu$_3$][B(C$_6$F$_5$)$_4$] (2.12): [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) was added to a solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) at RT. To the resulting mixture P^{n}Bu$_3$ (18 μL, 0.28 mmol) was added at RT and left to stir for 30

minutes. The solvent was removed *in vacuo*, and the amber oil was washed with pentanes (3 x 5 mL) before drying to afford a bright yellow solid (68 mg, 80 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 6.45 (d, 5H, $^{3}J_{P-H}$ = 1 Hz, $C_5\mathbf{H}_5$), 1.76 (m, 6H, $PC\mathbf{H}_2CH_2CH_2CH_3$), 1.56 (d, 27H, $^{3}J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.36 (m, 6H, $PCH_2C\mathbf{H}_2CH_2CH_3$), 1.30 (m, 6H, $PCH_2CH_2C\mathbf{H}_2CH_3$), 0.95 (t, 9H, $^{3}J_{H-H}$ = 7 Hz, $PCH_2CH_2CH_2C\mathbf{H}_3$), 0.83 (s, 3H, Ti-$C\mathbf{H}_3$). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.9 (d(m), $^{1}J_{C-F}$ = 240 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 138.9 (d(m), $^{1}J_{C-F}$ = 236 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 137.0 (d(m), $^{1}J_{C-F}$ = 250 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 124.8 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 114.7 (s, $\mathbf{C}_5H_5$), 64.5 (d, $^{2}J_{P-C}$ = 5 Hz, Ti-$\mathbf{C}H_3$), 42.2 (d, $^{1}J_{P-C}$ = 43 Hz, $\mathbf{C}(CH_3)_3$), 30.2 (s, $C(\mathbf{C}H_3)_3$), 26.3 (s, $P\mathbf{C}H_2CH_2CH_2CH_3$), 25.1 (d, $^{2}J_{P-C}$ = 13 Hz, $PCH_2\mathbf{C}H_2CH_2CH_3$), 24.4 (d, $^{3}J_{P-C}$ = 18 Hz, $PCH_2CH_2\mathbf{C}H_2CH_3$), 13.8 (s, $PCH_2CH_2CH_2\mathbf{C}H_3$). $^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.29 (s, 8F, $C_6\mathbf{F}_5$ (*o*-F)), −163.92 (t, 4F, $^{3}J_{F-F}$ = 20 Hz, $C_6\mathbf{F}_5$ (*p*-F)), −167.73 (t, 8F, $^{3}J_{F-F}$ = 18 Hz, $C_6\mathbf{F}_5$ (*m*-F)). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 52.2 (s, $N\mathbf{P}^{t}Bu_3$), 3.0 (s, $\mathbf{P}^{n}Bu_3$).

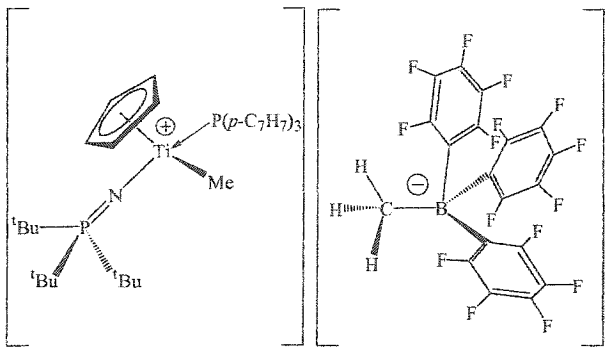


[Cp(NP^{t}Bu$_3$)TiMe·P(C$_6$H$_5$)$_3$][MeB(C$_6$F$_5$)$_3$] (2.13): A solution of $P(C_6H_5)_3$ (18 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT to a solution of $B(C_6F_5)_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) and stirred for 30 minutes. A white solid immediately formed. Subsequently, a solution of $Cp(NP^{t}Bu_3)TiMe_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added to the previous solution at RT and left to stir for another 30 minutes. The final solution was filtered through Celite, and the solvent was removed *in vacuo*. The resulting amber oil was washed with pentanes (3 x 5 mL), and dried. A bright yellow solid was recovered (69 mg, 87 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.54 (m, 9H, $PC_6\mathbf{H}_5$ (*o,p*-H)), 7.39 (t(m), 6H, $^{3}J_{P-H}$ = 2 Hz, $PC_6\mathbf{H}_5$ (*m*-H)), 6.31 (d, 5H, $^{3}J_{P-H}$ = 1 Hz, $C_5\mathbf{H}_5$), 1.41 (d, 27H, $^{3}J_{P-H}$ = 14 Hz, $C(C\mathbf{H}_3)_3$), 1.20 (s, 3H, Ti-$C\mathbf{H}_3$), 0.50 (s, br, 3H, $\mathbf{H}_3CB(C_6F_5)_3$). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^{1}J_{C-F}$ = 232 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 138.0 (d(m), $^{1}J_{C-F}$ = 245 Hz, C_6F_5 (*p*-C)), 136.9 (ddd, $^{1}J_{C-F}$ = 246 Hz, $^{2}J_{C-F}$ = 23

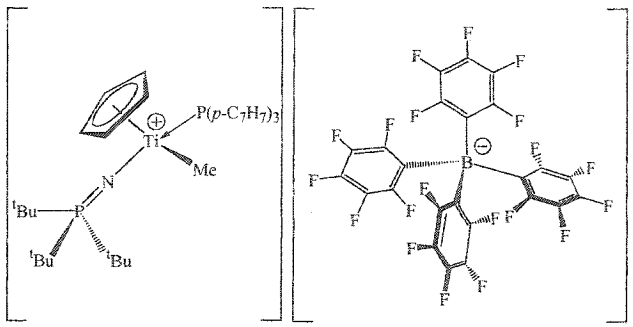
Hz, $^{3}J_{C-F}$ = 12 Hz, C_6F_5 (*m*-C)), 134.2 (d, $^{2}J_{P-C}$ = 12 Hz, PC_6H_5, (*o*-C)), 132.5 (d, $^{4}J_{P-C}$ = 2 Hz, PC_6H_5, (*p*-C)), 130.2 (d, $^{3}J_{P-C}$ = 10 Hz, PC_6H_5, (*m*-C)), 128.0 (d, $^{1}J_{P-C}$ = 36 Hz, PC_6H_5, (*ipso*-C)), 129.2 (s, br, C_6F_5 (*ipso*-C)), 115.9 (s, C_5H_5), 65.7 (d, $^{2}J_{P-C}$ = 5 Hz, Ti-CH_3), 42.2 (d, $^{1}J_{P-C}$ = 42 Hz, $C(CH_3)_3$), 30.0 (s, $C(CH_3)_3$), 10.4 (q, br, $^{1}J_{B-C}$ = 54 Hz, $H_3CB(C_6F_5)_3$). $^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −15.2 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.41 (d, 6F, $^{3}J_{F-F}$ = 22 Hz, C_6F_5 (*o*-F)), −165.59 (t, 3F, $^{3}J_{F-F}$ = 21 Hz, C_6F_5 (*p*-F)), −168.14 (t, 6F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 54.3 (s, NP^tBu_3), 15.1 (s, PPh_3).



[Cp(NP^{t}Bu$_3$)TiMe·P(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (2.14): A solution of $Cp(NP^tBu_3)TiMe_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $[C(C_6H_5)_3][B(C_6F_5)_4]$ (64 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), followed by the addition of $P(C_6H_5)_3$ (18 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was left to stir at RT for 30 minutes. The final solution was filtered through Celite, the solvent was removed *in vacuo*, and the recovered amber oil was washed with pentanes (3 x 5 mL) before drying to afford an amber-yellow solid (70 mg, 78 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.65 (t(m), 3H, $^{3}J_{P-H}$ = 2 Hz, PC_6H_5 (*p*-H)), 7.51 (t(m), 6H, $^{3}J_{P-H}$ = 2 Hz, PC_6H_5 (*o*-H)), 7.39 (t(m), 6H, $^{3}J_{P-H}$ = 2 Hz, PC_6H_5 (*m*-H)), 6.31 (d, 5H, $^{3}J_{P-H}$ = 1 Hz, C_5H_5), 1.40 (d, 27H, $^{3}J_{P-H}$ = 14 Hz, $C(CH_3)_3$), 1.21 (s, 3H, Ti-CH_3). $^{13}C\{^{1}H\}$ NMR (125.5 MHz, CD_2Cl_2) δ: 148.7 (d(m), $^{1}J_{C-F}$ = 242 Hz, C_6F_5 (*o*-C)), 138.8 (d(m), $^{1}J_{C-F}$ = 234 Hz, C_6F_5 (*p*-C)), 135.4 (d(m), $^{1}J_{C-F}$ = 251 Hz, C_6F_5 (*m*-C)), 134.1 (d, $^{2}J_{P-C}$ = 12 Hz, $P(C_6H_5)_3$, (*o*-C)), 132.5 (d, $^{4}J_{P-C}$ = 2 Hz, PC_6H_5, (*p*-C)), 130.1 (d, $^{3}J_{P-C}$ = 10 Hz, $P(C_6H_5)_3$, (*m*-C)), 128.0 (d, $^{1}J_{P-C}$ = 36 Hz, PC_6H_5, (*ipso*-C)), 124.2 (s, br, C_6F_5 (*ipso*-C)), 115.9 (s, C_5H_5), 65.7 (s, Ti-CH_3), 42.2 (d, $^{1}J_{P-C}$ = 43 Hz, $C(CH_3)_3$), 30.0 (s, $C(CH_3)_3$). $^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.9. ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.34 (s, 8F, C_6F_5 (*o*-F)), −163.95 (t, 4F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.75 (t, 8F, $^{3}J_{F-F}$ = 18 Hz, C_6F_5 (*m*-F)). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 54.3 (s, NP^tBu_3), 15.1 (s, $P(C_6H_5)_3$).

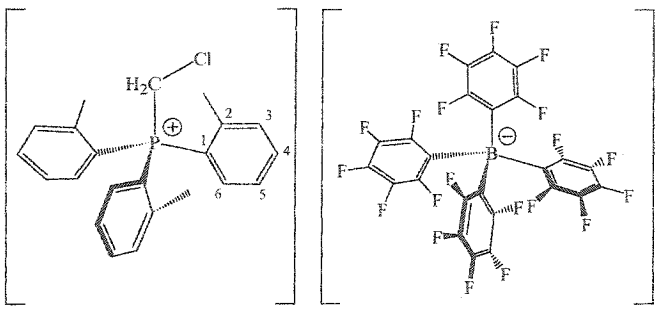


[Cp(NP^{t}Bu$_3$)TiMe·P(*p*-CH$_3$C$_6$H$_4$)$_3$][MeB(C$_6$F$_5$)$_3$] (2.15): A solution of P(*p*-CH$_3$C$_6$H$_4$)$_3$ (21 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT to a solution of B(C$_6$F$_5$)$_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) and stirred for 30 minutes. The colorless mixture was stirred for 30 min, during which time a white solid formed. A solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was then added to the previous solution at RT and the yellow mixture was left to stir for another 30 minutes. The solution was then filtered through Celite, the solvent removed *in vacuo*, and the oily residue was washed with pentane (3 x 5 mL) before drying to afford a yellow solid (72 mg, 87 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.30 (m, 12H, P(*p*-CH$_3$C$_6$**H**$_4$)), 6.29 (s, 5H, C$_5$**H**$_5$), 2.41 (s, 9H, P(*p*-C**H**$_3$C$_6$H$_4$)), 1.40 (d, 27H, $^3J_{P-H}$ = 14 Hz, C(C**H**$_3$)$_3$), 1.17 (s, 3H, Ti-C**H**$_3$), 0.50 (s, br, 3H, **H**$_3$CB(C$_6$F$_5$)$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 148.9 (d(m), $^1J_{C-F}$ = 235 Hz, **C**$_6$F$_5$ (*o*-C)), 143.2 (d, $^4J_{P-C}$ = 2 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*p*-C)), 138.1 (d(m), $^1J_{C-F}$ = 243 Hz, **C**$_6$F$_5$ (*p*-C)), 137.0 (ddd, $^1J_{C-F}$ = 247 Hz, $^2J_{C-F}$ = 23 Hz, $^3J_{C-F}$ = 11 Hz, **C**$_6$F$_5$ (*m*-C)), 134.1 (d, $^2J_{P-C}$ = 13 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*o*-C)), 130.8 (d, $^3J_{P-C}$ = 10 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*m*-C)), 129.2 (s, br, **C**$_6$F$_5$ (*ipso*-C)), 125.8 (d, $^1J_{P-C}$ = 38 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*ipso*-C)), 115.8 (s, **C**$_5$H$_5$), 65.1 (d, $^2J_{P-C}$ = 5 Hz, Ti-**C**H$_3$), 42.2 (d, $^1J_{P-C}$ = 42 Hz, **C**(CH$_3$)$_3$), 30.0 (s, C(**C**H$_3$)$_3$), 21.7 (s, P(*p*-**C**H$_3$C$_6$H$_4$), 10.6 (q, br, $^1J_{B-C}$ = 54 Hz, H$_3$**C**B(C$_6$F$_5$)$_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −15.2 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.68 (d, 6F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (*o*-F)), −165.58 (t, 3F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (*p*-F)), −168.11 (t, 6F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (*m*-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 53.6 (s, N**P**^{t}Bu$_3$), 13.6 (s, **P**(*p*-CH$_3$C$_6$H$_4$)$_3$).

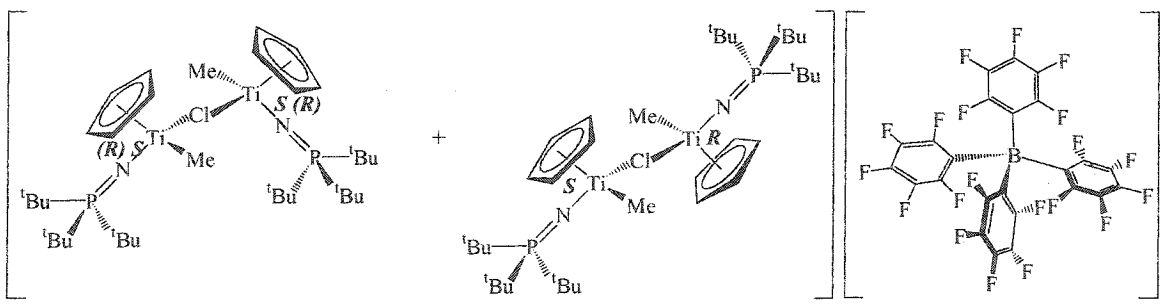


[Cp(NP^{t}Bu$_3$)TiMe·P(*p*-CH$_3$C$_6$H$_4$)$_3$][B(C$_6$F$_5$)$_4$] (2.16): A solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT to a solution of [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), followed by the addition at RT of P(*p*-CH$_3$C$_6$H$_4$)$_3$ (21 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was left to stir at RT for 30 minutes. The final solution was then filtered through Celite, the solvent was removed *in vacuo*, and the recovered orange oil was washed with pentanes (3 x 5mL) before drying to afford an orange solid (71 mg, 76 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.32 (m, 12H, P(*p*-CH$_3$C$_6$**H**$_4$)), 6.30 (s, 5H, C$_5$**H**$_5$), 2.41 (s, 9H, P(*p*-C**H**$_3$C$_6$H$_4$)), 1.40 (d, 27H, $^3J_{P-H}$ = 14 Hz, C(C**H**$_3$)$_3$), 1.19 (s, 3H, Ti-C**H**$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^1J_{C-F}$ = 240 Hz, **C**$_6$F$_5$ (*o*-C)), 143.1 (d, $^4J_{P-C}$ = 2 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*p*-C)), 138.7 (d(m), $^1J_{C-F}$ = 236 Hz, **C**$_6$F$_5$ (*p*-C)), 136.1 (d(m), $^1J_{C-F}$ = 250 Hz, **C**$_6$F$_5$ (*m*-C)), 134.0 (d, $^2J_{P-C}$ = 13 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*o*-C)), 130.8 (d, $^3J_{P-C}$ = 10 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*m*-C)), 124.7 (s, br, **C**$_6$F$_5$ (*ipso*-C)), 125.9 (d, $^1J_{P-C}$ = 38 Hz, P(*p*-CH$_3$**C**$_6$H$_4$) (*ipso*-C)), 115.9 (s, **C**$_5$H$_5$), 65.2 (d, $^2J_{P-C}$ = 5 Hz, Ti-**C**H$_3$), 42.2 (d, $^1J_{P-C}$ = 42 Hz, NP**C**(CH$_3$)$_3$), 29.9 (s, NPC(**C**H$_3$)$_3$), 21.8 (s, P(*p*-**C**H$_3$C$_6$H$_4$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.36 (s, 8F, C$_6$**F**$_5$ (*o*-F)), −164.04 (t, 4F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (*p*-F)), −167.81 (t, 8F, $^3J_{F-F}$ = 18 Hz, C$_6$**F**$_5$ (*m*-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 53.6 (s, N**P**^{t}Bu$_3$), 13.6 (s, **P**(*p*-CH$_3$-C$_6$H$_4$)$_3$).

[(*o*-CH$_3$C$_6$H$_4$)$_3$PCH$_2$Cl][B(C$_6$F$_5$)$_4$] (2.17) & [{Cp(NP^{t}Bu$_3$)TiMe}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (2.18): A solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was combined at RT with a solution of [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), followed by the addition at RT of a solution of P(*o*-CH$_3$C$_6$H$_4$)$_3$ (21 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was left to stir at RT for 30 minutes. The solvent was removed *in vacuo*, and the recovered orange oil was washed with pentanes (3 x 5 mL) before drying to afford an orange solid. 1 mL of CH_2Cl_2 was added to the dried solid, and layered with pentanes (3 mL). Characterization of **[(*o*-CH$_3$C$_6$H$_4$)$_3$PCH$_2$Cl][B(C$_6$F$_5$)$_4$] (2.17):**

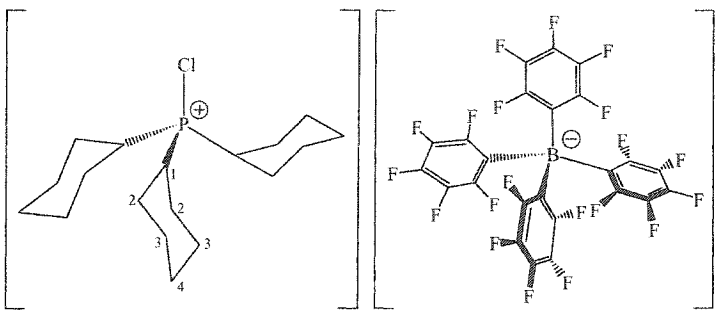


Colorless crystals were obtained, which were washed with pentanes (49 mg, 68 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.81 (m, 3H, P(*o*-$CH_3C_6\mathbf{H}_4$)), 7.60-7.47 (m, 9H, P(*o*-$CH_3C_6\mathbf{H}_4$)), 4.93 (s, br, 2H, (*o*-$CH_3C_6H_4)_3PC\mathbf{H}_2Cl$), 2.25 (s, 9H, P(*o*-$C\mathbf{H}_3C_6H_4)_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 148.7 (d(m), $^{1}J_{C-F}$ = 243 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 144.2 (d, $^{2}J_{P-C}$ = 9 Hz, P(*o*-$CH_3\mathbf{C}_6H_4$) (*2*-C)), 138.7 (d(m), $^{1}J_{C-F}$ = 250 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 137.0 (d, $^{4}J_{P-C}$ = 3 Hz, P(*o*-$CH_3\mathbf{C}_6H_4$) (*4*-C)), 136.8 (d(m), $^{1}J_{C-F}$ = 240 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 135.5 (d, $^{2}J_{P-C}$ = 12 Hz, P(*o*-$CH_3\mathbf{C}_6H_4$) (*6*-C)), 134.7 (d, $^{3}J_{P-C}$ = 11 Hz, P(*o*-$CH_3C_6H_4$) (5-C)), 128.9 (d, $^{3}J_{P-C}$ = 13 Hz, P(*o*-$CH_3\mathbf{C}_6H_4$) (3-C)), signal for P(*o*-$CH_3\mathbf{C}_6H_4$ (1-C)) was not observed, 124.7 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 42.2 (d, $^{1}J_{P-C}$ = 57 Hz, (*o*-$CH_3C_6H_4)_3P\mathbf{C}H_2Cl$), 23.0 (d, P(*o*-$\mathbf{C}H_3C_6H_4$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.77 (s, 8F, $C_6\mathbf{F}_5$ (*o*-F)), −163.84 (t, 4F, $^{3}J_{F-F}$ = 20 Hz, $C_6\mathbf{F}_5$ (*p*-F)), −167.71 (s, br, 8F, $^{3}J_{F-F}$ = 18 Hz, $C_6\mathbf{F}_5$ (*m*-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 29.1 (s). Compound **[{Cp(NP^{t}Bu$_3$)TiMe}$_2$(μ-Cl)][B(C$_6$F$_5$)$_4$] (2.18)** was additionally synthesized and characterized according to the following procedure:

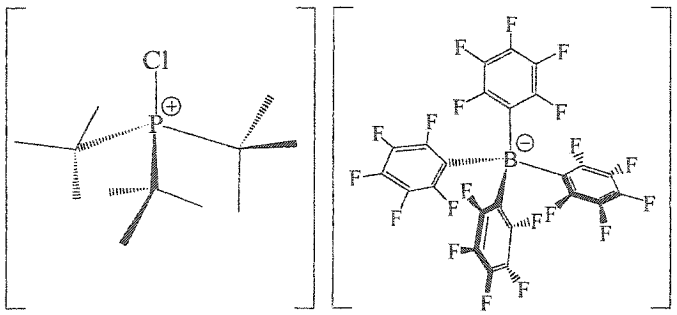


A solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was combined at RT with a solution of [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), and left to stir for 30 minutes. A second equivalent of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was incorporated into the reaction mixture. The solution was stirred at RT for another 30 minutes. The solvent was removed *in vacuo*. The recovered dark oil was washed with pentanes (3 x 5 mL) before drying to afford a red solid (88 mg, 89 %).

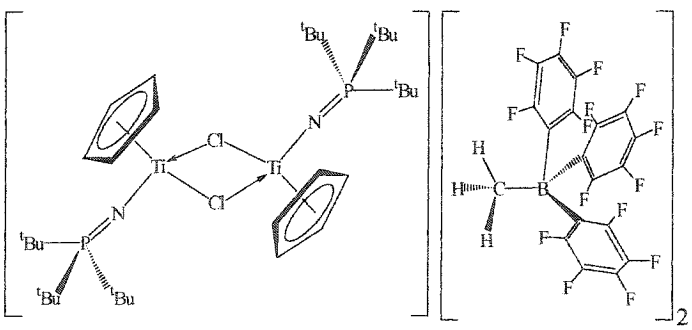
The *rac/meso* isomers were present in a 1:1 ratio and could not be specifically assigned. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 6.40, 6.36 (s, 10H, C_5H_5), 1.51, 1.49 (d, 54H, $^{3}J_{P-H}$ = 14 Hz, $C(CH_3)_3$), 1.11, 1.05 (s, 6H, Ti-CH_3). $^{13}C\{^{1}H\}$ NMR (125.75 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^{1}J_{C-F}$ = 240 Hz, C_6F_5 (*o*-C)), 138.8 (d(m), $^{1}J_{C-F}$ = 243 Hz, C_6F_5 (*p*-C)), 136.9 (d(m), $^{1}J_{C-F}$ = 246 Hz, C_6F_5 (*m*-C)), 124.2 (s, br, C_6F_5 (*ipso*-C)), 114.8, 114.7 (s, C_5H_5), 42.4 (d, $^{1}J_{P-C}$ = 43 Hz, $C(CH_3)_3$), 29.9 (s, $C(CH_3)_3$), 25.4 (s, Ti-CH_3). $^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.23 (s, 8F, C_6F_5 (*o*-F)), −163.99 (t, 4F, $^{3}J_{F-F}$ = 21 Hz, C_6F_5 (*p*-F)), −167.79 (s, 8F, C_6F_5 (*m*-F)). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 50.1 (s).



The compound **$[Cy_3PCl][B(C_6F_5)_4]$ (2.19)** was unexpectedly isolated from the following preparation: A solution of $Cp(NP^tBu_3)TiMe_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was combined at RT with a solution of $[C(C_6H_5)_3][B(C_6F_5)_4]$ (64 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), followed by the addition at RT of a solution of PCy_3 (20 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was left to stir at RT for 30 minutes. The solvent was removed *in vacuo*, and the recovered amber oil was washed with pentanes (3 x 5 mL) before drying to afford an orange solid. 1 mL of CH_2Cl_2 was added to the dried solid, and layered with pentanes (3 mL). Colorless crystals were obtained, which were washed with pentanes (44 mg, 63 %). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 2.25-1.32 (m, 33H, $P(C_6H_{11})_3$). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^{1}J_{C-F}$ = 240 Hz, C_6F_5 (*o*-C)), 138.9 (d(m), $^{1}J_{C-F}$ = 245 Hz, C_6F_5 (*p*-C)), 136.9 (d(m), $^{1}J_{C-F}$ = 248 Hz, C_6F_5 (*m*-C)), 125.1 (s, br, C_6F_5 (*ipso*-C)), 36.4 (d, $^{1}J_{P-C}$ = 31 Hz, $(C_6H_{11})_3PCl$ (1-C)), 26.8 (s, br, $(C_6H_{11})_3PCl$ (4-C)), 26.6 (d, $^{3}J_{P-C}$ = 18 Hz, $(C_6H_{11})_3PCl$ (3-C)), 25.5 (d, $^{2}J_{P-C}$ = 22 Hz, $(C_6H_{11})_3PCl$ (2-C)). $^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.29 (s, 8F, C_6F_5 (*o*-F)), −163.88 (t, 4F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.71 (s, br, 8F, $^{3}J_{F-F}$ = 18 Hz, C_6F_5 (*m*-F)). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 103.1 (s).

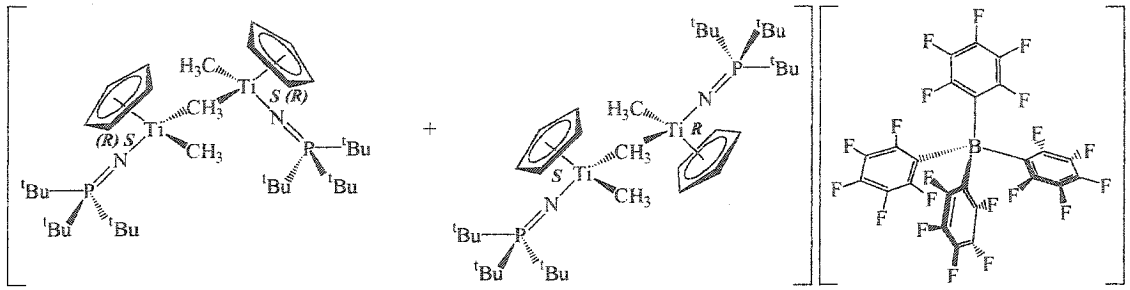


The compound **[^{t}Bu$_3$PCl][B(C$_6$F$_5$)$_4$] (2.20)** was unexpectedly isolated from the following preparation: A solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was combined at RT with a solution of [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), followed by the addition at RT of a solution of P^{t}Bu$_3$ (14 mg, 0.07 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was left to stir at RT for 30 minutes. The solvent was removed *in vacuo*, and the recovered yellow oil was washed with pentanes (3 x 5 mL) before drying to afford a yellow solid. NMR spectroscopic analyses revealed that multiple products were present. 1 mL of CH_2Cl_2 was added to the dried solid, and layered with pentanes (3 mL). Only a single colorless crystal was obtained and hence, spectroscopic characterization was not possible.



The compound **[{Cp(NP^{t}Bu$_3$)Ti-(μ-Cl)}$_2$][MeB(C$_6$F$_5$)$_3$]$_2$ (2.21)** was additionally synthesized and characterized according to the following procedure: A solution of Cp(NP^{t}Bu$_3$)TiMe$_2$ (25 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT to a solution of B(C$_6$F$_5$)$_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (2 mL), and was left to stir for 30 minutes. The solvent was removed *in vacuo* and the recovered oil was washed with pentanes (3 x 5 mL) before drying to afford an amber solid (106 mg, 85 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 6.76 (s, 10H, C$_5$**H**$_5$), 1.47 (d, 54H, $^3J_{P-H}$ = 14 Hz, C(C**H**$_3$)$_3$), 0.54 (s, br, 6H, **H**$_3$CB(C$_6$F$_5$)$_3$). ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2) δ: 148.9 (d(m), $^1J_{C-F}$ = 236 Hz, **C**$_6$F$_5$ (*o*-C)), 138.3 (d(m), $^1J_{C-F}$ = 242 Hz, **C**$_6$F$_5$ (*p*-C)), 137.0 (d(m), $^1J_{C-F}$ = 247 Hz, **C**$_6$F$_5$ (*m*-C)), 127.6 (s, br, **C**$_6$F$_5$ (*ipso*-C)), 117.6 (s, **C**$_5$H$_5$), 42.7 (d, $^1J_{P-C}$ = 40 Hz, **C**(CH$_3$)$_3$), 29.9 (s, C(**C**H$_3$)$_3$), 10.5 (s, br, H$_3$**C**B(C$_6$F$_5$)$_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −15.2 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.37 (d,

12F, $^{3}J_{F-F}$ = 23 Hz, C_6F_5 (*o*-F)), −165.61 (t, 6F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −168.13 (t, 12F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 60.7 (s).



[{Cp(NP^{t}Bu$_3$)TiMe}$_2$(μ-Me)][B(C_6F_5)$_4$] (2.23): A solution of Cp(NP^{t}Bu$_3$)$TiMe_2$ (25 mg, 0.07 mmol) in C_6H_5Cl (2 mL) was combined at RT with a solution of $[C(C_6H_5)_3][B(C_6F_5)_4]$ (64 mg, 0.07 mmol) in C_6H_5Cl (2 mL), and left to stir for 30 minutes. A second equivalent of Cp(NP^{t}Bu$_3$)$TiMe_2$ (25 mg, 0.07 mmol) in C_6H_5Cl (2 mL) was incorporated into the reaction mixture. The solution was stirred at RT for another 30 minutes. The solvent was removed *in vacuo* and the recovered purple oil was washed with pentanes (3 x 5 mL) before drying to afford a purple solid (77 mg, 79 %). The *rac/meso* isomers were present in a 1:1 ratio and could not be specifically assigned. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 6.29, 6.25 (s, 10H, $C_5\mathbf{H}_5$), 1.51, 1.50 (d, 54H, $^{3}J_{P-H}$ = 14 Hz, C(C$\mathbf{H}_3$)$_3$), 0.69, 0.66 (s, 6H, Ti-C$\mathbf{H}_3$), 0.14, 0.13 (s, 3H, μ-Ti-C$\mathbf{H}_3$). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.9 (d(m), $^{1}J_{C-F}$ = 236 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 139.0 (d(m), $^{1}J_{C-F}$ = 244 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 137.0 (d(m), $^{1}J_{C-F}$ = 247 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 126.6 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 113.6, 113.5 (s, $\mathbf{C}_5H_5$), 49.1, 49.0 (s, μ-Ti-$\mathbf{C}H_3$) confirmed by COSY NMR, 42.2 (d, $^{1}J_{P-C}$ = 44 Hz, $\mathbf{C}(CH_3)_3$), 30.7, 30.6 (s, Ti-$\mathbf{C}H_3$), 30.0 (s, C($\mathbf{C}H_3$)$_3$). $^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.34 (s, 6F, $C_6\mathbf{F}_5$ (*o*-F)), −163.91 (t, 3F, $^{3}J_{F-F}$ = 20 Hz, $C_6\mathbf{F}_5$ (*p*-F)), −167.73 (s, 6F, $C_6\mathbf{F}_5$ (*m*-F)). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 47.0 (s).

2.2.6. X-Ray Experimental

Single crystals for X-ray analysis were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer at 20 °C with Mo Kα radiation (λ = 0.71069 Å). The observed extinctions were consistent with the space groups determined for each sample. Measures of decay were obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the respective data collections. Empirical absorption corrections based on redundant data were applied to each data set. Subsequent solution and refinement were performed using the SHELXTL solution package.

Structure Solutions and Refinements: Non-hydrogen atomic scattering factors were taken from literature tabulations.[118] The heavy atom positions were determined using direct methods or Patterson techniques. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques of F, minimizing the function $\omega(|F_o|-|F_c|)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are observed and calculated structure factor amplitudes. In the final cycle of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C-H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.2 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom parameters were calculated but not refined.

X-ray structural solutions of $[Cp(NP^tBu_3)TiMe{\cdot}P(CH_3)_3][B(C_6F_5)_4]$ (**2.10**), $[(o{-}CH_3C_6H_4)_3PCH_2Cl][B(C_6F_5)_4]$ (**2.17**), $[(C_6H_{11})_3PCl][B(C_6F_5)_4]$ (**2.19**), $[^tBu_3PCl][B(C_6F_5)_4]$ (**2.20**) and $[Cp(NP^tBu_3)TiCl{\cdot}(4{-}DMAP)][B(C_6F_5)_4]$ (**2.22**) were performed as described above. The solution for structure $[\{Cp(NP^tBu_3)Ti(\mu{-}Cl)\}_2][B(C_6F_5)_4]_2$ (**2.21**) includes one molecule of CH_2Cl_2 with the central carbon disordered. No residual electron density remained in any of the solutions that was of any chemical significance. Cell parameters, R, R_w and GoF values are located in Table 2.1 and Table 2.2. ORTEP

drawings of **2.10**, **2.17**, **2.19**, **2.20**, **2.21** and **2.22** are shown in Figures 2.2, 2.6, 2.8, 2.9 and 2.10, with selected bond distances provided in the caption.

Table 2.1: Crystallographic parameters for $[Cp(NP^tBu_3)TiMe{\cdot}P(CH_3)_3][B(C_6F_5)_4]$ (**2.10**), $[(o\text{-}CH_3C_6H_4)_3PCH_2Cl][B(C_6F_5)_4]$ (**2.17**) and $[(C_6H_{11})_3PCl][B(C_6F_5)_4]$ (**2.19**).

	2.10	**2.17**	**2.19**
Molecular formula	$C_{45}H_{44}BF_{20}NP_2Ti$	$C_{46}H_{23}BClF_{20}P$	$C_{42}H_{33}BClF_{20}P$
Formula weight	1099.46	1032.87	994.91
a (Å)	15.707(9)	21.30(1)	26.15(1)
b (Å)	18.38(1)	7.996(5)	11.901(6)
c (Å)	18.20(1)	25.30(2)	16.170(8)
β (°)	108.84(1)	91.69(1)	122.03(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P2/c	Cc
Volume (Å^3)	4972(5)	4307(5)	4265(4)
D_{calc} (gcm^{-3})	1.469	1.593	1.549
Z	4	4	4
Abs coeff, μ mm^{-1}	0.344	0.248	0.246
θ range (°)	1.76-23.28	2.46-23.26	1.84-23.20
Reflections collected	20949	17533	8946
Data $F_o^2>3\sigma(F_o^2)$	3774	4180	3473
Parameters	631	623	586
R(%)	0.0409	0.0329	0.0453
R_w(%)	0.0812	0.0800	0.1188
Goodness of fit	1.020	0.851	0.987

The data was collected at 20°C with Mo Kα radiation (λ = 0.71073 Å)

$$R = \sum\left|\,|F_o| - |F_c|\,\right| / \sum |F_o|, \quad R_w = \left[\sum\left(|F_o| - |F_c|\right)^2 / \sum |F_o|^2\right]^{0.5}$$

Table 2.2: Crystallographic parameters for [^{t}Bu$_3$PCl][B(C$_6$F$_5$)$_4$] (**2.20**), [{Cp(NP^{t}Bu$_3$)Ti-(μ-Cl)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (**2.21**) and [Cp(NP^{t}Bu$_3$)TiCl·(4-DMAP)][B(C$_6$F$_5$)$_4$] (**2.22**).

	2.20	**2.21**	**2.22**
Molecular formula	$C_{36}H_{27}BClF_{20}P$	$C_{82}H_{64}B_2F_{40}N_2P_2Ti_2$	$C_{48}H_{42}BClF_{20}N_3PTi$
Formula weight	916.81	2016.74	1186.68
a (Å)	10.799(5)	12.489(6)	10.899(5)
b (Å)	12.945(6)	13.693(7)	27.24(1)
c (Å)	13.854(7)	14.974(7)	18.146(9)
α (°)	90.30(1)	93.12(1)	
β (°)	97.55(1)	109.771(9)	97.102(9)
γ (°)	99.425(9)	107.766(9)	
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	$P2_1/c$
Volume (Å^3)	1893.3(16)	2259.1(19)	5347(4)
D_{calc} (gcm^{-3})	1.608	1.7728	1.474
Z	2	2	4
Abs coeff, μ mm^{-1}	0.270	0.499	0.371
θ range (°)	2.29-23.27	1.88-23.28	1.23-23.25
Reflections collected	8152	9654	22759
Data $F_o^2 > 3\sigma(F_o^2)$	2540	4616	4294
Parameters	532	613	684
R(%)	0.0695	0.0327	0.0599
R_w(%)	0.1858	0.0954	0.1736
Goodness of fit	0.875	0.654	1.038

The data was collected at 20°C with Mo Kα radiation (λ = 0.71073 Å)

$$R = \sum \| F_o | - | F_c \| / \sum | F_o |, \quad R_w = \left[\sum \left(| F_o | - | F_c | \right)^2 / \sum | F_o |^2 \right]^{0.5}$$

2.3. Results and Discussion

2.3.1. Generation of the Titanium Complexes [Cp(NP^{t}Bu$_3$)TiMe·LB] [RB(C$_6$F$_5$)$_3$] (R = Me, C$_6$F$_5$) using Pyridines as Lewis Bases (LB)

Several substituted pyridines were utilized as Lewis bases (LB) to stabilize the titanium species Cp(NP^{t}Bu$_3$)TiMe(μ-MeB(C$_6$F$_5$)$_3$) and [Cp(NP^{t}Bu$_3$)TiMe][B(C$_6$F$_5$)$_4$] by forming the ion pair [Cp(NP^{t}Bu$_3$)TiMe·LB][RB(C$_6$F$_5$)$_4$] (R = Me, C$_6$F$_5$). Since the syntheses of titanium methyl cationic complexes with pyridine in CH_2Cl_2 have been previously described,[119,120] the experiments within this chapter were performed using CH_2Cl_2 as the solvent. Dichloromethane appeared to be an ideal solvent for these reactions as it is a non-coordinative polar solvent that can solubilize the zwitterions or cations generated from Cp(NP^{t}Bu$_3$)TiMe$_2$. Because the species generated from the titanium complex Cp(NP^{t}Bu$_3$)TiMe$_2$ will be charged, their solubility becomes poor in solvents such as toluene, benzene, hexane or pentane. If solvents like THF and Et_2O are utilized, the solvent can coordinate to the metal and will compete with the Lewis base.

The pyridines employed in the pursuit of stabilizing titanium cyclopentadienyl tri-*t*-butylphosphinimide charged complexes were pyridine (Py), 4-*tert*-butylpyridine (4-^{t}BuPy), 4-ethylpyridine (4-EtPy) and 4-dimethylaminopyridine (4-DMAP). It was observed that, depending on the activator used to generate the charged titanium species, the order of addition was relevant.

In the reaction using B(C$_6$F$_5$)$_3$ as the activator, the substituted pyridine was added to Cp(NP^{t}Bu$_3$)TiMe$_2$, followed by the addition of a solution of B(C$_6$F$_5$)$_3$ in CH_2Cl_2 (Figure 2.3a). The products obtained from the reactions performed in this sequence were characterized by NMR spectroscopy. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{11}B{^{1}H} and ^{19}F NMR analyses identified the compounds as [Cp(NP^{t}Bu$_3$)TiMe·Py][MeB(C$_6$F$_5$)$_3$] (**2.1**), [Cp(NP^{t}Bu$_3$)TiMe·(4-^{t}BuPy)][MeB(C$_6$F$_5$)$_3$] (**2.3**), [Cp(NP^{t}Bu$_3$)TiMe·(4-EtPy)][MeB(C$_6$F5)$_3$] (**2.5**) and [Cp(NP^{t}Bu$_3$)TiMe·(4-DMAP)][MeB(C$_6$F$_5$)$_3$] (**2.7**). Selected NMR data are displayed in Table 2.3 (p.51).

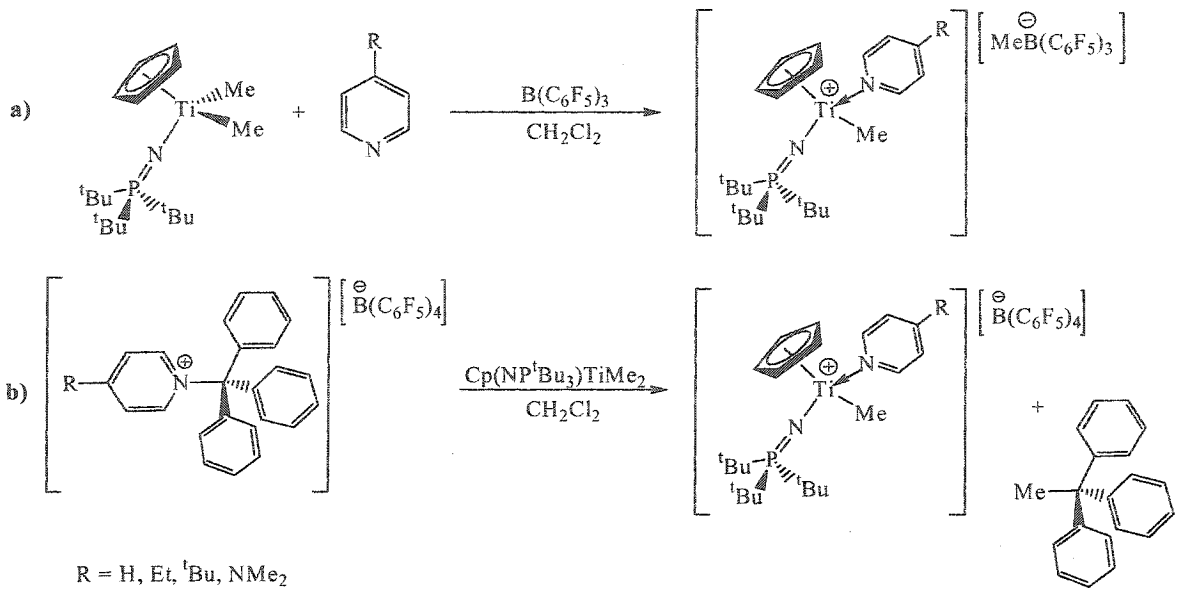


Figure 2.3: Generation of the complex $[Cp(NP^tBu_3)TiMe{\cdot}(4\text{-}RPy)][RB(C_6F_5)_3]$ (R = Me, C_6F_5) using (**a**) $B(C_6F_5)_3$ and (**b**) $[C(C_6H_5)_3][B(C_6F_5)_4]$ as the activators.

If the order of addition of the reagents were to be changed, the reaction between the substituted pyridines and $B(C_6F_5)_3$ takes place, forming the corresponding adduct preventing the generation of the active complex

The stabilized complexes $[Cp(NP^tBu_3)TiMe{\cdot}(4\text{-}RPy)][B(C_6F_5)_4]$ (R = H, Et, ^{t}Bu, NMe_2) using $[C(C_6H_5)_3][B(C_6F_5)_4]$, were best obtained by first reacting the substituted pyridine with trityl borate, followed by the addition of the titanium complex $Cp(NP^tBu_3)TiMe_2$ (Figure 2.3b). Using this procedure, the ion pairs $[Cp(NP^tBu_3)$-$TiMe{\cdot}Py][B(C_6F_5)_4]$ (**2.2**), $[Cp(NP^tBu_3)TiMe{\cdot}(4\text{-}^t BuPy)][B(C_6F_5)_4]$ (**2.4**), $[Cp(NP^tBu_3)$-$TiMe{\cdot}(4\text{-}EtPy)][B(C_6F_5)_4]$ (**2.6**) and $[Cp(NP^tBu_3)TiMe{\cdot}(4\text{-}DMAP)][B(C_6F_5)_4]$ (**2.8**) were synthesized. These complexes were characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and ^{19}F NMR spectroscopy and selected NMR data are shown in Table 2.3.

Table 2.3: Selected spectroscopic data for the stabilized titanium complexes **2.1** to **2.8**. Chemical shifts are given in ppm.

COMPOUND	$^{31}P\{^{1}H\}$ NMR δ	^{1}H NMR δ	$^{13}C\{^{1}H\}$ NMR δ	$^{11}B\{^{1}H\}$ NMR δ	^{19}F NMR δ
$Cp(NP^tBu_3)TiMe_2$	33.8	6.07 (C_5H_5) 0.03 (Ti-CH_3)	110.4 (C_5H_5) 38.1 (Ti-CH_3)	-	-
$[Cp(NP^tBu_3)TiMe{\cdot}Py][MeB(C_6F_5)_3]$ **2.1**	51.7	6.46 (C_5H_5) 1.28 (Ti-CH_3)	115.6 (C_5H_5) 54.9 (Ti-CH_3)	−15.2	−133.35 (*o*-F) −165.54 (*p*-F) −168.10 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}Py][B(C_6F_5)_4]$ **2.2**	51.7	6.46 (C_5H_5) 1.29 (Ti-CH_3)	115.5 (C_5H_5) 54.9 (Ti-CH_3)	−16.8	−133.24 (*o*-F) −163.85 (*p*-F) −167.70 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}4\text{-}^tBuPy][MeB(C_6F_5)_3]$ **2.3**	51.1	6.44 (C_5H_5) 1.27 (Ti-CH_3)	115.4 (C_5H_5) 54.4 (Ti-CH_3)	−15.1	−133.39 (*o*-F) −165.56 (*p*-F) −168.09 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}4\text{-}^tBuPy][B(C_6F_5)_4]$ **2.4**	51.1	6.44 (C_5H_5) 1.27 (Ti-CH_3)	115.4 (C_5H_5) 54.5 (Ti-CH_3)	−16.8	−133.22 (*o*-F) −163.91 (*p*-F) −167.71 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}4\text{-}EtPy][MeB(C_6F_5)_3]$ **2.5**	51.1	6.43 (C_5H_5) 1.24 (Ti-CH_3)	115.4 (C_5H_5) 54.5 (Ti-CH_3)	−15.1	−133.41 (*o*-F) −165.54 (*p*-F) −168.09 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}4\text{-}EtPy][B(C_6F_5)_4]$ **2.6**	51.2	6.44 (C_5H_5) 1.24 (Ti-CH_3)	115.5 (C_5H_5) 54.6 (Ti-CH_3)	−16.8	−133.30 (*o*-F) −163.91 (*p*-F) −167.72 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}(4\text{-}DMAP)][MeB(C_6F_5)_3]$ **2.7**	49.1	6.37 (C_5H_5) 1.10 (Ti-CH_3)	114.7 (C_5H_5) 52.1 (Ti-CH_3)	−15.2	−133.42 (*o*-F) −165.52 (*p*-F) −168.15 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}\ (4\text{-}DMAP)][B(C_6F_5)_4]$ **2.8**	48.9	6.38 (C_5H_5) 1.12 (Ti-CH_3)	114.6 (C_5H_5) 52.3 (Ti-CH_3)	−16.8	−133.34 (*o*-F) −163.89 (*p*-F) −167.72 (*m*-F)

The starting material $Cp(NP^tBu_3)TiMe_2$ shows a $^{31}P\{^1H\}$ NMR chemical shift at δ 33.8 ppm. The $^{31}P\{^1H\}$ NMR resonances of the complexes at δ ca. 50 ppm corresponding to the phosphorous atom of the NP^tBu_3 moiety, indicated that the starting material was no longer present. The formation of complexes **2.1** to **2.8** were confirmed by ^1H and $^{13}C\{^1H\}$ NMR analyses (Table 2.3). For the starting material the ^1H NMR chemical shifts for Cp and Ti-Me are δ 6.07 ppm and δ0.03 ppm respectively The ^1H NMR signals corresponding to the Cp ring (δ ca. 6.40 ppm) and Ti-Me (δ ca. 1.20 ppm) in compounds **2.1** to **2.8** are found downfield compared to the signals of $Cp(NP^tBu_3)TiMe_2$. This difference found in the ^1H NMR chemical shift for the Cp ligand and Ti-Me is consistent with cationic nature of the metal complex.

The Cp ligand in both base-free complexes $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ show a chemical shift at δ6.62 ppm in the ^1H NMR spectrum, and at δ116.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum. When pyridine derivatives are coordinated to the titanium center, the ^1H NMR chemical shift for the Cp ligand moves upfield, indicating that electron density is being donated from the coordinated pyridine (Lewis base) to the metal center (Table 2.3). From these complexes, it is noticed that Py is the weakest electron donor used, with **2.1** and **2.2** showing a ^1H NMR chemical shift at δ 6.46 ppm for the Cp ring and δ ca. 1.29 ppm for Ti-Me. Of the four pyridines used ^1H NMR data reflected that 4-DMAP is the strongest electron donor. The species **2.7** and **2.8** had the largest ^1H NMR chemical shifts upfield for the Cp ligand and Ti-Me, when compared to the other complexes stabilized by the other pyridines (Py, 4-^{t}BuPy and 4-EtPy) (δ ca. 6.38 ppm for the Cp and δ ca. 1.11 ppm for Ti-Me) (Table 2.3). The pK_a[121,122,c] values of each pyridine (Table 2.4) also indicate that Py is the weakest electron donor and 4-DMAP is the strongest one.

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[c] The pK_a[121,122] values listed for each Lewis base refer to their corresponding conjugate acid (Figure 2.a).

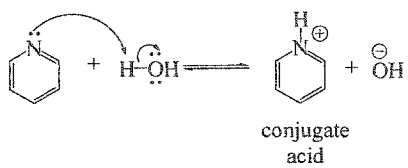


Figure 2.a: Equilibrium between the Lewis base Py and its conjugate acid PyH^+.

Table 2.4: Pyridines listed in increasing order of basicity according to the pK_a[121,122] value.

Pyridines	Py	4-^{t}BuPy	4-EtPy	4-DMAP[121]
pK_a[122]	5.14	5.99	6.02	9.14

The $^{11}B\{^1H\}$ NMR chemical shifts found for the reactions performed with $B(C_6F_5)_3$, were δca. − 15.2 ppm. ^{19}F NMR spectroscopy showed that the environments of the *ortho*-, *meta*- and *para*-F atoms on the aryl groups coordinated to the boron atom remained essentially the same after the counterion $[MeB(C_6F_5)_3]^-$ was formed. An analogous observation can be made for the reactions performed with trityl borate $[C(C_6H_5)_3][B(C_6F_5)_4]$. It is not apparent by NMR analyses that there is any influence of the anion on the cation.

The experiments revealed that the trityl carbocation $[C(C_6H_5)_3]^+$ has a stronger affinity for the methyl group bound to the titanium center in $Cp(NP^tBu_3)TiMe_2$ than to any of the 4-RPy (R = H, Et, ^{t}Bu, NMe_2). When the titanium complex is added to the pyridinium borate salt ($[4\text{-}RPyC(C_6H_5)_3][B(C_6F_5)_4]$), the pyridinium salt must dissociate (Figure 2.4) in order for the trityl cation to abstract the methyl group in $Cp(NP^tBu_3)TiMe_2$, promoting the formation of the titanium complex $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$, which is stabilized by the 4-RPy Lewis base (Figure 2.3b). The reaction equilibrium between $Cp(NP^tBu_3)TiMe_2$ and $[C(C_6H_5)_3]^+$ tends to the formation of $MeC(C_6H_5)_3$, which is removed from the solution mixture after work up of the reaction.

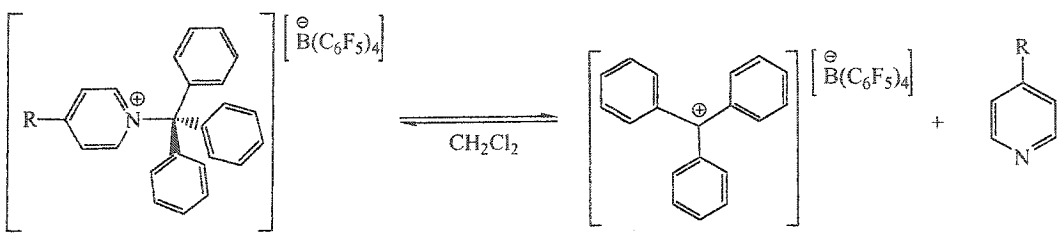


Figure 2.4: Dissociation of $[4\text{-}RPyC(C_6H_5)_3][B(C_6F_5)_4]$ to $[C(C_6H_5)_3][B(C_6F_5)_4]$ and 4-RPy (R = H, Et, ^{t}Bu, NMe_2)

2.3.2. Generation of the Complexes $[Cp(NP^tBu_3)TiMe{\cdot}LB][RB(C_6F_5)_3]$ (R = Me, C_6F_5) using Tertiary Phosphines as Lewis Bases (LB)

The stabilization of the titanium complexes $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ and $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ was also accomplished using tertiary phosphines. The order of addition of the reagents to generate the complexes $[Cp(NP^tBu_3)TiMe{\cdot}PR_3][R'B(C_6F_5)_3]$ (PR_3 = tertiary phosphine; R' = Me, C_6F_5) proved to be important, depending on the activator and phosphine used.

The complexes $[Cp(NP^tBu_3)TiMe{\cdot}PR_3][MeB(C_6F_5)_3]$ (R = Me, ^{n}Bu), were prepared by mixing the tertiary phosphine and $Cp(NP^tBu_3)TiMe_2$, followed by the addition of a solution of $B(C_6F_5)_3$ (Figure 2.5a). The reaction of $Cp(NP^tBu_3)TiMe_2$ with one equivalent of PMe_3 and $B(C_6F_5)_3$ as the activator, gave a mixture of products. Different stoichiometric ratios of the titanium complex and the phosphine were tried. The complex $[Cp(NP^tBu_3)TiMe{\cdot}PMe_3][MeB(C_6F_5)_3]$ (**2.9**) proved to be easily obtained, when an excess of phosphine ($Cp(NP^tBu_3)TiMe_2$:PMe_3 = 1:5) was added to the reaction mixture before the addition of $B(C_6F_5)_3$ in order to drive the reaction towards the formation of the product. From the spectroscopic NMR analyses, no free phosphine was observed after work up of the reaction. The sole species present in solution was **2.9**. The $^{31}P\{^1H\}$ NMR resonance at δ 52.1 ppm is indicative of the phosphorus atom of the phosphinimide ligand, and δ −18.6 ppm corresponds to the phosphorus atom of the phosphine now coordinated to the metal (Table 2.5, p. 60). The analogous reaction using one equivalent of P^nBu_3 gave $[Cp(NP^tBu_3)TiMe{\cdot}P^nBu_3][MeB(C_6F_5)_3]$ (**2.11**) as the only product. For **2.11** the phosphorus resonances in the $^{31}P\{^1H\}$ NMR analysis were present at δ 52.1 and 3.0 ppm.

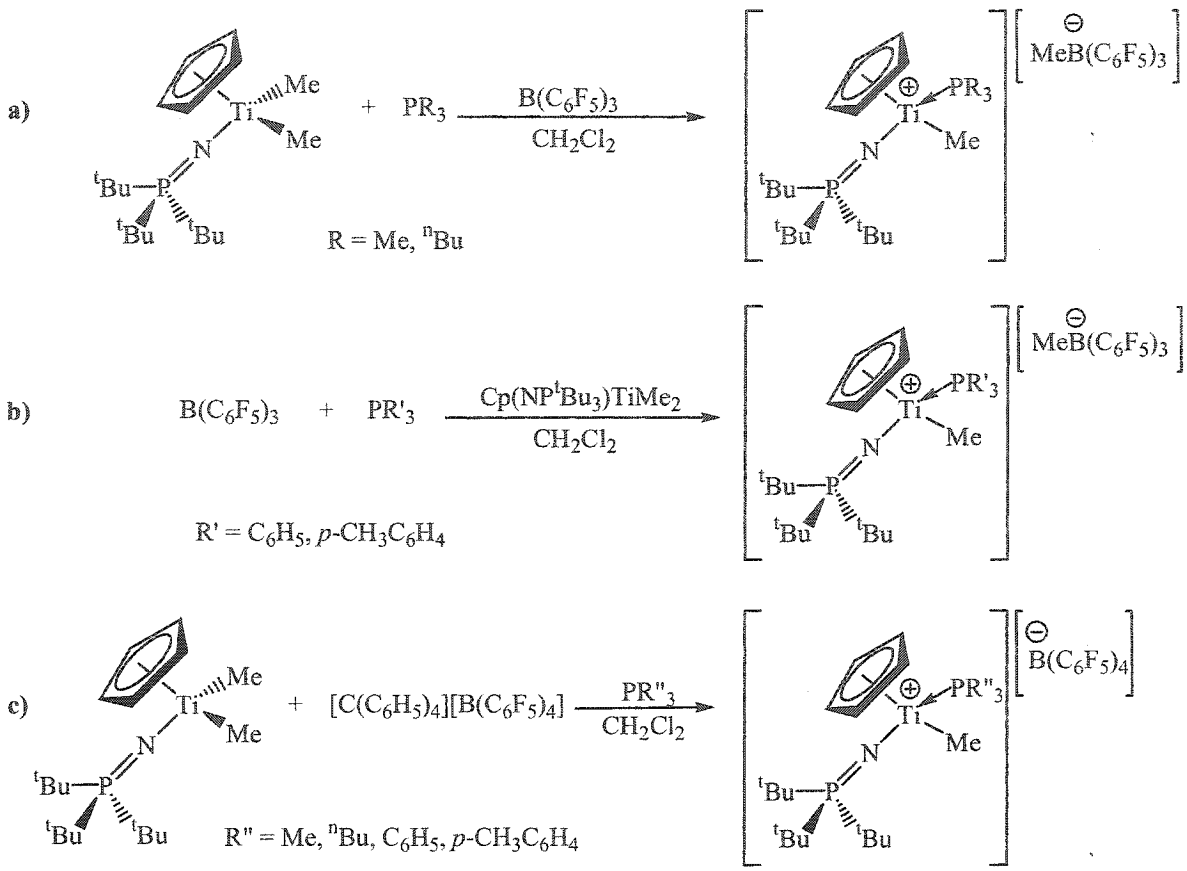


Figure 2.5: Syntheses of the stabilized complex $[Cp(NP^tBu_3)TiMe{\cdot}PR_3][RB(C_6F_5)_3]$ (R = Me, C_6F_5) using (**a**) $B(C_6F_5)_3$ as the activator and trialkyl phosphines as Lewis bases; (**b**) $B(C_6F_5)_3$ as the activator and triaryl phosphines as Lewis bases; and (**c**) trityl borate as an activator and PR_3 (R = Me, ^{n}Bu, C_6H_5, p-$CH_3C_6H_4$).

The complexes $[Cp(NP^tBu_3)TiMe{\cdot}PR_3][MeB(C_6F_5)_3]$, (R = C_6H_5, p-$CH_3C_6H_4$) were afforded by first reacting $B(C_6F_5)_3$ with the triaryl phosphine for 30 minutes. Then, the titanium complex was added to the resulting mixture and left to react for another 30 minutes at room temperature (Figure 2.5b). In the case of $P(C_6H_5)_3$, the product $[Cp(NP^tBu_3)TiMe{\cdot}P(C_6H_5)_3][MeB(C_6F_5)_3]$ (**2.13**) was characterized. The $^{31}P\{^1H\}$ NMR resonance (δ 54.3 ppm) corresponds to the phosphorus atom of the (NP^tBu_3) moiety, and δ 15.1 ppm is indicative of the phosphorus atom of the coordinated phosphine $P(C_6H_5)_3$. The phosphine $P(p\text{-}CH_3C_6H_4)_3$ behaved in a similar manner, giving the ion pair $[Cp(NP^tBu_3)TiMe{\cdot}P(p\text{-}CH_3C_6H_4)_3][MeB(C_6F_5)_3]$ (**2.15**). In this case, the $^{31}P\{^1H\}$ NMR

resonances were found at δ 53.6 ppm (NP^tBu_3) and δ 13.6 ppm ($P(p\text{-}CH_3C_6H_4)_3$) (Table 2.5).

The titanium complex activator, trityl borate $[C(C_6H_5)_3][B(C_6F_5)_4]$ was used to generate the species $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$. A solution of the titanium complex in CH_2Cl_2 was combined with $[C(C_6H_5)_3][B(C_6F_5)_4]$ at room temperature. PR_3 (R = Me, ^{n}Bu, C_6H_5, p-$CH_3C_6H_4$) was immediately incorporated to the mixture (Figure 2.5c). Experimental work confirmed that if $[C(C_6H_5)_3][B(C_6F_5)_4]$ is combined first with PR_3, the phosphonium salt does not dissociate, not allowing the formation of the ion pair $[Cp(NP^tBu_3)TiMe{\cdot}PR_3][B(C_6F_5)_4]$. The stabilized complexes obtained in this manner were characterized by NMR spectroscopy (Table 2.5), and identified as $[Cp(NP^tBu_3)TiMe{\cdot}PMe_3][B(C_6F_5)_4]$ (**2.10**)[d] (confirmed also by X-ray crystallography, Figure 2.6), $[Cp(NP^tBu_3)TiMe{\cdot}P^nBu_3][B(C_6F_5)_4]$ (**2.12**), $[Cp(NP^tBu_3)TiMe{\cdot}PPh_3][B(C_6F_5)_4]$ (**2.14**), and $[Cp(NP^tBu_3)TiMe{\cdot}P(p\text{-}CH_3C_6H_4)_3][B(C_6F_5)_4]$ (**2.16**), respectively.

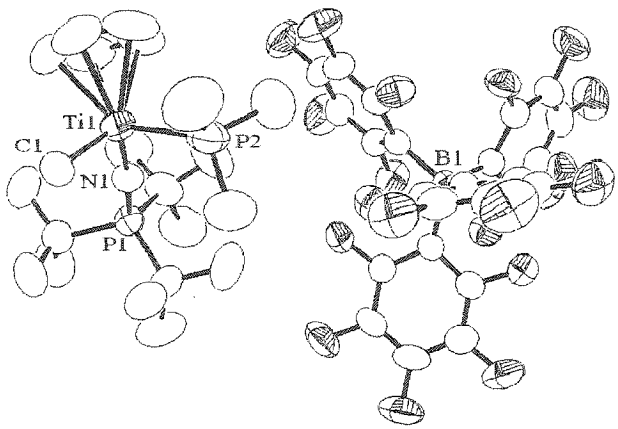


Figure 2.6: ORTEP diagram of the stabilized complex $[Cp(NP^tBu_3)TiMe{\cdot}PMe_3][B(C_6F_5)_4]$ (**2.10**) (hydrogen atoms are omitted for clarity; 50% thermal ellipsoids). Selected bond lengths (Å): Ti(1)–C(1) 2.187(3); Ti(1)–P(2) 2.673(2); Ti(1)–N(1) 1.768(3); N(1)–P(1) 1.617(3).

[d] **2.10** was obtained by adding an excess of phosphine ($Cp(NP^tBu_3)TiMe_2$:PMe_3 = 1:5) to the reaction mixture.

Table 2.5: Selected spectroscopic data for the stabilized titanium complexes **2.9** to **2.16**. * Chemical shifts of the free phosphines. Chemical shifts are given in ppm.

COMPOUND	$^{31}P\{^{1}H\}$ NMR δ*	$^{31}P\{^{1}H\}$ NMR δ	^{1}H NMR δ	$^{13}C\{^{1}H\}$ NMR δ	$^{11}B\{^{1}H\}$ NMR δ	^{19}F NMR δ
$Cp(NP^tBu_3)TiMe_2$	-	33.8 (NP^tBu_3)	6.07 (C_5H_5) 0.03 (Ti-CH_3)	110.4 (C_5H_5) 38.1 (Ti-CH_3)	-	-
$[Cp(NP^tBu_3)TiMe{\cdot}PMe_3][MeB(C_6F_5)_3]$ **2.9**	−62.0	52.1 (NP^tBu_3) −18.6 (PMe_3)	6.45 (C_5H_5) 0.80 (Ti-CH_3)	114.9 (C_5H_5) 63.9 (Ti-CH_3)	−15.2	−133.70 (*o*-F) −165.64 (*p*-F) −168.14 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}PMe_3][B(C_6F_5)_4]$ **2.10**	−62.0	52.2 (NP^tBu_3) −18.9 (PMe_3)	6.45 (C_5H_5) 0.80 (Ti-CH_3)	114.8 (C_5H_5) 63.9 (Ti-CH_3)	−16.9	−133.26 (*o*-F) −163.87 (*p*-F) −167.69 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}P^nBu_3][MeB(C_6F_5)_3]$ **2.11**	−31.5	52.1 (NP^tBu_3) 3.0 (P^nBu_3)	6.44 (C_5H_5) 0.83 (Ti-CH_3)	114.6 (C_5H_5) 64.1 (Ti-CH_3)	−15.2	−133.34 (*o*-F) −165.64 (*p*-F) −168.15 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}P^nBu_3][B(C_6F_5)_4]$ **2.12**	−31.5	52.2 (NP^tBu_3) 3.0 (P^nBu_3)	6.45 (C_5H_5) 0.83 (Ti-CH_3)	114.7 (C_5H_5) 64.5 (Ti-CH_3)	−16.9	−133.29 (*o*-F) −163.92 (*p*-F) −167.73 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}P(C_6H_5)_3][MeB(C_6F_5)_3]$ **2.13**	−5.1	54.3 (NP^tBu_3) 15.1 ($P(C_6H_5)_3$)	6.31 (C_5H_5) 1.20 (Ti-CH_3)	115.9 (C_5H_5) 65.7 (Ti-CH_3)	−15.2	−133.41 (*o*-F) −165.59 (*p*-F) −168.14 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}P(C_6H_5)_3][B(C_6F_5)_4]$ **2.14**	−5.1	54.3 (NP^tBu_3) 15.1 ($P(C_6H_5)_3$)	6.31 (C_5H_5) 1.21 (Ti-CH_3)	115.9 (C_5H_5) 65.7 (Ti-CH_3)	−16.9	−133.34 (*o*-F) −163.95 (*p*-F) −167.75 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}P(p\text{-}CH_3C_6H_4)_3][MeB(C_6F_5)_3]$ **2.15**	−7.7	53.6 (NP^tBu_3) 13.6 ($P(p\text{-}CH_3C_6H_4)_3$)	6.29 (C_5H_5) 1.17 (Ti-CH_3)	115.8 (C_5H_5) 65.1(Ti-CH_3)	−15.2	−133.68 (*o*-F) −165.58 (*p*-F) −168.11 (*m*-F)
$[Cp(NP^tBu_3)TiMe{\cdot}P(p\text{-}CH_3C_6H_4)_3][B(C_6F_5)_4]$ **2.16**	−7.7	53.6 (NP^tBu_3) 13.6 ($P(p\text{-}CH_3C_6H_4)_3$)	6.30 (C_5H_5) 1.19 (Ti-CH_3)	115.9 (C_5H_5) 65.2 (Ti-CH_3)	−16.9	−133.36 (*o*-F) −164.04 (*p*-F) −167.81 (*m*-F)

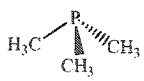
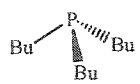
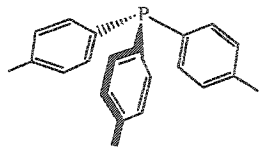
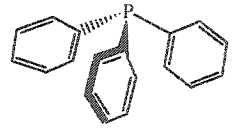
The formation of complexes **2.9** to **2.16** was confirmed by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, $^{11}B\{^{1}H\}$ and ^{19}F NMR spectroscopy. In the $^{31}P\{^{1}H\}$ NMR spectra of these reactions the chemical shift of the starting material corresponding to the $NP^{t}Bu_3$ ligand was no longer present (δ 33.8 ppm), showing in contrast two different signals after the reaction. One signal corresponded to the phosphorus atom in the ligand $NP^{t}Bu_3$ and the other to phosphorus atom of the coordinated tertiary phosphine (Table 2.5).

Based on the observations described, it can be rationalized that the size of the phosphine plays an important role in the formation of the desired product. The size of the tertiary phosphine ($P^{n}Bu_3$, $P(C_6H_5)_3$ and $P(p\text{-}CH_3C_6H_4)_3$), is increased by the substituents at the phosphorus atom. PMe_3 is smaller in contrast with PR3 (^{n}Bu, C_6H_5, $p\text{-}CH_3C_6H_4$). This difference in size might be the reason why when using one equivalent of PMe_3 in the reaction, multiple products are obtained[123,124] instead of the desired product **2.9** or **2.10**. Possibly, by increasing the concentration of PMe_3, such problem is overcome, allowing the formation of the PMe_3 stabilized ion pair complexes.

The titanium complexes stabilized by the trialkyl phosphines PMe_3 and $P^{n}Bu_3$, show a $^{31}P\{^{1}H\}$ NMR chemical shift downfield from the free phosphine, where $\Delta\delta$ ($\delta_{\text{coord-phosphine}} - \delta_{\text{free phosphine}}$) was 43.4 and 34.5 ppm for PMe_3 and $P^{n}Bu_3$ respectively. The $\Delta\delta$ found for the complexes stabilized by triaryl phosphines **2.13**, **2.14** and **2.15**, **2.16** were 20.2 ppm and 21.3 ppm respectively (Table 2.5). The $\Delta\delta$ tends to be less for the larger ligands. This is because the R–P–R angles of the phosphines with larger substituents generally open less on the coordination.[125]

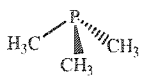
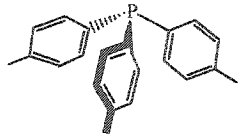
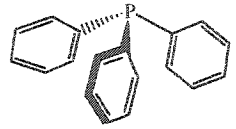
The electron density donated by the tertiary phosphines to the titanium is reflected in the chemical shifts obtained from the ^{1}H NMR spectra (Table 2.5). The chemical shifts for Ti–Me in the Lewis base stabilized complexes for the trialkyl phosphines (**2.9** to **2.12**) appear further upfield compared to the complexes stabilized by triaryl phosphines (**2.13** to **2.16**). ^{1}H NMR analyses showed that the chemical shifts for Ti–Me groups tend to go upfield as the ability of the tertiary phosphines to act as electron donors increases (Table 2.6).

Table 2.6: Relation between ^{1}H NMR chemical shift of Ti-Me and Lewis basicity of PR_3 (R = Me, ^{n}Bu, C_6H_5, *p*-$CH_3C_6H_4$). Phosphines are listed in decreasing order of basicity with respect to their pK_a value.

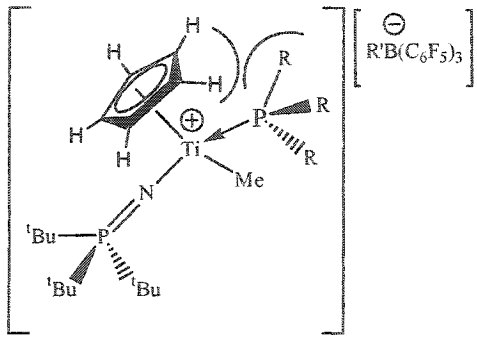
Phosphine	PMe_3 	P^nBu_3 	$P(p\text{-}CH_3C_6H_4)_3$ 	$P(C_6H_5)_3$ 
pK_a[126,127]	8.65	8.69	3.84	2.73
^{1}H NMR δ (ppm) Ti-Me	0.80 (**2.9**) 0.80 (**2.10**)	0.83 (**2.11**) 0.83 (**2.12**)	1.20 (**2.13**) 1.21 (**2.14**)	6.17 (**2.15**) 6.19 (**2.16**)

An anomaly is observed in ^{1}H NMR spectra when chemical shifts of the Cp ring signals are compared. As the ability of the phosphine to act as a Lewis base decreases, the chemical shift for the Cp ring appears to be more shielded. This trend parallels also with the size of the phosphine. As the cone angle of the phosphine increases, the chemical shift of the Cp ring appears further upfield (Table 2.7). Such an anomaly is not observed in ^{1}H NMR analyses of the complexes stabilized by pyridines. The coordination of tertiary phosphines seems to have a dependency on their substituents' size as on their electron donating ability (Table 2.7).

Table 2.7: ^{1}H NMR chemical shifts of the Cp ring in the complexes stabilized by PR_3 (R = Me, ^{n}Bu, C_6H_5, p-$CH_3C_6H_4$) in relation to the Lewis basicity (pK_a).

Phosphine	PMe_3 	$P^{n}Bu_3$ 	$P(p\text{-}CH_3C_6H_4)_3$ 	$P(C_6H_5)_3$ 
pK_a[126,127]	8.65	8.69	3.84	2.73
Tolman Cone Angle[126,127]	118°	132°	145°	145°
^{1}H NMR δ (ppm) Cp ring	6.45 (**2.9**) 6.45 (**2.10**)	6.45 (**2.11**) 6.44 (**2.12**)	6.31 (**2.13**) 6.31 (**2.14**)	6.29 (**2.15**) 6.30 (**2.16**)

This can be interpretated in steric factors. As the size of the phosphine increases, the distance between the phosphorus atom and the metal center, titanium, increases also. This enhancement can affect the interaction between the phosphine substituents and the protons at the Cp ligand. However, as the size of the substituent at the phosphine increases, so does the cone angle of such phosphine. This can promote an interaction between the protons at the Cp ligand and the substituents at the phosphine, since they could be relatively close. The anomaly observed by ^{1}H NMR spectroscopic analysis does not distinguish which case is the cause. Probably both situations contribute, and it appears that in both cases is the size of the phosphine the one that dictates such phenomenon (Figure 2.7).



R = Me, ^{n}Bu, C_6H_5, *p*-$CH_3C_6H_4$
R' = Me, C_6F_5

Figure 2.7: Steric interactions between the protons at the Cp ligand and the substituents of the tertiary phosphine.

The $^{11}B\{^1H\}$ NMR analysis for the systems where the counterion is $[MeB(C_6F_5)_3]^-$ (**2.9**, **2.11**, **2.13** and **2.15**) gave single resonances at the same chemical shift value (δ −15.2 ppm) independent of which phosphine was used. Similarly, the ^{19}F NMR chemical shifts for the *ortho*-, *meta*- and *para*-F atoms present in the aryl groups of the counterion showed no significant change. This is an indication that there is no interaction between the cation and the counterion. A similar conclusion can be made for the case where the counterion is $[B(C_6F_5)_4]^-$ for the complexes **2.10**, **2.12**, **2.14** and **2.16**.

2.3.3. Steric Effects of Bulky Tertiary Phosphines in the Reactions with the Complex [Cp(NP^{t}Bu$_3$)TiMe][RB(C$_6$F$_5$)$_3$] (R = Me, C$_6$F$_5$)

Stabilization of the cationic moiety $[Cp(NP^tBu_3)TiMe]^+$ was also attempted with the Lewis base P(*o*-$CH_3C_6H_4)_3$. The ion pair complex was first generated by reacting $Cp(NP^tBu_3)TiMe_2$ with the activator ($B(C_6F_5)_3$ or $[C(C_6H_5)_3][B(C_6F_5)_4]$); P(*o*-$CH_3C_6H_4)_3$ was then added to the resulting mixture and left to react for 30 minutes at room temperature (Figure 2.8). $^{31}P\{^1H\}$ NMR data obtained from the reactions using either $B(C_6F_5)_3$ or $[C(C_6H_5)_3][B(C_6F_5)_4]$ provided the same information.

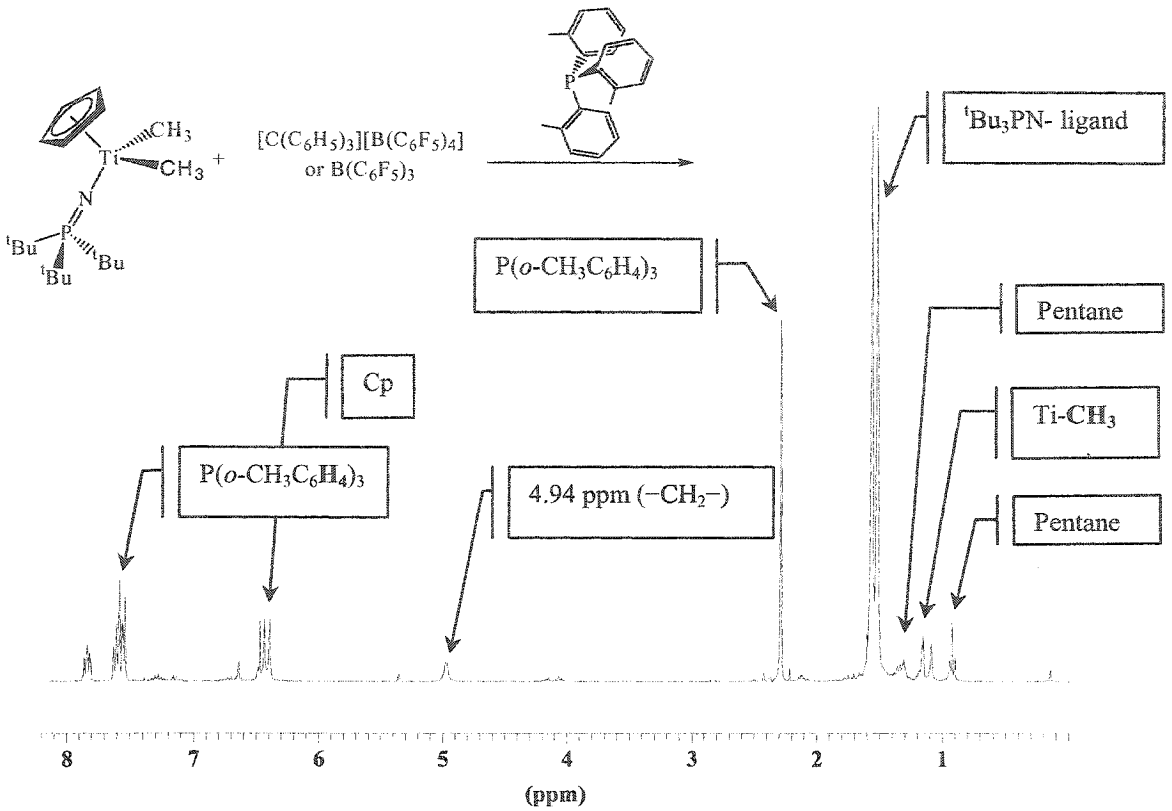


Figure 2.8: ^{1}H NMR spectrum of the final products of the reaction of Cp(NP^{t}Bu$_3$)TiMe$_2$, P(*o*-CH$_3$C$_6$H$_4$)$_3$ and [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] in CH$_2$Cl$_2$.

A DEPT spectrum was obtained and a HETCOR NMR experiment was performed. The data collected showed that the signal at δ35.9 ppm in the ^{13}C{^{1}H} NMR spectrum and the signal at δ4.94 ppm in the ^{1}H NMR spectrum (Figure 2.8) correspond to a methylene carbon. A low temperature ^{1}H NMR spectrum at – 40 °C was carried out (Figure 2.9), which showed the signal corresponding to the phosphinimide ligand split into two sets of doublets, suggesting inequivalent *t*-butyl groups. The three signals assigned to the Cp ring became two and the signals for the methyl groups were two sharp singlets at δ1.01 ppm and δ0.88 ppm. The singlet at δ4.94 ppm defined as a methylene split into two sets of doublet of doublets, suggesting the protons are diastereotopic, where the geminal coupling constant $|^{2}J_{H-H}|$ is 15 Hz. A ^{31}P{^{1}H} NMR spectrum was also run at – 40 °C. It was found that the ^{31}P{^{1}H} NMR signal of δ50.3 ppm obtained at 30 °C split in two, where the new resonances appeared at δ 50.1 ppm and δ49.9 ppm (Figure 2.10).

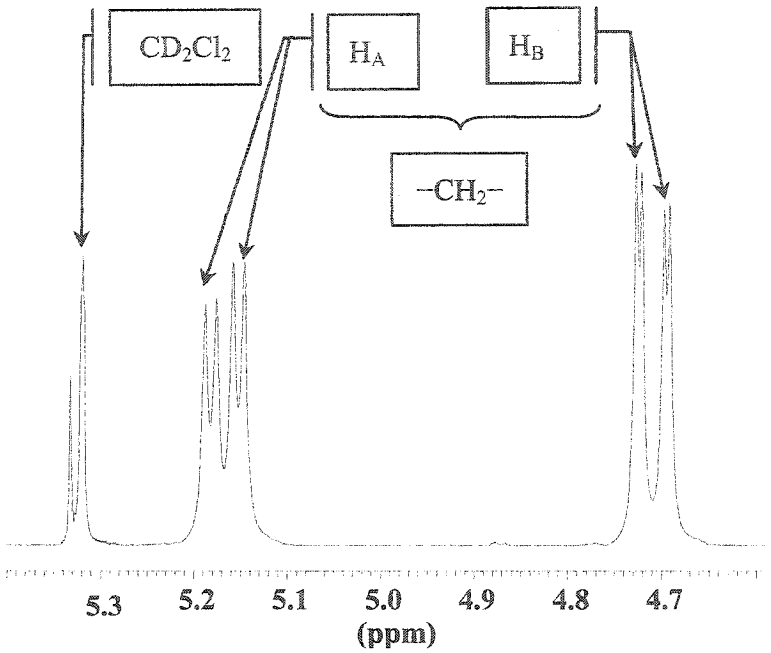


Figure 2.9: ^{1}H NMR spectrum at − 40 °C, showing the splitting of the signal originally found at δ4.94 ppm in the ^{1}H NMR spectrum at RT, suggesting the methylene protons are diastereotopic (δ_{H_A} 5.17 ppm; δ_{H_B} 4.71 ppm; $|^2J_{AB}|$ = 15 Hz).

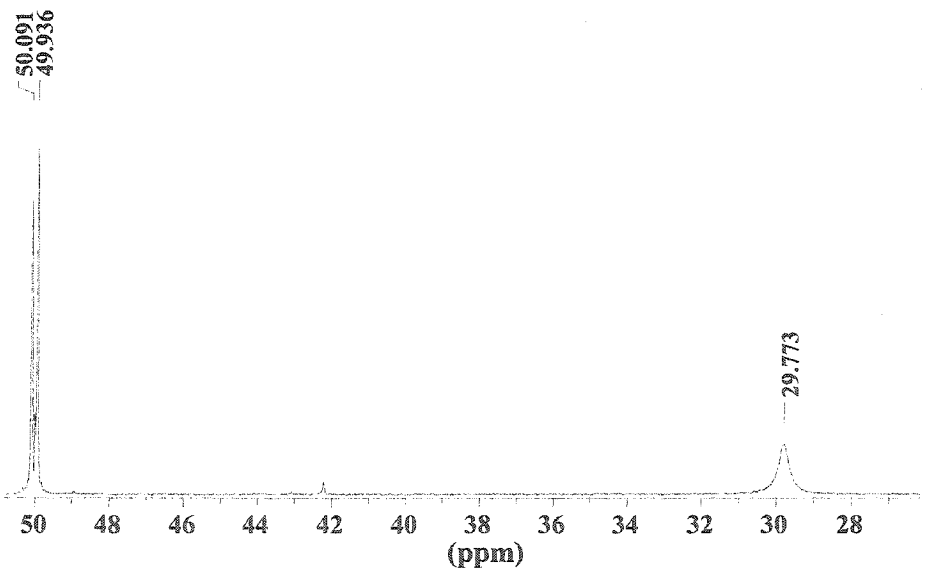


Figure 2.10: $^{31}P\{^1H\}$ NMR spectrum at – 40 °C, revealing two signals corresponding to the phosphinimide ligand.

These data are consistent with the two products isolated from the reaction. One of them is the phosphonium salt $[(o\text{-}CH_3C_6H_4)_3PCH_2Cl][B(C_6F_5)_4]$ (**2.17**), which was confirmed by X-ray analysis from crystals obtained by fractional crystallization (Figure 2.11). The second product is proposed to be the dimeric complex $[(Cp(NP^tBu_3)TiMe)_2(\mu\text{–}Cl)][B(C_6F_5)_4]$ (**2.18**) (Figure 2.12). It is possible that this complex is present in solution as diastereomers with *racemic/meso* configuration where the molecule is chiral at the titanium atom. This explains the inequivalence observed in the ^1H NMR signals attributed to the Cp ligand, phosphinimide moiety and methyl groups coordinated to the titanium center; and the presence of two signals in the $^{31}P\{^1H\}$ NMR spectrum performed at −40°C. Further work provides support to this hypothesis, which will be discussed in Section 2.3.4.

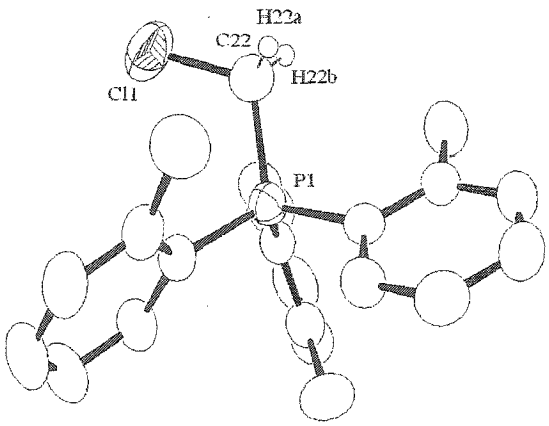


Figure 2.11: ORTEP diagram of the phosphonium salt $[(o\text{-}CH_3C_6H_4)_3PCH_2Cl][B(C_6F_5)_4]$ (**2.17**). (Borate anion and hydrogen atoms, except H22a and H22b are omitted for clarity; 50% thermal ellipsoids). Selected bond lengths (Å): P(1)–C(22) 1.837(2); C(22)–Cl(1) 1.776(3).

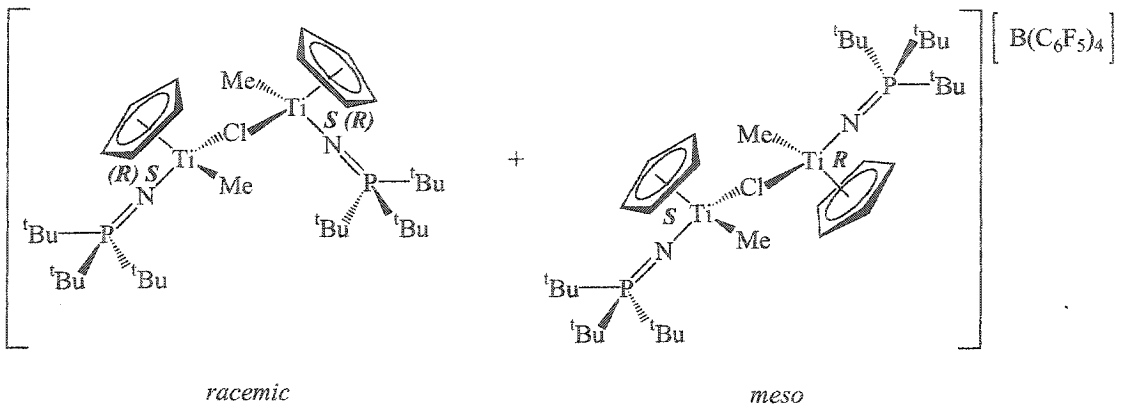


Figure 2.12: Structure proposed for the second product **2.18**.

The results obtained for the reaction involving P(*o*-$CH_3C_6H_4)_3$ suggest that the course of the reaction may depend more on the steric properties of the phosphine ligands than on their Lewis basicity. P(*o*-$CH_3C_6H_4)_3$ has a pK_a value of 3.08, which lies in the range of the values for P(*p*-$CH_3C_6H_4)_3$ (pK_a = 3.84) and P($C_6H_5)_3$ (pK_a = 2.73). Whereas P(*p*-$CH_3C_6H_4)_3$ and P($C_6H_4)_3$ have a cone angle of 145°, P(*o*-$CH_3C_6H_4)_3$ has a cone angle of 194°.

Similar reactions with other sterically bulky phosphines were performed (Table 8). The $^{31}P\{^1H\}$ NMR spectroscopic analyses of the final solutions of the reactions of P^iPr_3, PCy_3 and P^tBu_3 with Cp(NP^tBu_3)$TiMe_2$ and $B(C_6F_5)_3$ showed multiple signals, what was interpretated as an indication that multiple products were formed. For the reactions involving PCy_3 and P^tBu_3, with $[C(C_6H_5)_3][B(C_6F_5)_4]$ as the activator, fractional crystallization afforded suitable crystals for X-ray diffraction. The structures $[Cy_3PCl][B(C_6F_5)_4]$ (**2.19**) and $[^tBu_3PCl][B(C_6F_5)_4]$ (**2.20**) are shown in Figure 2.13. Since the spectroscopic data for the reaction performed with P^iPr_3 are analogous to the data obtained using P^tBu_3 and PCy_3, it is proposed that one of the products might be $[^iPr_3PCl][B(C_6F_5)_4]$. The signal observed for both reactions with $B(C_6F_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$ in the $^{31}P\{^1H\}$ NMR spectra at δ117.0 ppm are assigned to the phosphorus atom of the phosphonium salt $[^iPr_3PCl][RBR'_3]$ (R' = C_6F_5; R = C_6F_5, Me) (Table 2.9).

Table 2.8: List of sterically bulky tertiary phosphines PR_3 (R = ^{t}Bu, Cy, ^{i}Pr) in decreasing order of basicity with respect to their pK_a value.

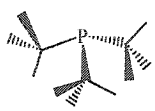
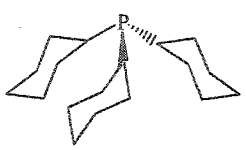
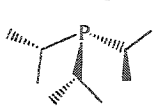
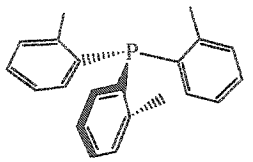
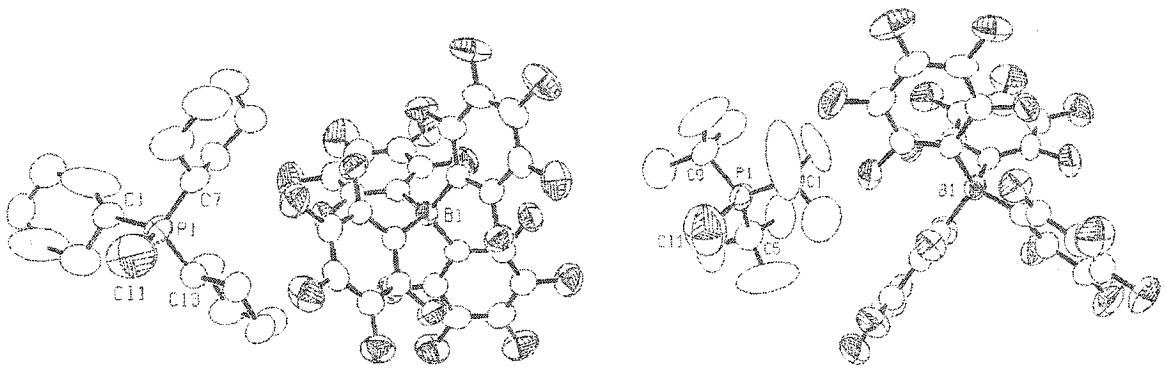
Phosphine	P^tBu_3 	PCy_3 	P^iPr_3 	$P(o\text{-}CH_3C_6H_4)_3$ 
pK_a[126,127]	11.4	9.7	9.3	3.08
Tolman Cone Angle[126,127]	182°	170°	160°	194°

Table 2.9: [a] Selected $^{31}P\{^1H\}$ NMR downfield chemical shifts found in the final reaction mixture for P^tBu_3 and PCy_3 that correspond to $[R_3PCl][R'B(C_6F_5)_3]$ (R = ^{t}Bu, Cy ; R' = Me, C_6F_5). and P^iPr_3. [b] $^{31}P\{^1H\}$ NMR downfield signals might correspond to the phosphonium salt $[^iPr_3PCl][R'B(C_6F_5)_3]$

PR_3	$B(C_6F_5)_3$	$[C(C_6H_5)_3][B(C_6F_5)_4]$
P^tBu_3	123.1[a]	123.3[a]
PCy_3	103.3[a]	103.3[a]
P^iPr_3	117.0[b]	117.0[b]

The mechanism the reaction follows is not clear, but the results suggest that CH_2Cl_2 is activated, probably by the active species of the titanium complex, allowing the generation of such salts. In the case of the reaction with $P(o\text{-}CH_3C_6H_4)_3$ it can be thought that after the active species is formed, the solvent could then coordinate at the titanium. The phosphine in solution could then promote a S_N2 step, yielding $[(o\text{-}CH_3C_6H_4)_3PCH_2Cl]^+$ and $Cp(NP^tBu_3)TiMeCl$ (Figure 2.14). $Cp(NP^tBu_3)TiMeCl$ could then coordinate to the cationic moiety $[Cp(NP^tBu_3)TiMe]^+$, to yield the μ-Cl bridge dimer. In the cases where the reaction takes place with P^iPr_3, PCy_3 and P^tBu_3 is not possible to formulate a plausible reaction mechanism, since there was not enough information.



2.19 **2.20**

Figure 2.13: ORTEP diagram of the products **2.19** and **2.20**. (Hydrogen atoms are omitted for clarity; 50% thermal ellipsoids). (**2.19**) Selected bond distance (Å): P(1)–Cl(1) 1.976(3); (**2.20**) Selected bond distance (Å): P(1)–Cl(1) 2.001(4).

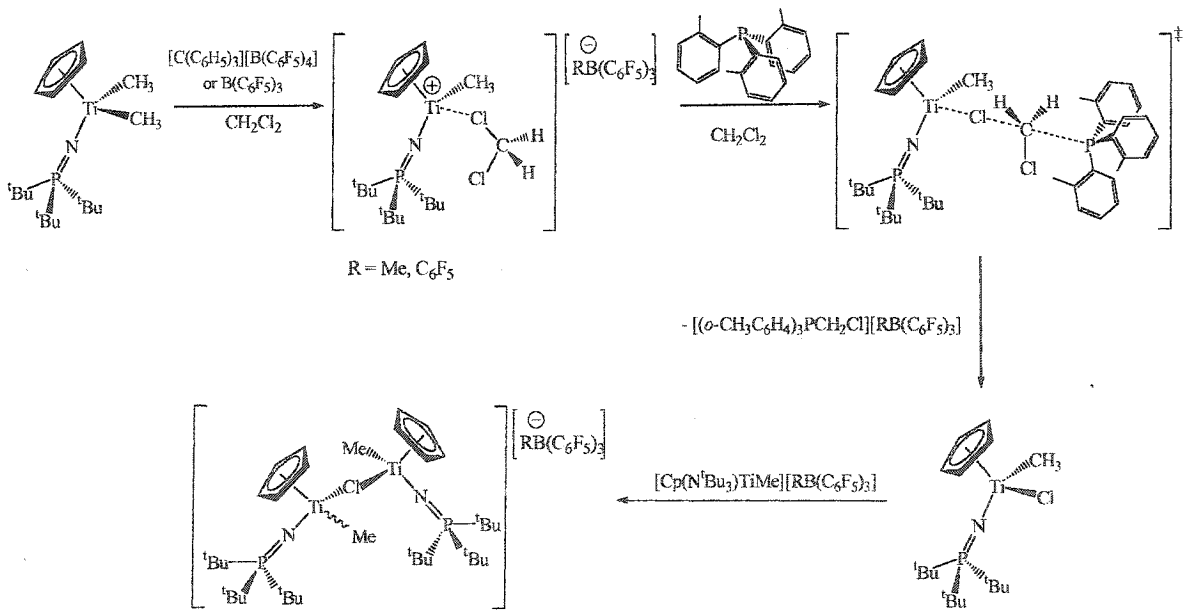


Figure 2.14: Mechanism for the reaction of $P(o\text{-}CH_3C_6H_4)_3$ with $[Cp(NP^tBu_3)Ti\ Me]^+$.

2.3.4. Solvent Interference

In attempts to obtain the species $[Cp(NP^tBu_3)TiMe{\cdot}LB][RB(C_6F_5)_3]$ (LB = Lewis base; R = Me, C_6F_5), as stated previously, it was found that the order of addition of the reactants was important, as well as the identity of the solvent employed. The generation of the zwitterion $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ and ion-pair $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ in hexanes has been reported.[82] However, in reactions where the metal complex $Cp(NP^tBu_3)TiMe_2$ and activator were mixed in CH_2Cl_2 and left to react for 30 minutes before adding the Lewis base, multiple products were obtained (Figure 2.15)[e]. Interestingly, in all the reactions with either $B(C_6F_5)_3$ or $[C(C_6H_5)_3][B(C_6F_5)_4]$ as the activator, it was found by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR analyses that $[Cp(NP^tBu_3)TiMe{\cdot}LB][RB(C_6F_5)_3]$ was not formed. In general, the resonances for the Ti–Me group in the ^1H and $^{13}C\{^1H\}$ NMR spectra were no longer present; $^{31}P\{^1H\}$ NMR spectra showed a peak at around δ60 ppm. It is possible that CH_2Cl_2 reacts with $[Cp(NP^tBu_3)TiMe]^+$, to give the complex $[\{Cp(NP^tBu_3)Ti(\mu\text{-}Cl)\}_2][RB(C_6F_5)_3]_2$ (R = Me, C_6F_5) (Figure 2.15). This solvent interference in the reaction of coordinative unsaturated metal complexes, where a chloride is abstracted from the solvent, has been previously reported.[32,128] The X-ray structure of $[\{Cp(NP^tBu_3)Ti(\mu\text{-}Cl)\}_2][B(C_6F_5)_4]_2$ (**2.21**) shown in Figure 2.16, confirms the suspected reaction with CH_2Cl_2.

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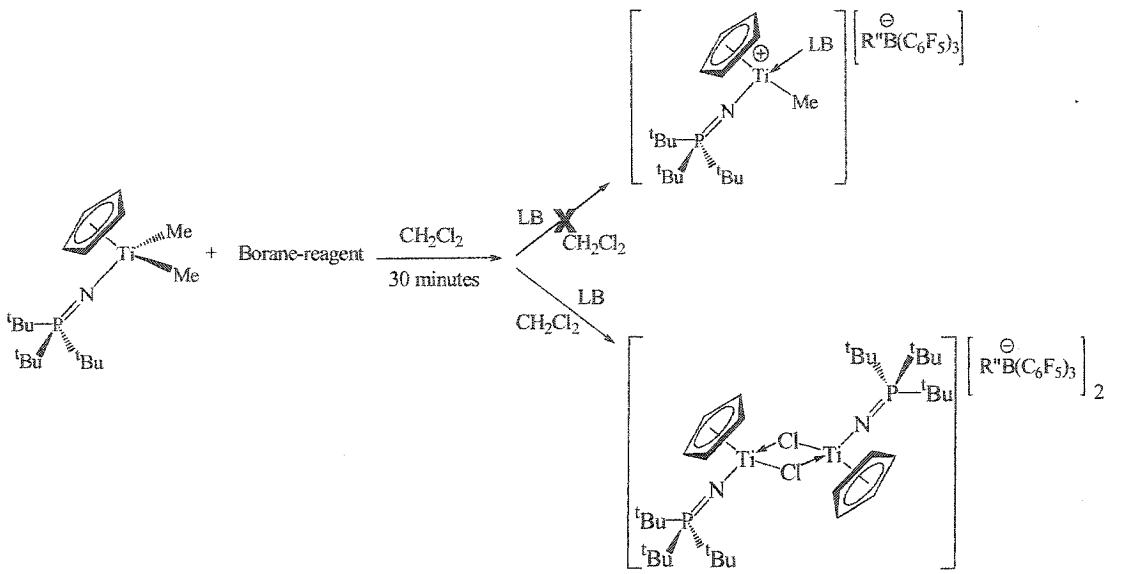
[e] The difference between the reactions performed with trityl *tetrakis*(pentafluorophenyl) borate to afford the stabilized ion pair (Section 2.3.2) with tertiary phosphines and the reactions described in this section lays in the reaction time. To stablilize the ion pair (Section 2.3.2), the phosphine was added immediately after the addition of $[C(C_6H_5)_3][B(C_6F_5)_4]$ to the complex $Cp(NP^tBu_3)TiMe_2$. In the case described here, the phosphine is added after 30 minutes have elapsed from the addition of $[C(C_6H_5)_3][B(C_6F_5)_4]$ to the metal complex.



LB = 4-RPy, PR'_3

R = H, Et, ^{t}Bu, NMe_2

R' = Me, ^{n}Bu, C_6H_5, *p*-$CH_3C_6H_4$, Cy, ^{i}Pr, ^{t}Bu, *o*-$CH_3C_6H_4$

R'' = Me, C_6F_5

Figure 2.15: The stabilized titanium complex $[Cp(NP^tBu_3)TiMe{\cdot}LB][RB(C_6F_5)_3]$ (LB = Lewis base; R = Me, C_6F_5) is not obtained if the complex $[Cp(NP^tBu_3)TiMe][RB(C_6F_5)_3]$ is prepared before the addition of the Lewis base. The reaction intermediates of the reaction were not identified.

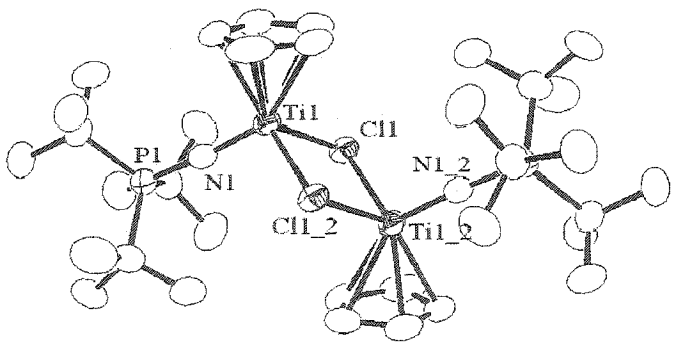


Figure 2.16: ORTEP diagram of $[\{Cp(NP^tBu_3)Ti(\mu\text{-}Cl)\}_2][BC_6F_5)_4]_2$ (**2.21**) (counterions and hydrogen atoms are omitted for clarity; 50% thermal ellipsoids). Selected bond distances (Å): Ti(1)–Cl(1) 2.4606(13); Ti(1)–Cl(1_2) 2.454(1); Ti(1)–N(1) 1.7506(2); N(1)–P(1) 1.652(2).

Table 2.10: $^{31}P\{^{1}H\}$ NMR chemical shifts in CD_2Cl_2 at room temperature for the tertiary phosphine and pyridine base-free complexes (R = Me, C_6F_5). [a] C_6D_5Br was used as solvent. [b] Chemical shifts obtained at -40°C. [c] Average of both isomers.

Titanium complex	$^{31}P\{^{1}H\}$ NMR δ	^{1}H NMR δ	$^{13}C\{^{1}H\}$ NMR δ
$Cp(NP^tBu_3)TiMe_2$	33.8	6.07 (C_5H_5) 0.03 (Ti-CH_3)	110.4 (C_5H_5) 38.1 (Ti-CH_3)
$[Cp(NP^tBu_3)TiMe][RB(C_6F_5)_3]$	56.0[a]	6.62[a] (C_5H_5) 1.35[a] (Ti-CH_3)	116.4[a] (C_5H_5) 61.4[a] (Ti-CH_3)
$[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-Cl})][RB(C_6F_5)_3]$ **(2.18)**	50.09[b] 49.93[b]	6.38[c] (C_5H_5) 1.08[c] (Ti-CH_3)	114.8[c] (C_5H_5) 35.4[c] (Ti-CH_3)
$[\{Cp(NP^tBu_3)Ti(\mu\text{-Cl})\}_2][RB(C_6F_5)_3]_2$ **(2.21)**	60.7	6.76 (C_5H_5) N/A (Ti-CH_3)	117.6 (C_5H_5) N/A (Ti-CH_3)
$[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-Me})][RB(C_6F_5)_3]$ **(2.23)**	47.0	6.27[c] (C_5H_5) 0.67[c] (Ti-CH_3)	113.6[c] (C_5H_5) 30.7[c] (Ti-CH_3)
$Cp(NP^tBu_3)TiCl_2$	49.4	6.46 (C_5H_5) N/A (Ti-CH_3)	114.4 (C_5H_5) N/A (Ti-CH_3)

The stable dimeric complexes $[\{Cp(NP^tBu_3)Ti(\mu\text{-Cl})\}_2][\ RB(C_6F_5)_3]_2$, **2.21** (Table 2.10),[115,129] can be obtained as a single product by mixing equimolar amounts of $Cp(NP^tBu_3)TiMe_2$ and $B(C_6F_5)_3$ with CH_2Cl_2 as solvent, without the Lewis base in the reaction mixture. Lancaster *et al.* reported the dimer, $[NEt_4]_2[\{C_5H_4B(C_6F_5)_3\}Zr(\mu\text{-Cl})Cl_2]_2$, however in this case, the ionic pair was afforded by reacting $[NEt_4][\{C_5H_4B(C_6F_5)_3\}Zr(NMe_2)_3]$ with an excess of Me_3SiCl.[130]

An interesting case is the formation of the complex $[Cp(NP^tBu_3)TiCl\cdot(4\text{-DMAP})][B(C_6F_5)_4]$ **(2.22)**. From a solution containing **2.8**, where the solvent was CH_2Cl_2, crystals were obtained and the crystallographic structure was found (Figure 2.17). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopic analyses of **2.22** did not show the signals corresponding to the methyl group bound to the titanium (Ti-**Me**), which will indicate the presence of **2.8**. Interestingly, the $^{31}P\{^{1}H\}$ NMR spectrum showed a signal at 49.0 ppm. The difference between the $^{31}P\{^{1}H\}$ chemical shifts of **2.8** and **2.22** is insignificant. The methyl group

bound to the titanium, has been displaced by a chloride, which presumably comes from the solvent.

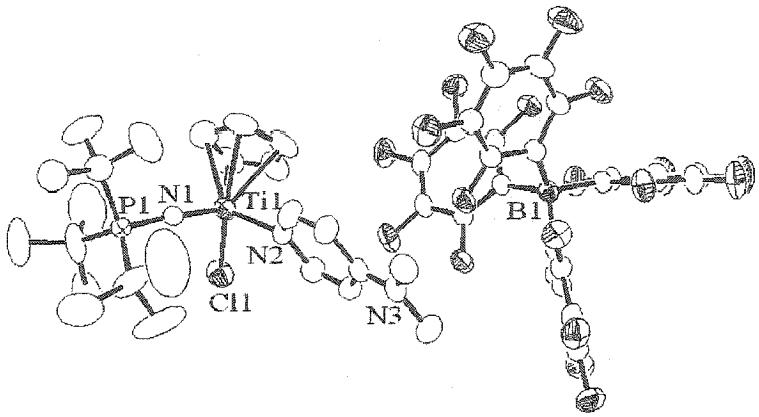


Figure 2.17: ORTEP diagram of the product **2.22**. (Hydrogen atoms are omitted for clarity; 30% thermal ellipsoids). Selected bond distances (Å): Ti(1)–Cl(1) 2.305(2); Ti(1)–N(2) 2.110(4); Ti(1)–N(1) 1.763(4); N(1)–P(1) 1.607(4).

It was also found that the dimeric species **2.18** is produced when two equivalents of $Cp(NP^tBu_3)TiMe_2$ and one equivalent of trityl borate are mixed in CH_2Cl_2 (Figure 2.18). The data obtained from NMR analyses confirmed the generation of the dimer (Table 2.10). The chloride-bridged complex $[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (**2.18**) can be viewed as an adduct between $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ and $Cp(NPtBu_3)TiMeCl$. Analogous complexes $[\{\eta^5\text{-}(C_5H_3Me_2)_2ZrMe\}_2(\mu\text{-}F)][MeB(C_6F_5)_3]$ and $[\{Cp_2ZrMe\}_2(\mu\text{-}F)]$ [MePNB] (PNB = *tris*(β-perfluoronaphthyl)borane) have been reported.[37,44]

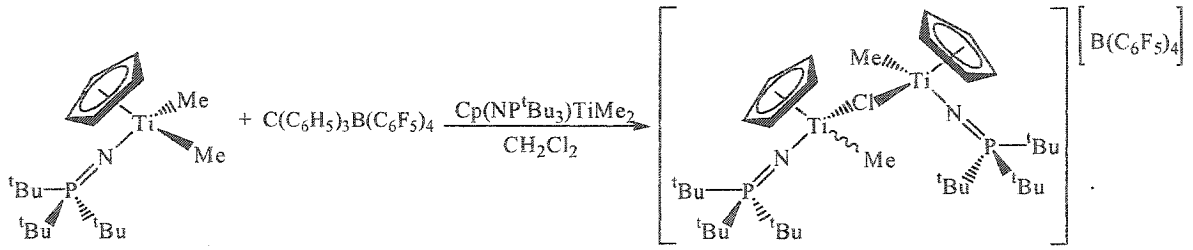


Figure 2.18: The synthesis of $[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (**2.18**) involving two equivalents of $Cp(NP^tBu_3)TiMe_2$ and one equivalent of trityl borate.

Dimerization can be avoided if the Lewis base is added to the activated catalyst before it can react with the solvent; the Lewis base coordinates to the metal center, stabilizing it and protecting it from the reaction with CH_2Cl_2. It can be interpretated that the Lewis base is strongly coordinated to the metal, since there is no evidence of displacement of it by the solvent. This was also confirmed with a series of experiments involving the generation of the Lewis base stabilized complex in C_6H_5Cl as solvent, following the procedure described in this section. C_6H_5Cl has a lower dielectric constant ($\epsilon = 5.71$) compared to CH_2Cl_2 ($\epsilon = 9.08$), but is high enough to promote the dissociation of the ion pairs obtained.[131-133]

The reactions involving $Cp(NP^tBu_3)TiMe_2$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$ with 4-RPy (R = H, ^{t}Bu, Et, NMe_2) as Lewis bases were performed again to generate the pyridine stabilized ion pair complexes. NMR spectroscopic analysis was employed to characterize the products, which were identified as the ionic systems $[Cp(NP^tBu_3)TiMe\cdot(4\text{-}RPy)][B(C_6F_5)_4]$ (**2.2**, **2.4**, **2.6** and **2.8**). The reactions of $Cp(NP^tBu_3)TiMe_2$ with PR_3 (R = Me, ^{n}Bu, C_6H_5, *p*-$CH_3C_6H_4$) and $B(C_6F_5)_3$, were carried out as well. The final products of these reactions were isolated and characterize by NMR spectroscopy as $[Cp(NP^tBu_3)TiMe\cdot PR_3][MeB(C_6F_5)_3]$ (**2.9**, **2.11**, **2.13** and **2.15**). In the cases where the activator was trityl borate $[C(C_6H_5)_3][B(C_6F_5)_4]$ the Lewis base stabilized complexes **2.10**, **2.12**, **2.14** and **2.16** were yielded.

Reactions using P(*o*-$CH_3C_6H_4)_3$ were also performed. The NMR analyses of these revealed that two species were present, the free phosphine and the active catalyst $[Cp(NP^tBu_3)TiMe][RB(C_6F_5)_3]$ (R = Me, C_6F_5). This indicates no reaction occurs

between the moiety $[Cp(NP^tBu_3)TiMe]^+$ and $P(o\text{-}CH_3C_6H_4)_3$. For the cases involving P^iPr_3, PCy_3 and P^tBu_3, the $^{31}P\{^1H\}$ NMR spectra showed multiple signals. Attempts to promote the formation or isolation of a major product failed.[f]

The same reaction for the formation of **2.18** was performed using C_6H_5Cl as the solvent, and in this case the product was $[Cp(NP^tBu_3)TiMe\}_2(\mu\text{-Me})][B(C_6F_5)_4]$ (**2.23**) (Table 2.10), which was characterized by NMR spectroscopic analyses. Zhang and Piers[56] prepared an analogous dimer, with a ketimide ligand instead of a phosphinimide ligand coordinated to the metal center. The ^1H NMR spectroscopic data reported was compared with data generated for this product. The most diagnostic peaks are those of the μ-Me groups which appear at δ 0.01 ppm, and those for Ti-CH_3 which appear at δ 0.77 ppm and δ 0.75 ppm. Unlike the dimers reported by Zhang and Piers, the dimer **2.23** (Figure 2.19) is stable at room temperature for days in a C_6H_5Cl solution. Examples of other metallocene dimers which are stable at room temperature have also been reported.[43,44,134,135]

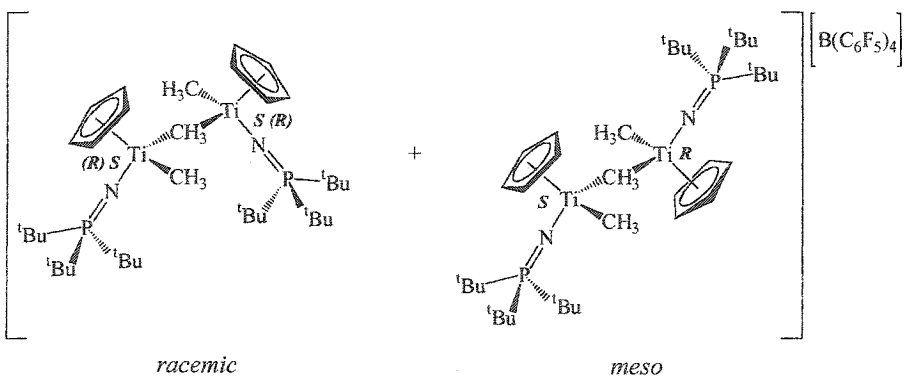


Figure 2.19: Product **2.23** from the reaction involving two equivalents of $Cp(NP^tBu_3)TiMe_2$ with trityl borate in C_6H_5Cl as solvent.

C_6H_5Cl as a solvent does not react with the activated catalyst in the same way as CH_2Cl_2. It is apparent that after $[Cp(NP^tBu_3)TiMe][RB(C_6F_5)_3]$ is generated, a C_6H_5Cl molecule coordinates to the active site of the complex. The Lewis bases, such as

[f] It is possible that steric properties of the phosphines do not allow the formation of the stabilized ion pair.

pyridines, the tertiary phosphines (PMe_3, P^nBu_3, $P(C_6H_5)_3$, $P(p\text{-}CH_3C_6H_4)_3$) or $Cp(NP^tBu_3)TiMe_2$ could then coordinate to the metal center by displacing the solvent molecule that stabilized the cationic moiety of the complex.

The explanation for the lack of reactivity between C_6H_5Cl and the titanium active species can rest in the carbon orbital hybridization of the solvent. The carbon in CH_2Cl_2 has a sp^3 hybridization while the carbon atoms at C_6H_5Cl have a sp^2. The orbitals at C_6H_5Cl have more s character than CH_2Cl_2. Therefore the bond between the chloride and the carbon will be stronger in C_6H_5Cl than in CH_2Cl_2; being easier for the titanium active species to abstract the chloride from CH_2Cl_2 than C_6H_5Cl.

2.4. Summary

The complexes $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ and $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ were stabilized using a series of substituted pyridines and tertiary phosphines as Lewis bases. The use of substituted pyridines showed the effect that they have in the cationic moiety of the titanium complex when they donate electron density to the metal center. The lack of bulky substituents at the α-carbon at the ring in all the substituted pyridines provided suitable Lewis bases that could be used to probe (by ^1H NMR spectroscopy) the electronic effect that they have in the stabilized titanium ion pair complexes; where the steric factor is not taken in account.

The complexes stabilized by tertiary phosphines appeared to be mainly influenced by the size of the substituents on the phosphine. The steric effect induced by the tertiary phosphine seems to play an important role in addition to its electron donating ability as a Lewis base. As the cone angle of the phosphine increased from 132° (P^nBu_3) to 145° ($P(C_6H_5)_3$) it was apparent by ^1H NMR spectroscopy that the chemical shift for the protons at the Cp ligand in the titanium complex were susceptible to the size of the substituents of the phosphine (**2.13**, **2.14**, **2.15**, **2.16**), suggesting an interaction between the substituents of the phosphine and the protons at the Cp ligand. As the cone angle of the phosphine is increased, phosphonium salts are obtained as products (**2.17**, **2.19**, **2.20**).

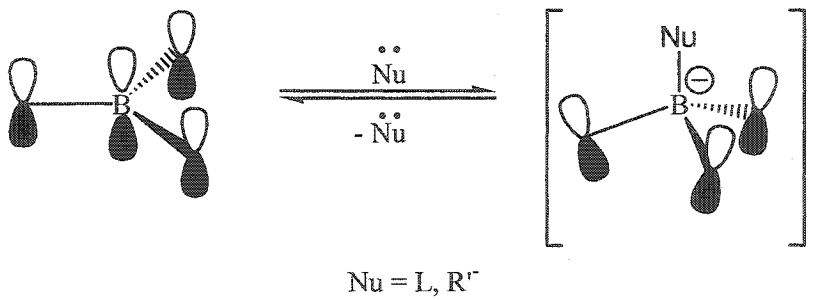
It was found that the stabilization reactions between the activated complex and Lewis bases (substituted pyridines and tertiary phosphines) can be performed in C_6H_5Cl. The generation of the dimeric species **2.18**, **2.21** and **2.23** is also dependent on the solvent employed and the ratio between activator ($B(C_6F_5)_3$ or $[C(C_6H_5)_3][B(C_6F_5)_4]$) and the metal complex $Cp(NP^tBu_3)TiMe_2$. **2.18** and **2.21** are obtained using CH_2Cl_2 as solvent, while **2.23** is generated in C_6H_5Cl.

From the studies performed, the size of the Lewis base proved to be relevant to the stabilization of the complex $Cp(NP^tBu_3)TiMe_2$. The choice of solvent is of significance. CH_2Cl_2 undergoes further reactions with the active species $[Cp(NP^tBu_3)TiMe]^+$ after coordinating to the metal center. C_6H_5Cl allows a better control of the species existing in solution, since it does not react after coordinating to the metal center of the active species.

3. Lewis Base-Borane Compounds and Borate Salts

3.1. *Introduction*

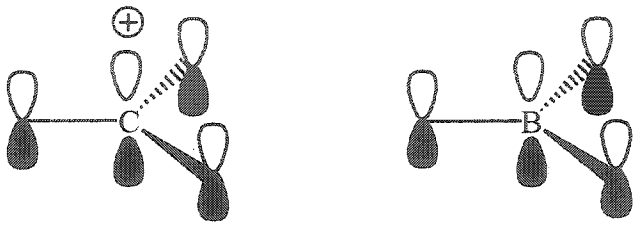
Lewis acids/base (donor/acceptor) systems have been known for ca. 80 years, and yet they continue to be a subject of interest.[95,136-140] Since the boron atom in triorganoboranes (BR_3) has an empty 2p-orbital, it can accept electrons from, either a neutral donor (L), or an anion (R'^-) to form a $R_3B{\cdot}L$ adduct or a $[R_3BR']^-$ anion. The neutral donor (L) or anion (R'^-) will donate electron density into the LUMO (Figure 3.1),[139] changing the symmetry of the molecule from the planar tricoordinate to the distorted tetrahedral tetracoordinate, as it changes from borane to borate.



Nu = L, R'^-

Figure 3.1: Change from a tricoordinate borane to tetracoordinate borate when the empty 2p-orbital accepts the electrons from a fourth nucleophile (Nu).

The electron-deficient carbocations are both, isolectronic and isostructural with neutral tertiary boron (Figure 3.2).[141] Such as triphenylmethyl (trityl) cation which contains a sp^2-hybridized electron-deficient carbon atom, with six valence electrons.[142] For both isoelectronic species, an analogous reactivity can be expected.



a b

Figure 3.2: Graphic representation of the isoelectronic and isostructural species, triphenyl cation (**a**) and borane (**b**).

Reactions between the triphenylmethyl cation and Group 15 compounds have been previously reported.[106-112] There is also precedence for the isoelectronic borane adducts formed by a coordinate bond (or dative bond)[g] between tertiary boranes and tertiary derivatives of Group 15, particularly those of nitrogen and phosphorus.[97,103,105,139,140,143,144]

Tri-substituted nitrogen atoms have a pair of unshared electrons that are available to complete the octet of the electron-deficient Lewis acids (borane and carbocation). Phosphine also interacts *via* its lone pair with the vacant 2p-orbital on both Lewis acids resulting in intermolecular bonding to form Lewis acids/phosphine systems.[105]

In this chapter the Lewis acids *tris*(pentafluorophenyl)borane $B(C_6F_5)_3$ and trityl borate $[C(C_6H_5)_3][B(C_6F_5)_4]$ were reacted with a series of Lewis bases (substituted pyridines and tertiary phosphines). The obtained products were characterized by NMR spectroscopic analyses.

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[g] Coordinate bonds or dative bonds are similar to covalent bonds. The difference is in the source of the electrons that make up the bond pair. In covalent bonds each atom participating in the bond donates an electron, both of which are shared by the two atoms. With coordinate bonds, only one of the atoms donates both electrons and these are then shared by both of the atoms participating in the bond. Compounds of the type BR_3 tend to accept electron pairs from suitable electron donors in order to complete its outer shell of electrons and obtain the most favorable electronic configuration.

3.2. *Experimental*

3.2.1. General Comments

All experiments were performed with exclusion of oxygen and moisture in oven-dried (140°C) glassware in a nitrogen-filled Vacuum Atmospheres glovebox.

The multinuclear NMR spectroscopy and X-ray crystallography was analogous to those described in Section 2.2.1, with the exception that the only deuterated solvent employed was dichloromethane-d_2 (CD_2Cl_2).

3.2.2. Solvents

Dichloromethane-d_2 (CD_2Cl_2) (Cambridge Isotopes Laboratories) was degassed and dried over CaH_2, and vacuum-transferred and stored over 4 Å molecular sieves under a nitrogen atmosphere.

The reagent grade solvents dichloromethane and pentane were purchased from Aldrich Chemical Co., and pre-dried using Grubbs' column systems, manufactured by Innovative Technologies, Inc.[117] Dichloromethane was further distilled from CaH_2, and pentane was distilled from Na prior to use.

3.2.3. Materials

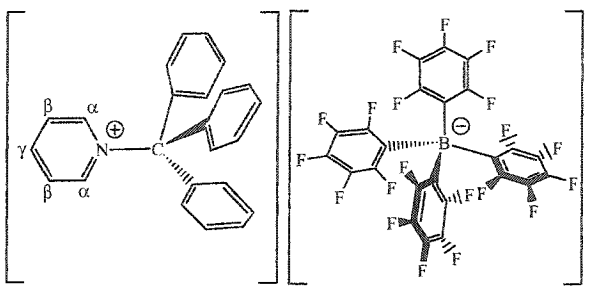
4 Å molecular sieves were purchased from Aldrich Chemical Co. and were dried at 100°C *in vacuo* for 24 h prior to use.

3.2.4. Reagents

The starting materials $B(C_6F_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$ were generously donated by Nova Chemicals Co. and used as received.

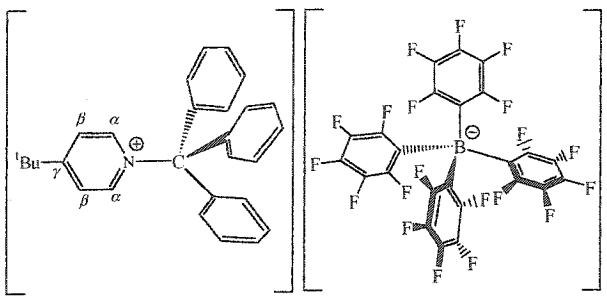
The reagents Py, 4-EtPy, 4-^{t}BuPy, 4-DMAP, PMe_3 (1.0 M in toluene), $P(C_6H_{11})_3$ and P^tBu_3 were purchased from Aldrich Chemical Co.. $P(CH_3)_3$, $P(C_6H_{11})_3$ and P^tBu_3 were used as received. Py, 4-EtPy and 4-^{t}BuPy were dried over CaH_2 and fractionally distilled, then stored in contact with 4 Å molecular sieves. 4-DMAP was recrystallized from toluene prior to use. P^iPr_3, P^nBu_3, $P(p\text{-}CH_3C_6H_4)_3$ and $P(o\text{-}CH_3C_6H_4)_3$ were obtained from Strem Chemicals and used as received. $P(C_6H_5)_3$ was obtained from Strem Chemicals and recrystallized from pentanes prior to use.

3.2.5. Syntheses

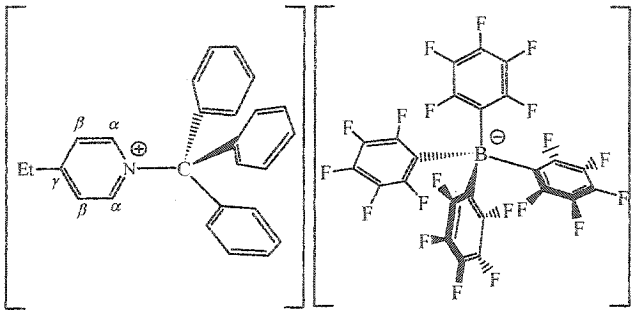


$[PyC(C_6H_5)_3][B(C_6F_5)_4]$ (3.1): To a solution of $[C(C_6H_5)_3][B(C_6F_5)_4]$ (128 mg, 0.14 mmol) in CH_2Cl_2 (4 mL), a solution of Py (12 µL, 0.14 mmol) in CH_2Cl_2 (2 mL) was added at RT. The mixture was stirred for 30 minutes, after which time the solvent was reduced *in vacuo* to ca. 1 mL. Addition of pentane to the CH_2Cl_2 solution resulted in the formation of a light yellow precipitate. The solvent was decanted and the precipitate was dried *in vacuo* (136 mg, 97 %).^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.76 (d, 2H, $^3J_{H-H}$ = 6 Hz, $C_5\mathbf{H}_5N$, (α-H)), 8.54 (t, 1H, $^3J_{H-H}$ = 7 Hz, $C_5\mathbf{H}_5N$, (γ-H)), 7.99 (t, 2H, $^3J_{H-H}$ = 7 Hz, $C_5\mathbf{H}_5N$, (β-H)), 7.51-7.45 (m, 9H, $C(C_6\mathbf{H}_5)_3$, *o,p*-H), 7.15 (m, 6H, $C(C_6\mathbf{H}_5)_3$, *m*-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.6 (d(m), $^1J_{C-F}$ = 227 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 145.2 (s, $\mathbf{C}_5H_5N$, (α-C)), 138.6 (s, $C(\mathbf{C}_6H_5)_3$, (*ipso*-C)), 138.8 (d(m), $^1J_{C-F}$ = 250 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 136.9 (d(m), $^1J_{C-F}$ = 241 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 130.7 (s, $\mathbf{C}_5H_5N$, (γ-C)), 130.6 (s, $C(\mathbf{C}_6H_5)_3$, (*o,m*-C)), 130.0 (s, $C(\mathbf{C}_6H_5)_3$, (*p*-C)), 128.3 (s, $\mathbf{C}_5H_5N$, (β-C)), 124.5 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), 91.0 (s, $\mathbf{C}(C_6H_5)_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −17.0 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.39 (s, 8F, $C_6\mathbf{F}_5$ (*o*-F)), −163.82 (t, 4F, $^3J_{F-F}$ = 20 Hz, $C_6\mathbf{F}_5$ (*p*-F)), −167.72 (t, 8F, $^3J_{F-F}$ = 17 Hz, $C_6\mathbf{F}_5$ (*m*-F)). Elemental analysis calculation for $C_{48}H_{20}BF_{20}N$: C, 57.57; H, 2.01; N, 1.04; Found: C, 57.71; H, 2.24; N, 1.11.

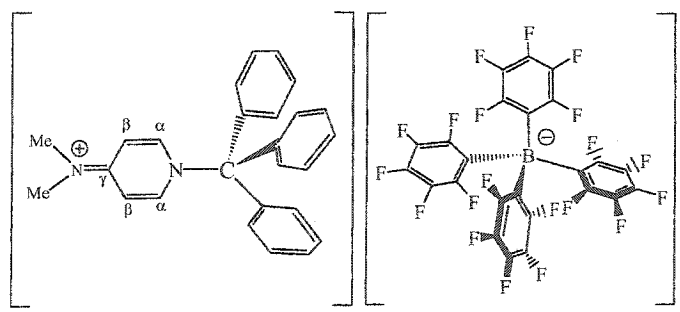
Synthesis of [4-^{t}BuPyC(C_6H_5)$_3$][B(C_6F_5)$_4$] (3.2), [4-EtPyC(C_6H_5)$_3$][B(C_6F_5)$_4$] (3.3) and [(4-DMAP)C(C_6H_5)$_3$][B(C_6F_5)$_4$] (3.4): These compounds were prepared in a similar manner using the appropriate substituted pyridine 4-RPy (R = H, Et, ^{t}Bu, NMe_2), and thus only a representative preparation is detailed. To a solution of [C(C_6H_5)$_3$][B(C_6F_5)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (4 mL), a solution of 4-RPy (0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT. The mixture was stirred for 30 minutes, after which time the solvent was reduced *in vacuo* to ca. 1 mL. Addition of pentane to the CH_2Cl_2 solution resulted in the formation of a precipitate. The solvent was decanted and the precipitate was dried *in vacuo*.



[4-^{t}BuPyC(C_6H_5)$_3$][B(C_6F_5)$_4$] (3.2): 4-^{t}BuPy (10 μL, 0.07 mmol); white solid (61 mg, 82.4 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.58 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-(C(CH_3)$_3$)C_5H_4N, (α-H)), 7.90 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-(C(CH_3)$_3$)C_5H_4N, (β-H)), 7.50-7.43 (m, 9H, C(C_6H_5)$_3$, (*o,p*-H)), 7.14 (m, 6H, C(C_6H_5)$_3$, (*m*-H)), 1.42 (s, 9H, 4-(C(CH_3)$_3$)C_5H_4N). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 174.9 (s, 4-(C(CH_3)$_3$)C_5H_4N, (γ-C)), 148.7 (d(m), $^1J_{C-F}$ = 241 Hz, C_6F_5 (*o*-C)), 144.3 (s, 4-(C(CH_3)$_3$)C_5H_4N, (α-C)), 138.8 (d(m), $^1J_{C-F}$ = 247 Hz, C_6F_5 (*p*-C)), 138.8 (s, C(C_6H_5)$_3$, (*ipso*-C)), 136.8 (d(m), $^1J_{C-F}$ = 244 Hz, C_6F_5 (*m*-C)), 128.7 (s, br, C_6F_5 (*ipso*-C)), 130.5 (s, C(C_6H_5)$_3$, (*o,m*-C)), 129.8 (s, C(C_6H_5)$_3$, (*p*-C)), 125.2 (s, 4-(C(CH_3)$_3$)C_5H_4N, (β-C)), 89.9 (s, C(C_6H_5)$_3$), 37.5 (s, 4-(C(CH_3)$_3$)C_5H_4N), 30.1 (s, 4-(C(CH_3)$_3$)C_5H_4N). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −17.0 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.33 (s, 8F, C_6F_5 (*o*-F)), −163.85 (t, 4F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.73 (t, 8F, $^3J_{F-F}$ = 17 Hz, C_6F_5 (*m*-F)). Elemental analysis calculation for $C_{52}H_{28}BF_{20}N$: C, 59.06; H, 2.67; N, 1.32; Found: C, 59.12; H, 2.78; N, 1.48.

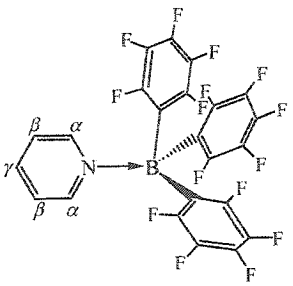


[4-EtPyC(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] (3.3): 4-EtPy (8 μL, 0.07 mmol); white solid (70 mg, 97 %).^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.56 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-CH_3CH_2-C_5H_5N, (α-H)), 7.75 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-CH_3CH_2-C_5H_5N, (β-H)), 7.51-7.44 (m, 9H, C(C_6H_5)$_3$, *o,p*-H), 7.14 (m, 6H, C(C_6H_5)$_3$, *m*-H), 2.99 (q, 2H, $^3J_{H-H}$ = 8 Hz, 4-CH_3CH_2-C_5H_5N), 1.37 (t, 3H, $^3J_{H-H}$ = 8 Hz, 4-CH_3CH_2-C_5H_5N). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 162.8 (s, 4-CH_3CH_2-C_5H_4N, (γ-C)), 148.8 (d(m), $^1J_{C-F}$ = 244 Hz, C_6F_5 (*o*-C)), 144.2 (s, 4-CH_3CH_2-C_5H_4N, (α-C)), 138.9 (s, C(C_6H_5)$_3$, (*ipso*-C)), 138.8 (d(m), $^1J_{C-F}$ = 244 Hz, C_6F_5 (*p*-C)), 136.8 (d(m), $^1J_{C-F}$ = 249 Hz, C_6F_5 (*m*-C)), 130.5 (s, C(C_6H_5)$_3$, (*o,m*-C)), 129.9 (s, C(C_6H_5)$_3$, (*p*-C)), 127.3 (s, 4-CH_3CH_2-C_5H_4N, (β-C)), 124.7 (s, br, C_6F_5 (*ipso*-C)), 89.7 (s, C(C_6H_5)$_3$), 29.6 (s, 4-CH_3CH_2-C_5H_4N), 13.2 (s, 4-CH_3CH_2-C_5H_4N). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −17.0 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.35 (s, 8F, C_6F_5 (*o*-F)), −163.82 (t, 4F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.70 (t, 8F, $^3J_{F-F}$ = 17 Hz, C_6F_5 (*m*-F)). Elemental analysis calculation for $C_{50}H_{24}BF_{20}N$: C, 58.33; H, 2.35; N, 1.36; Found: C, 57.91; H, 2.66; N, 1.38.



[(4-DMAP)C(C$_6$H$_4$)$_3$][B(C$_6$F$_5$)$_4$] (3.4): 4-DMAP (9 mg, 0.07 mmol); white solid (68 mg, 93%).^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.95 (d, 2H, $^3J_{H-H}$ = 8 Hz, 4-$(CH_3)_2N$-C_5H_5N, (α-H)), 7.43 (m, 6H, C(C_6H_5)$_3$, (*m*-H)), 7.18 (m, 9H, C(C_6H_5)$_3$, (*o,p*-H)), 6.67 (d, 2H, $^3J_{H-H}$ = 8 Hz, 4-$(CH_3)_2N$-C_5H_5N, (β-H)), 3.21 (s, 6H, 4-$(CH_3)_2N$-C_5H_5N). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 156.8 (s, 4-$(H_3C)_2N$-C_5H_4N, (γ-C)), 148.8 (d(m), $^1J_{C-F}$ = 242 Hz, C_6F_5 (*o*-C)), 144.2 (s, 4-$(C(CH_3)_3)C_5H_4N$, (α-C)), 138.9 (s, C(C_6H_5)$_3$, (*ipso*-C)), 138.9 (d(m), $^1J_{C-F}$ = 242 Hz,

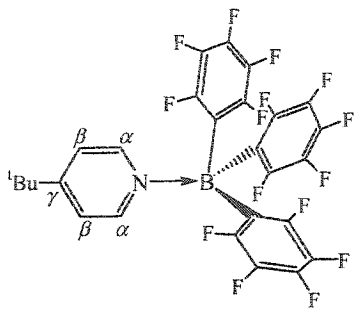
C_6F_5 (*p*-C)), 136.9 (d(m), $^1J_{C-F}$ = 248 Hz, C_6F_5 (*m*-C)), 130.5 (s, $C(C_6H_5)_3$, (*o,m*-C)), 129.6 (s, $C(C_6H_5)_3$, (*p*-C)), 129.3 (s, 4-$(C(CH_3)_3)C_5H_4N$, (*β*-C)), 124.7 (s, br, C_6F_5 (*ipso*-C)), 89.7 (s, $C(C_6H_5)_3$), 40.7 (s, 4-$(H_3C)_2N$-C_5H_4N). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) *δ*: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) *δ*: −133.38 (s, 8F, C_6F_5 (*o*-F)), −163.95 (t, 4F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.81 (t, 8F, $^3J_{F-F}$ = 17 Hz, C_6F_5 (*m*-F)). Elemental analysis calculation for $C_{50}H_{25}BF_{20}N_2$: C, 57.49; H, 2.41; N, 2.68; Found: C, 57.32; H, 2.50; N, 2.75.



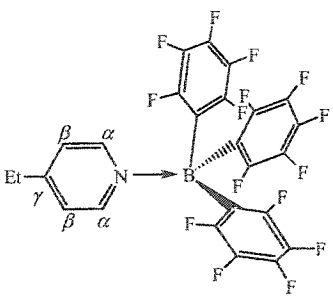
Py·B(C_6F_5)$_3$ (3.5): To a solution of $B(C_6F_5)_3$ (72 mg, 0.14 mmol) in 4 mL of CH_2Cl_2, a solution of Py (12 μL, 0.14 mmol) in 2 mL of CH_2Cl_2 was added at RT. The mixture was stirred for 30 minutes, after which time the solvent was reduced *in vacuo* to ca. 1 mL. Addition of pentane to the CH_2Cl_2 solution resulted in the formation of a white precipitate. The solvent was decanted and the precipitate was dried *in vacuo* (68 mg, 81.9 %). ^1H NMR (500 MHz, CD_2Cl_2) *δ*: 8.61 (s br, 2H, C_5H_5N, (*α*-H)), 8.21 (t, 1H, $^3J_{H-H}$ = 8 Hz, C_5H_5N, (*γ*-H)), 7.71 (t, 2H, $^3J_{H-H}$ = 8 Hz, C_5H_5N, (*β*-H)). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) *δ*: 148.3 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*o*-C)), 147.3 (s, C_5H_5N, (*β*-C)), 143.4 (s, C_5H_5N, (*γ*-C)), 140.8 (d(m), $^1J_{C-F}$ = 237 Hz, C_6F_5 (*p*-C)), 137.7 (d(m), $^1J_{C-F}$ = 243 Hz, C_6F_5 (*m*-C)), 126.4 (s, C_5H_5N, (*α*-C)), 118.9 (s, br, C_6F_5 (*ipso*-C)). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) *δ*: −3.88 (s, $B(C_6F_5)_3$). ^{19}F NMR (282.34 MHz, CD_2Cl_2) *δ*: −132.15 (d, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*o*-F)), −157.83 (t, 3F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −164.28 (t, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). Elemental analysis calculation for $C_{33}H_5BF_{15}N$: C, 46.74; H, 0.85; N, 2.37; Found: C, 46.60; H, 0.90; N, 2.71.

Synthesis of 4-^{t}BuPy·B(C_6F_5)$_3$ (3.6), 4-EtPy·B(C_6F_5)$_3$ (3.7) and (4-DMAP)·B(C_6F_5)$_3$ (3.8)[103,140]**:** These compounds were prepared in a similar manner using the appropriate substituted pyridine 4-RPy (R = H, Et, ^{t}Bu, NMe_2), and thus only a representative preparation is detailed. To a solution of $B(C_6F_5)_3$ (36 mg, 0.07 mmol) in CH_2Cl_2 (4 mL), a solution of 4-RPy (0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT. The mixture was

stirred for 30 minutes, after which time the solvent was reduced *in vacuo* to ca. 1 mL. Addition of pentane to the CH_2Cl_2 solution resulted in the formation of a precipitate. The solvent was decanted and the precipitate was dried *in vacuo*.

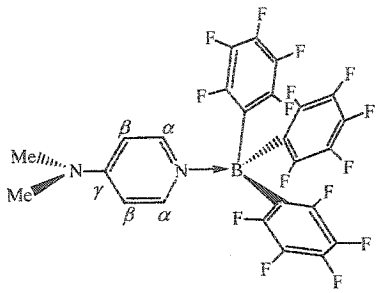


4-^{t}BuPy·B(C_6F_5)$_3$ (3.6): 4-^{t}BuPy (10 μL, 0.07 mmol); white solid (40 mg, 88.8 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.45 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-(C(CH_3)$_3$)C_5H_4N, (α-H)), 7.63 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-(C(CH_3)$_3$)C_5H_4N, (β-H)), 1.38 (s, 9H, 4-(C(CH_3)$_3$)C_5H_4N). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 169.1 (s, 4-(C(CH_3)$_3$)C_5H_4N, (γ-C)), 148.3 (d(m), $^1J_{C-F}$ = 250 Hz, $^2J_{C-F}$ = 14 Hz, C_6F_5 (*o*-C)), 146.6 (s, 4-(C(CH_3)$_3$)C_5H_4N, (α-C)), 140.7 (d(m), $^1J_{C-F}$ = 237 Hz, C_6F_5 (*p*-C)), 137.7 (d(m), $^1J_{C-F}$ = 235 Hz, C_6F_5 (*m*-C)), 123.4 (s, 4-(C(CH_3)$_3$)C_5H_4N, (β-C)), 118.8 (s, br, C_6F_5 (*ipso*-C)), 36.5 (s, 4-(C(CH_3)$_3$)C_5H_4N), 30.1 (s, 4-(C(CH_3)$_3$)C_5H_4N). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −4.37 (s, B(C_6F_5)$_3$). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −132.15 (d, 6F, $^3J_{F-F}$ = 17 Hz, C_6F_5 (*o*-F)), −158.14 (t, 3F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −164.44 (t, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). Elemental analysis calculation for $C_{27}H_{13}BF_{15}N$: C, 50.11; H, 2.02; N, 2.16; Found: C, 49.79; H, 2.07; N, 2.16.



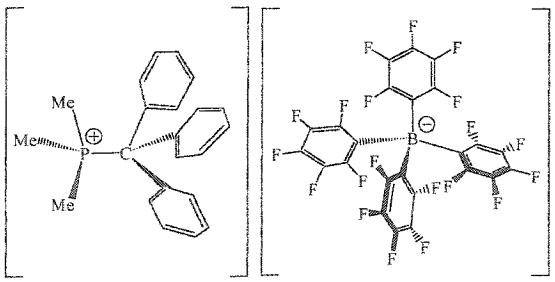
4-EtPy·B(C_6F_5)$_3$ (3.7): 4-EtPy (8 μL, 0.07 mmol); white solid (39 mg, 90.7 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 8.43 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-CH_3CH_2-C_5H_5N, (α-H)), 7.49 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-CH_3CH_2-C_5H_5N, (β-H)), 2.86 (q, 2H, $^3J_{H-H}$ = 8 Hz, 4-CH_3CH_2-C_5H_5N), 1.33 (t, 3H, $^3J_{H-H}$ = 8 Hz, 4-CH_3CH_2-C_5H_5N). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 162.4 (s, 4-CH_3CH_2-C_5H_4N, (γ-C)), 148.3 (d(m), $^1J_{C-F}$ = 250 Hz, C_6F_5 (*o*-C)), 140.8 (d(m), $^1J_{C-F}$ = 238 Hz, C_6F_5 (*p*-C)), 137.7 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*m*-C)), 118.7 (s, br, C_6F_5 (*ipso*-C)), 149.9 (s, 4-CH_3CH_2-C_5H_4N, (α-C)), 125.7 (s, 4-CH_3CH_2-C_5H_4N, (β-C)), 29.1 (s, 4-CH_3CH_2-C_5H_4N), 13.6 (s, 4-CH_3CH_2-C_5H_4N). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −4.29 (s, B(C_6F_5)$_3$). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −132.20 (d, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*o*-F)), −158.09 (t, 3F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −164.40 (t, 6F,

$^3J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). Elemental analysis calculation for $C_{25}H_9BF_{15}N$: C, 48.50; H, 1.47; N, 2.26; Found: C, 48.59; H, 1.76; N, 2.20.

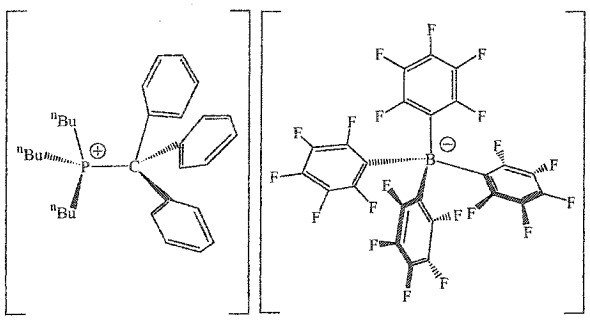


(4-DMAP)·B(C_6F_5)$_3$ (3.8): 4-DMAP (9 mg, 0.07 mmol); white solid (40 mg, 90.9 %). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 7.90 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-$(CH_3)_2$N-C_5H_4N, (α-H)), 6.60 (d, 2H, $^3J_{H-H}$ = 7 Hz, 4-$(CH_3)_2$N-C_5H_4N, (β-H)), 3.13 (s, 6H, 4-$(CH_3)_2$N-C_5H_4N), ^{13}C{^{1}H} NMR (125.77 MHz, CD_2Cl_2) δ: 156.4 (s, 4-$(CH_3)_2$N-C_5H_4N, (γ-C)), 148.6 (d(m), $^1J_{C-F}$ = 245 Hz, C_6F_5 (*o*-C)), 140.5 (d(m), $^1J_{C-F}$ = 253 Hz, C_6F_5 (*p*-C)), 137.8 (d(m), $^1J_{C-F}$ = 255 Hz, C_6F_5 (*m*-C)), 145.8 (s, 4-$(CH_3)_2$N-C_5H_4N, (α-C)), 106.8 (s, 4-$(CH_3)_2$N-C_5H_4N, (β-C)), 40.1 (s, 4-$(CH_3)_2$N-C_5H_5N). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −5.5 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −132.89 (d, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*o*-F)), −159.16 (t, 3F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −165.02 (t, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). Elemental analysis calculation for $C_{25}H_{10}BF_{20}N_2$: C, 47.35; H, 1.59; N, 4.42; Found: C, 47.86; H, 2.40; N, 4.27.

Synthesis of [$Me_3PC(C_6H_5)_3$][B(C_6F_5)$_4$] (3.9), [$^nBu_3PC(C_6H_5)_3$][B(C_6F_5)$_4$] (3.10), [$(C_6H_5)_3PC(C_6H_5)_3$][B(C_6F_5)$_4$][148] (3.11), [(p-$CH_3C_6H_4)_3PC(C_6H_5)_3$][B($C_6F_5$)$_4$] (3.12), [($p$-$^iPr_3$P-$C_6H_4$)($C_6H_5)_2$CH][B($C_6F_5$)$_4$] (3.13), [(4-$PCy_3$-$C_6H_5$)$C(C_6H_5)_2$][B($C_6F_5$)$_4$] (3.14) and [(4-$P^tBu_3$-$C_6H_5$)$C(C_6H_5)_2$][B($C_6F_5$)$_4$] (3.15): These compounds were prepared in a similar manner using the appropriate tertiary phosphine PR_3 (R = Me, ^{n}Bu, C_6H_5, p-$CH_3C_6H_4$, ^{i}Pr, Cy, ^{t}Bu), and thus only a representative preparation is detailed. To a solution of [$C(C_6H_5)_3$][B(C_6F_5)$_4$] (64 mg, 0.07 mmol) in CH_2Cl_2 (4 mL), a solution of PR_3 (0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT. The mixture was stirred for 30 minutes, after which time the solvent was reduced *in vacuo* to ca. 2 ml. Addition of pentane to the CH_2Cl_2 solution resulted in the formation of a precipitate. The solvent was decanted and the precipitate was dried *in vacuo*.

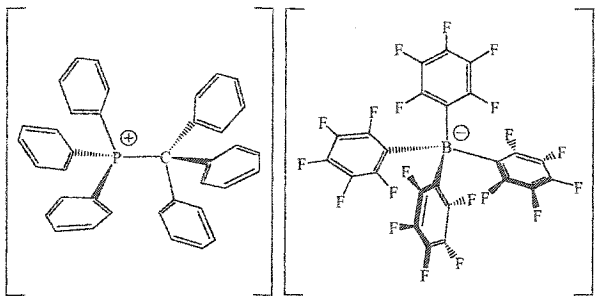


$[Me_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (3.9): PMe_3 (1.0 M in toluene; 70 μL, 0.07 mmol); orange solid (57 mg, 82.6 %). ^1H NMR (300 MHz, CD_2Cl_2) δ: 7.50 (m, 9H, $C(C_6H_5)_3$, (*o,p*-H)), 7.07 (m, 6H, $C(C_6H_5)_3$, (*m*-H)), 1.95 (d, 9H, $^3J_{H-H}$ = 12 Hz, PCH_3). $^{13}C\{^1H\}$ NMR (125.75 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^1J_{C-F}$ = 241 Hz, C_6F_5 (*o*-C)), 138.8 (d(m), $^1J_{C-F}$ = 243 Hz, C_6F_5 (*p*-C)), 137.5 (s, $C(C_6H_5)_3$, (*ipso*-C)), 136.9 (d(m), $^1J_{C-F}$ = 244 Hz, C_6F_5 (*m*-C)), 130.3 (s, $C(C_6H_5)_3$, (*o,m,p*-C)), 124.8 (s, br, C_6F_5 (*ipso*-C)), signal for $C(C_6H_5)_3$ was not observed, 13.4 (d, $^1J_{C-F}$ = 52 Hz, PCH_3). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.18 (s, 8F, C_6F_5 (*o*-F)), −163.80 (t, 4F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.63 (t, 8F, $^3J_{F-F}$ = 17 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 38.7 (s). Elemental analysis calculation for $C_{46}H_{24}BF_{20}P$: C, 55.34; H, 2.42; N, 0.00; Found: C, 55.37; H, 1.84; N, 0.07.

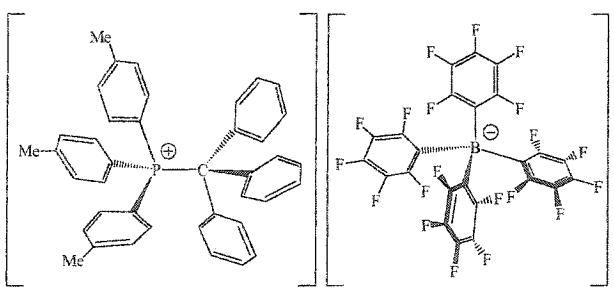


$[^nBu_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (3.10): P^nBu_3 (18 μL, 0.07 mmol); white solid (68 mg, 87.2 %). ^1H NMR (500 MHz, CD_2Cl_2) δ: 7.51-7.44 (m, 9H, $C(C_6H_5)_3$), 7.07 (m, 6H, $C(C_6H_5)_3$, 2.25 (m, 6H, $PCH_2CH_2CH_2CH_3$), 1.34 (m, 12H, $PCH_2CH_2CH_2CH_3$), 0.82 (t, 9H, $^3J_{H-H}$ = 7 Hz, $PCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^1J_{C-F}$ = 244 Hz, C_6F_5 (*o*-C)), 138.8 (d(m), $^1J_{C-F}$ = 246 Hz, C_6F_5 (*p*-C)), 138.0 (s, $C(C_6H_5)_3$, (*ipso*-C)), 136.9 (d(m), $^1J_{C-F}$ = 250 Hz, C_6F_5 (*m*-C)), 130.7 (d, $^3J_{P-C}$ = 5 Hz, $C(C_6H_5)_3$, (*o,m*-C)), 130.4 (s, $C(C_6H_5)_3$, (*p*-C)), 130.3 (s, $C(C_6H_5)_3$, (*p*-C)), 124.8 (s, br, C_6F_5 (*ipso*-C)), 65.0 (d, $^1J_{P-C}$ = 38 Hz, $C(C_6H_5)_3$), 26.2 (d, $^1J_{P-C}$ = 6 Hz, $PCH_2CH_2CH_2CH_3$), 24.6 (d, $^2J_{P-C}$ = 15 Hz, $PCH_2CH_2CH_2CH_3$), 23.4 (d, $^3J_{P-C}$ = 41 Hz, $PCH_2CH_2CH_2CH_3$), 13.3 (s, $PCH_2CH_2CH_2CH_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.31 (s, 8F, C_6F_5 (*o*-F)), −164.02 (t, 4F, $^3J_{F-F}$ = 21 Hz, C_6F_5 (*p*-F)), −167.86 (s, 8F, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$

NMR (121.5 MHz, CD_2Cl_2) δ: 42.8 (s). Elemental analysis calculation for $C_{55}H_{42}BF_{20}P$: C, 58.74; H, 3.76; N, 0.00; Found: C, 58.28; H, 3.69; N, 0.06.

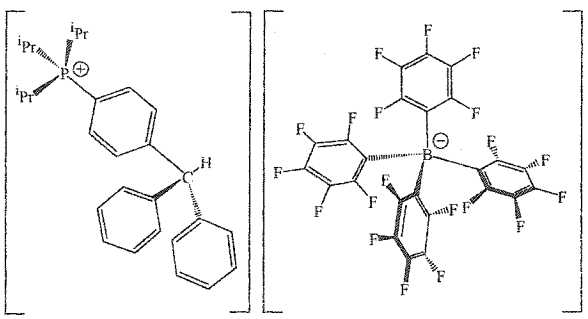


$[(C_6H_5)_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (3.11): $P(C_6H_5)_3$ (18 mg, 0.07 mmol); white solid (73 mg, 89 %). ^1H NMR (500 MHz, CD_2Cl_2) δ: 7.79 (d, 3H, $^3J_{H-H}$ = 8 Hz, $P(C_6\mathbf{H}_5)_3$, (*p*-H)), 7.54 (d, 3H, $^3J_{H-H}$ = 8 Hz, $C(C_6\mathbf{H}_5)_3$, (*p*-H)), 7.33 (t, 6H, $^3J_{H-H}$ = 8 Hz, $C(C_6\mathbf{H}_5)_3$, (*m*-H)), 7.46 (dd, 6H, $^3J_{H-H}$ = 8 Hz, $^4J_{P-H}$ = 3 Hz, $P(C_6\mathbf{H}_5)_3$, (*m*-H)), 7.00 (d, 6H, $^3J_{H-H}$ = 8 Hz, $C(C_6\mathbf{H}_5)_3$, (*o*-H)), 6.83 (m, 6H, $P(C_6\mathbf{H}_5)_3$, (*o*-H)). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.9 (d(m), $^1J_{C-F}$ = 240 Hz, $\mathbf{C}_6F_5$ (*o*-C)), 138.8 (d(m), $^1J_{C-F}$ = 249 Hz, $\mathbf{C}_6F_5$ (*p*-C)), 136.9 (d(m), $^1J_{C-F}$ = 242 Hz, $\mathbf{C}_6F_5$ (*m*-C)), 135.9 (s, $C(\mathbf{C}_6H_5)_3$, ((*ipso*-C))), 135.7 (d, $^2J_{P-C}$ = 8 Hz, $P(\mathbf{C}_6H_5)_3$, (*o*-C)), 132.6 (d, $^4J_{P-C}$ = 5 Hz, $P(\mathbf{C}_6H_5)_3$, (*p*-C)), 131.0 (s, $P(\mathbf{C}_6H_5)_3$ (*m*-C)), 130.9 (s, $C(\mathbf{C}_6H_5)_3$, (*o,m*-C)), 129.8 (s, $C(\mathbf{C}_6H_5)_3$, (*p*-C)), 120.9 (d, $^1J_{P-C}$= 75 Hz, $P(\mathbf{C}_6H_5)_3$, (*ipso*-C)), 124.0 (s, br, $\mathbf{C}_6F_5$ (*ipso*-C)), signal for $\mathbf{C}(C_6H_5)_3$ was not observed. $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.9 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.43 (s, 8F, $C_6\mathbf{F}_5$ (*o*-F)), −164.10 (t, 4F, $^3J_{F-F}$ = 21 Hz, $C_6\mathbf{F}_5$ (*p*-F)), −167.93 (t, 8F, $^3J_{F-F}$ = 17 Hz, $C_6\mathbf{F}_5$ (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 24.6 (s). Elemental analysis calculation for $C_{61}H_{30}BF_{20}P$: C, 61.85; H, 2.55; N, 0.00; Found: C, 61.30; H, 2.90; N, 0.06.

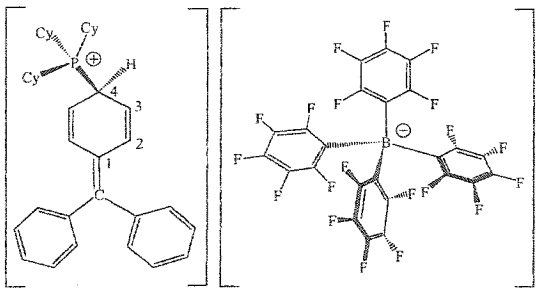


$[(p\text{-}CH_3C_6H_4)_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (3.12): $P(p\text{-}CH_3C_6H_4)_3$ (21 mg, 0.07 mmol); white solid (77 mg, 90.6 %). ^1H NMR (500 MHz, CD_2Cl_2) δ: 7.52 (t, 3H, $^3J_{H-H}$ = 8 Hz, $C(C_6\mathbf{H}_5)_3$, (*p*-H)), 7.33 (t, 6H, $^3J_{H-H}$ = 8 Hz, $C(C_6\mathbf{H}_5)_3$, (*m*-H)), 7.25 (dd, 6H, $^3J_{H-H}$ = 8 Hz, $^4J_{P-H}$ = 3 Hz, $P(p\text{-}CH_3C_6\mathbf{H}_4)_3$, (*m*-H)), 7.03 (d, 6H, $^3J_{H-H}$ = 8 Hz, $C(C_6\mathbf{H}_5)_3$, (*o*-H)), 6.71 (m, 6H, $P(p\text{-}CH_3C_6\mathbf{H}_4)_3$, (*o*-H)), 2.44 (s, 9H, $P(p\text{-}C\mathbf{H}_3C_6H_4)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 148.9 (d(m), $^1J_{C-F}$ = 241 Hz,

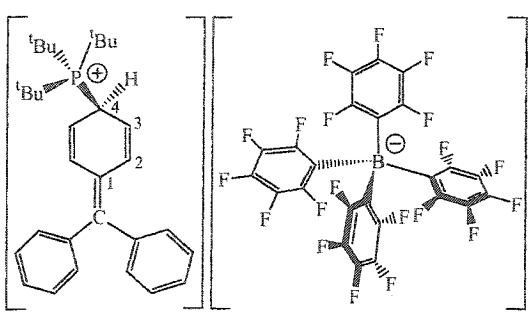
C_6F_5 (*o*-C)), 147.6 (s, C(C_6H_5)$_3$, (*ipso*-C)), 138.9 (d(m), $^1J_{C-F}$ = 245 Hz, C_6F_5 (*p*-C)), 136.9 (d(m), $^1J_{C-F}$ = 250 Hz, C_6F_5 (*m*-C)), 135.7 (d, $^2J_{P-C}$ = 9 Hz, P(*p*-$CH_3C_6H_4$)$_3$, (*o*-C)), 132.7 (d, $^4J_{P-C}$ = 5 Hz, P(*p*-$CH_3C_6H_4$)$_3$, (*p*-C)), 131.7 (d, $^3J_{P-C}$ = 12 Hz, P(*p*-$CH_3C_6H_4$)$_3$ (*m*-C)), 130.6 (s, C(C_6H_5)$_3$, (*o,m*-C)), 129.7 (s, C(C_6H_5)$_3$, (*p*-C)), 124.7 (s, br, C_6F_5 (*ipso*-C)), 117.8 (d, $^1J_{P-C}$ = 78 Hz, P(*p*-$CH_3C_6H_4$)$_3$ (*ipso*-C)), 68.6 (d, $^1J_{P-C}$ = 41 Hz, C(C_6H_5)$_3$), 21.9 (s, P(*p*-$CH_3C_6H_4$)$_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.35 (s, 8F, C_6F_5 (*o*-F)), −164.02 (t, 4F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.79 (t, 8F, $^3J_{F-F}$ = 15 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 24.6 (s). Elemental analysis calculation for $C_{64}H_{36}BF_{20}P$: C, 62.66; H, 2.96; N, 0.00; Found: C, 62.50; H, 2.64; N, 0.07.



[(*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH][B(C_6F_5)$_4$] (3.13): P^{i}Pr$_3$ (15 µL, 0.07 mmol); pink solid (63 mg, 84 %).^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.60-7.11 (m, 14H, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH,), 5.69 (s, 1H, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$C**H**), 3.00 (m, 3H, $^3J_{H-H}$ = 7 Hz, P(C**H**(CH$_3$)$_2$)), 1.39 (dd, 18H, $^3J_{H-H}$ = 7 Hz, $^3J_{P-H}$ = 16 Hz, P(C**H**(CH$_3$)$_2$)). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 152.6 (s, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*p*-C), 148.3 (d(m), $^1J_{C-F}$ = 239 Hz, C_6F_5 (*o*-C)), 142.2 (s, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*ipso*-C)), 138.4 (d(m), $^1J_{C-F}$ = 246 Hz, C_6F_5 (*p*-C)), 136.5 (d(m), $^1J_{C-F}$ = 246, C_6F_5 (*m*-C)), 132.6 (s, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*o*-C)), 131.8 (d, $^2J_{P-C}$ = 11 Hz, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*m*-C)), 129.4 (s, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*m*-C)), 128.9 (s, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*o*-C)), 127.2 (s, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*p*-C)), 124.8 (s, br, C_6F_5 (*ipso*-C)), 110.1 (d, $^1J_{P-C}$ = 75 Hz, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH, (*p*-C)), 56.9 (s, (*p*-^{i}Pr$_3$P-C_6H_4)(C_6H_5)$_2$CH), 21.1 (d, $^1J_{P-C}$ = 43 Hz, P(CH(CH$_3$)$_2$)$_3$), 16.4 (s, P(CH(CH$_3$)$_2$)$_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −17.0 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.33 (s, 8F, C_6F_5 (*o*-F)), −163.91 (t, 4F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.80 (s, br, 8F, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 40.4 (s). Elemental analysis calculation for $C_{52}H_{36}BF_{20}P$: C, 57.69; H, 3.35; N, 0.00; Found: C, 57.74; H, 3.71; N, 0.03.



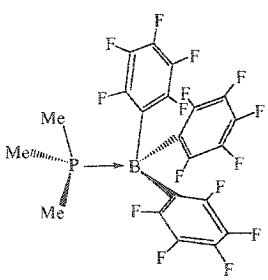
[(4-PCy$_3$-C$_6$H$_5$)C(C$_6$H$_5$)$_2$][B(C$_6$F$_5$)$_4$] (3.14): PCy$_3$ (20 mg, 0.07 mmol); yellow solid (75 mg, 89.3 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.37 (m, 6H, (4-PCy$_3$-C$_6$H$_5$)C(C$_6$**H**$_5$)$_2$, (*p,o*-H)), 7.15 (dd, 4H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz (4-PCy$_3$-C$_6$H$_5$)C(C$_6$**H**$_5$)$_2$, (*m*-H)), 6.86 (d(m), 2H, $^3J_{H-H}$ = 10 Hz, (4-PCy$_3$-C$_6$**H**$_5$)C(C$_6$H$_5$)$_2$, (2-H)), 5.69 (m, 2H, $^3J_{H-H}$ = 10 Hz, (4-PCy$_3$-C$_6$**H**$_5$)C(C$_6$H$_5$)$_2$, (3-H)), 4.46 (d(m), $^2J_{P-H}$ = 28 Hz, (4-PCy$_3$-C$_6$**H**$_5$)C(C$_6$H$_5$)$_2$, (4-H)), 1.33-2.45 (m, br, 33H, P(C$_6$**H**$_{11}$)$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 148.7 (d(m), $^1J_{C-F}$ = 237 Hz, **C**$_6$F$_5$ (*o*-C)), 140.8 (d, $^5J_{P-C}$ = 4 Hz, (4-PCy$_3$-C$_6$H$_5$)**C**(C$_6$H$_5$)$_2$), 138.1 (d(m), $^1J_{C-F}$ = 244 Hz, **C**$_6$F$_5$ (*p*-C)), 136.9 (d(m), $^1J_{C-F}$ = 257, **C**$_6$F$_5$ (*m*-C)), 134.5 (d, $^3J_{P-C}$ = 11 Hz, (4-PCy$_3$-**C**$_6$H$_5$)C(C$_6$H$_5$)$_2$ (2-C)), 130.6 (s, (4-PCy$_3$-C$_6$H$_5$)C(**C**$_6$H$_5$)$_2$, (*o*-C)), 129.3 (s, (4-PCy$_3$C$_6$H$_5$) C(**C**$_6$H$_5$)$_2$, (*ipso*-C)), 129.0 (s, (4-PCy$_3$-C$_6$H$_5$)C(**C**$_6$H$_5$)$_2$, (*p*-C)), 128.9 (s, (4-PCy$_3$-C$_6$H$_5$)C(**C**$_6$H$_5$)$_2$, (*m*-C)), 125.8 (d, $^4J_{P-C}$ = 11 Hz, (4-PCy$_3$-**C**$_6$H$_5$)C(C$_6$H$_5$)$_2$ (1-C)), 124.2 (s, br, **C**$_6$F$_5$ (*ipso*-C)), 118.3 (d, $^2J_{P-C}$ = 9 Hz, (4-PCy$_3$-**C**$_6$H$_5$)C(C$_6$H$_5$)$_2$ (3-C)), 33.7 (d, $^1J_{P-C}$ = 42 Hz, P(**C**$_6$H$_{11}$)$_3$ (1-C)), 32.0 (d, $^1J_{P-C}$ = 35 Hz, 4-PCy$_3$**C**$_6$H$_5$)C(C$_6$H$_5$)$_2$, (4-C)), 28.0 (d, $^3J_{P-C}$ = 4 Hz, P(**C**$_6$H$_{11}$)$_3$ (3-C)), 27.5 (d, $^2J_{P-C}$ = 11 Hz, P(**C**$_6$H$_{11}$)$_3$ (2-C)), 25.4 (s, P(**C**$_6$H$_{11}$)$_3$ (4-C)). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.31 (s, 8F, C$_6$**F**$_5$ (*o*-F)), −163.94 (t, 4F, $^3J_{F-F}$ = 20 Hz, C$_6$**F**$_5$ (*p*-F)), −167.74 (t, 8F, $^3J_{F-F}$ = 17 Hz, C$_6$**F**$_5$ (*m*-F)). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 28.1 (s, **P**(C$_6$H$_{11}$)$_3$). Elemental analysis calculation for $C_{61}H_{48}BF_{20}P$: C, 60.91; H, 4.02; N, 0.00; Found: C, 60.72; H, 3.83; N, 0.03.



[(4-P^{t}Bu$_3$-C$_6$H$_5$)C(C$_6$H$_5$)$_2$][B(C$_6$F$_5$)$_4$] (3.15): P^{t}Bu$_3$ (14 mg, 0.07 mmol); yellow solid (67 mg, 85.9 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.36 (m, 6H, (4-P^{t}Bu$_3$-C$_6$H$_5$)C(C$_6$**H**$_5$)$_2$, (*m,p*-H)), 7.14 (m, 4H, (4-P^{t}Bu$_3$-C$_6$H$_5$)-C(C$_6$**H**$_5$)$_2$, (*o*-H)), 6.87 (d(m), 2H, $^3J_{H-H}$ = 10 Hz, (4-P^{t}Bu$_3$-C$_6$**H**$_5$)C(C$_6$H$_5$)$_2$, (2-H)), 6.12 (d(m), 2H, $^3J_{H-H}$ = 10 Hz, (4-P^{t}Bu$_3$-C$_6$**H**$_5$)C(C$_6$H$_5$)$_2$, (3-H)), 4.67 (d(m), 1H, $^2J_{P-H}$ = 27 Hz, (4-P^{t}Bu$_3$-C$_6$**H**$_5$)C(C$_6$H$_5$)$_2$, (4-H)),

1.71 (d, 27H, $^{3}J_{P-H}$ = 14 Hz, P(C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ: 148.8 (d(m), $^{1}J_{C-F}$ = 240 Hz, C_6F_5 (*o*-C)), 140.7(d, $^{5}J_{P-C}$ = 4 Hz, (4-P^{t}Bu$_3$C$_6$H$_5$)C(C$_6$H$_5$)$_2$), 138.8 (d(m), $^{1}J_{C-F}$ = 245 Hz, C_6F_5 (*p*-C)), 136.9 (d(m), $^{1}J_{C-F}$ = 246 Hz, C_6F_5 (*m*-C)), 134.4 (d, $^{3}J_{P-C}$ = 10 Hz, (4-P^{t}Bu$_3$C$_6$H$_5$)C(C$_6$H$_5$)$_2$, (2-C)), 130.8 (s, (4-P^{t}Bu$_3$C$_6$H$_5$)-C(C$_6$H$_5$)$_2$, (*o*-C)), 129.0 (s, (4-P^{t}Bu$_3$C$_6$H$_5$)C(C$_6$H$_5$)$_2$, (*p*-C)), 128.9 (s, (4-P^{t}Bu$_3$C$_6$H$_5$)-C(C$_6$H$_5$)$_2$, (*m*-C)) 128.5 (s, (4-P^{t}Bu$_3$C$_6$H$_5$)C(C$_6$H$_5$)$_2$, (*ipso*-C)), 125.3 (d, $^{4}J_{P-C}$ = 10 Hz, (4-P^{t}Bu$_3$C$_6$H$_5$)C(C$_6$H$_5$)$_2$, (1-C)), 124.2 (s, br, C_6F_5 (*ipso*-C)), 121.0 (d, $^{2}J_{P-C}$ = 10 Hz, (4-P^{t}Bu$_3$C$_6$H$_5$)C(C$_6$H$_5$)$_2$, (3-C)), 42.3 (d, $^{1}J_{P-C}$ = 21 Hz, P(C(CH$_3$)$_3$), 38.9 (d, $^{1}J_{P-C}$ = 31 Hz, 4-P^{t}Bu$_3$C$_6$H$_5$)C(C$_6$H$_5$)$_2$, (4-C)), 31.0 (s, PC(CH$_3$)$_3$). ^{11}B{^{1}H} NMR (96.25 MHz, CD_2Cl_2) δ: −16.8 (s). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −133.28 (s, 8F, C_6F_5 (*o*-F)), −163.85 (t, 4F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −167.73 (d, 8F, $^{3}J_{F-F}$ = 17 Hz, C_6F_5 (*m*-F)).^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2) δ: 50.2 (s, ^{t}Pr$_3$PC$_6$H$_4$). Elemental analysis calculation for $C_{55}H_{42}BF_{20}P$: C, 58.74; H, 3.76; N, 0.00; Found: C, 58.02; H, 3.61; N, 0.04.

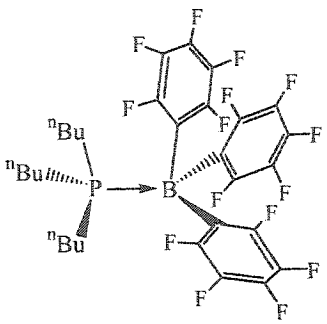
Synthesis of Me$_3$P·B(C$_6$F$_5$)$_3$ (3.16), ^{n}Bu$_3$P·B(C$_6$F$_5$)$_3$ (3.17), (C$_6$H$_5$)$_3$P·B(C$_6$F$_5$)$_3$ (3.18), (*p*-CH$_3$C$_6$H$_4$)$_3$P·B(C$_6$F$_5$)$_3$ (3.19), (*p*-^{i}Pr$_3$P-C$_6$F$_4$)(C$_6$F$_5$)$_2$BF (3.20) and (*p*-Cy$_3$P-C$_6$F$_4$)(C$_6$F$_5$)$_2$BF (3.21): These compounds were prepared in a similar manner using the appropriate tertiary phosphine PR_3 (R = Me, ^{n}Bu, C_6H_5, *p*-$CH_3C_6H_4$, ^{i}Pr, Cy, ^{t}Bu), and thus only a representative preparation is detailed. To a solution of $[C(C_6H_5)_3][B(C_6F_5)_4]$ (64 mg, 0.07 mmol) in CH_2Cl_2 (6 mL), a solution of PR_3 (0.07 mmol) in CH_2Cl_2 (2 mL) was added at RT. The mixture was stirred for 30 minutes, after which time the solvent was reduced *in vacuo* to ca. 2 ml. Addition of pentane to the CH_2Cl_2 solution resulted in the formation of a precipitate. The solvent was decanted and the precipitate was dried *in vacuo*.



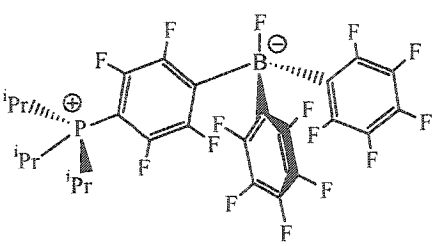
Me$_3$P·B(C$_6$F$_5$)$_3$ (3.16): PMe$_3$ (1.0 M in toluene; 70 µL, 0.07 mmol) white solid (38 mg, 92.7 %). Elemental analysis calculation for $C_{21}H_{29}F_{15}BP$: C, 42.89; H, 1.54; N, 0.00; Found: C, 42.17; H, 1.82; N, 0.005.

$C_{36}H_{15}F_{15}BP$ (3.17): $P(C_6H_5)_3$ (18 mg, 0.07 mmol) white solid (50 mg, 90.6 %). Elemental analysis calculation for $C_{36}H_{15}F_{15}BP$: C, 55.84; H, 1.95; N, 0.00; Found: C, 55.61; H, 1.99; N, 0.04.

$C_{39}H_{21}F_{15}BP$ (3.18): $P(p\text{-}CH_3C_6H_4)_3$ (21 mg, 0.07 mmol) white solid (54 mg, 92.9 %). Elemental analysis calculation for $C_{39}H_{21}F_{15}BP$: C, 57.38; H, 2.59; N, 0.00; Found: C, 56.90; H, 2.58; N, 0.06.

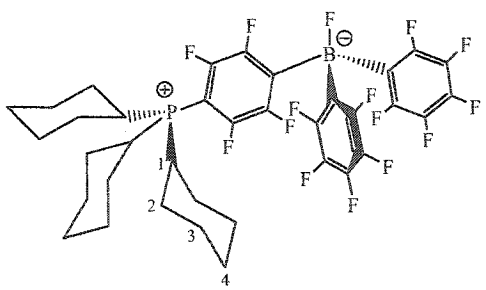


$^nBu_3P{\cdot}B(C_6F_5)_3$ (3.19): P^nBu_3 (18 μL, 0.07 mmol); white solid (44 mg, 88 %).^{1}H NMR (500 MHz, CD_2Cl_2) δ: 1.74 (m, 6H, $PCH_2CH_2CH_2CH_3$), 1.42 (m, 6H, $PCH_2CH_2CH_2CH_3$), 1.43 (m, 6H, $PCH_2CH_2CH_2CH_3$), 0.88 (t, 9H, $^3J_{H-H}$ = 7 Hz, $PCH_2CH_2CH_2CH_3$), $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2) δ: 149.2 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*o*-C)), 140.5 (d(m), $^1J_{C-F}$ = 250 Hz, C_6F_5 (*p*-C)), 137.8 (d(m), $^1J_{C-F}$ = 240 Hz, C_6F_5 (*m*-C)), 116.8 (s, br, C_6F_5 (*ipso*-C)), 26.5 (d, $^1J_{P-C}$ = 7 Hz, $PCH_2CH_2CH_2CH_3$), 25.0 (d, $^2J_{P-C}$ = 12 Hz, $PCH_2CH_2CH_2CH_3$), 21.3 (d, $^3J_{P-C}$ = 90 Hz, $PCH_2CH_2CH_2CH_3$), 13.7 (s, $PCH_2CH_2CH_2CH_3$). $^{11}B\{^1H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −15.6 (d, $^1J_{P-B}$ = 60 Hz, $B(C_6F_5)_3$). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −129.85 (d, 6F, $^3J_{F-F}$ = 23 Hz, C_6F_5 (*o*-F)), −157.58 (t, 3F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −164.44 (pseudo t, 6F, $^3J_{F-F}$ = 20 Hz, C_6F_5 (*m*-F)). $^{31}P\{^1H\}$ NMR (121.5 MHz, 30°C, CD_2Cl_2) δ: 0.56 (d, br, $^1J_{B-P}$ = 95 Hz, P^nBu_3). $^{31}P\{^1H\}$ NMR (202.5 MHz, −20°C, CD_2Cl_2) δ: −1.2 (s, br). Elemental analysis calculation for $C_{30}H_{27}F_{15}BP$: C, 50.44; H, 3.81; N, 0.00; Found: C, 50.27; H, 3.83; N, 0.003.



$(p\text{-}^iPr_3P\text{-}C_6F_4)(C_6F_5)_2BF$ (3.20): P^iPr_3 (15 μL, 0.07 mmol); white solid (40 mg, 85.5 %).^{1}H NMR (300 MHz, CD_2Cl_2) δ: 3.23 (m, 3H, $CHCH_3$), 1.47 (dd, 18H, $^3J_{P-H}$ = 18 Hz, $^3J_{H-H}$ = 6 Hz, $CH(CH_3)_2$), $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2) δ: 149.8 (d(m),

$^{1}J_{C-F}$ = 247 Hz, (*p*-$^{i}Pr_3P$-C_6F_4), (*o*-C)),148.2 (d(m), $^{1}J_{C-F}$ = 231 Hz, C_6F_5 (*o*-C)), 147.0 (d(m), $^{1}J_{C-F}$ = 255 Hz, (*p*-$^{i}Pr_3P$-C_6F_4), (*m*-C)), 143.7 (s, br, (*p*-$^{i}Pr_3P$-C_6F_4), (*ipso*-C)), 139.3 (d(m), $^{1}J_{C-F}$ = 246 Hz, C_6F_5 (*p*-C)), 136.9 (d(m), $^{1}J_{C-F}$ = 244 Hz, C_6F_5 (*m*-C)), 122.4 (s, br, C_6F_5 (*ipso*-C)), 89.3 (d(m), $^{1}J_{P-C}$ = 70 Hz, C_6F_4 (*p*-C)), 23.8 (d, $^{1}J_{P-C}$ = 40 Hz, $CH(CH_3)_2$), 17.2 (s, $CH(CH_3)_2$). $^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −0.89 (d, $^{1}J_{B-F}$ = 64 Hz). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −124.84 (s, 2F, $^{i}Pr_3PC_6F_4$ (*o*-F)), −127.71 (t, 2F, $^{3}J_{F-F}$ = 11 Hz, $^{i}Pr_3PC_6F_4$ (*m*-F)), −132.14 (t, 4F, $^{3}J_{F-F}$ = 10 Hz, C_6F_5 (*o*-F)), −158.11 (t, 2F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −163.07 (t, 4F, $^{3}J_{F-F}$ = 16 Hz, C_6F_5 (*m*-F)), −189.37 (d, 1F, $^{1}J_{B-F}$ = 82 Hz). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 53.2 (m). Elemental analysis calculation for $C_{27}H_{21}BF_{15}P$: C, 48.24; H, 3.15; N, 0.00; Found: C, 48.24; H, 3.15; N, 0.00.



(*p*-Cy_3P-C_6F_4)(C_6F_5)$_2$BF (3.21): PCy_3 (20 mg, 0.07 mmol); white solid (48 mg, 87.3 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 63.08-1.22 (m, br, 11H, $P(C_6H_{11})_3$). $^{13}C\{^{1}H\}$ NMR (125.75 MHz, CD_2Cl_2) δ: 150.4 (d(m), $^{1}J_{C-F}$ = 245 Hz, C_6F_4 (*o*-C)), 148.7 (d(m), $^{1}J_{C-F}$ = 242 Hz, C_6F_5 (*o*-C)), 147.6 (dd(m), $^{1}J_{C-F}$ = 256 Hz, $^{2}J_{C-F}$ = 18 Hz, C_6F_4 (*m*-C)), 143.2 (s, br, C_6F_4 (*ipso*-C)), 139.8 (d(m), $^{1}J_{C-F}$ = 248 Hz, C_6F_5 (*p*-C)), 137.4 (ddd, $^{1}J_{C-F}$ = 250 Hz, $^{2}J_{C-F}$ = 22 Hz, $^{3}J_{C-F}$ = 11 Hz, C_6F_5 (*m*-C)), 123.2 (s, br, C_6F_5 (*ipso*-C)), 90.0 (d(m), $^{1}J_{P-C}$ = 69 Hz, C_6F_4 (*p*-C)), 33.3 (d, $^{1}J_{P-C}$ = 39 Hz, $P(C_6H_{11})_3$) (1-C)), 28.2 (d, $^{2}J_{P-C}$ = 3 Hz, $P(C_6H_{11})_3$), (2-C)), 27.4 (d, $^{3}J_{P-C}$ = 12 Hz, $P(C_6H_{11})_3$) (3-C)), 25.9 (s, $P(C_6H_{11})_3$, (4-H)).$^{11}B\{^{1}H\}$ NMR (96.25 MHz, CD_2Cl_2) δ: −0.7 (d, $^{1}J_{B-F}$ = −58 Hz). ^{19}F NMR (282.34 MHz, CD_2Cl_2) δ: −128.76 (s, 2F, $Cy_3PC_6F_4$ (*o*-F)), −132.03 (t, 2F, $^{3}J_{F-F}$ = 13 Hz, $Cy_3PC_6F_4$ (*m*-F)), −135.81 (t, 4F, $^{3}J_{F-F}$ = 12 Hz, C_6F_5 (*o*-F)), −161.92 (t(m), 2F, $^{3}J_{F-F}$ = 20 Hz, C_6F_5 (*p*-F)), −166.83 (t(m), 4F, $^{3}J_{F-F}$ = 16 Hz, C_6F_5 (*m*-F)), −193.11 (d, 1F, $^{1}J_{B-F}$ = 72 Hz).$^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) δ: 41.6 (m). Elemental analysis calculation for $C_{36}H_{33}BF_{15}P$: C, 54.57; H, 4.20; N, 0.00; Found: C, 54.03; H, 4.14; N, 0.03.

3.2.6. X-Ray Experimental

X-ray structural solution of $[(p\text{-}^{i}Pr_3P\text{-}C_6H_4)(C_6H_5)_2CH][B(C_6F_5)_4]$ (**3.19**) were obtained using direct methods or by a Patterson map. The solution for structure $p\text{-}^{i}Pr_3P\text{-}C_6F_4)(C_6F_5)_2BF$ (**3.25**) include one molecule of CH_2Cl_2 in the cell. Cell parameters, R, R_w and GoF values are located in Table 3.1. No residual electron density remained in any of the solutions that was of any chemical significance. ORTEP drawings of **3.19** and **3.25** are shown in Figures 3.5 and 3.10, with selected bond distances provided in the caption text.

Table 3.1: Crystallographic parameters for $[(p\text{-}^{i}Pr_3P\text{-}C_6H_4)(C_6H_5)_2CH][B(C_6F_5)_4]$ **(3.13)** and $(p\text{-}^{i}Pr_3P\text{-}C_6F_4)(C_6F_5)_2BF$ **(3.20)**

	3.13	**3.20**
Molecular formula	$C_{52}H_{36}BPF_{20}.CH_2Cl_2$	$C_{27}H_{20}BF_{15}P$
Formula weight	1166.51	671.21
a (Å)	10.901(5)	9.544(6)
b (Å)	13.168(6)	18.426(11)
c (Å)	19.539(9)	17.134(10)
α (°)	96.262(9)	90
β (°)	100.806(9)	105.156(12)
γ(°)	109.261(8)	90
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2(1)/c
Volume (Å^3)	2556(2)	2908(3)
D_{calc} (gcm^{-3})	1.515	1.533
Z	2	4
Abs coeff, μ mm^{-1}	0.269	0.208
θ range (°)	2.07-23.27	2.21-23.20
Reflections collected	10903	12247
Data $F_o^2>3\sigma(F_o^2)$	5003	2650
Parameters	694	398
R(%)	0.0674	0.0388
R_w(%)	0.1955	0.1066
Goodness of fit	1.016	0.946

The data were collected at 20°C with Mo Kα radiation (λ = 0.71073 Å)

$$R = \sum \| F_o | - | F_c \| / \sum | F_0 |, \quad R_w = \left[\sum \left(| F_o | - | F_c | \right)^2 / \sum | F_o |^2 \right]^{0.5}$$

3.3. Results and Discussion

3.3.1. Reactions Between Substituted Pyridine and Trityl Borate

In order to generate the trityl pyridinium borate salts $[(C_6H_5)_3C(4\text{-}RPy)][B(C_6F_5)_4]$ (R = H, Et, ^{t}Bu, NMe_2), equimolar amounts of both reagents, the corresponding pyridine and trityl borate ($[(C_6H_5)_3C(4\text{-}RPy)][B(C_6F_5)_4]$) were used. The solutions were prepared in CH_2Cl_2, mixed at room temperature and left to stir for 30 minutes (Figure 3.3). The trityl pyridinium borate salts $[PyC(C_6H_5)_3][B(C_6F_5)_4]$ **(3.1)**, $[(4\text{-}^t BuPy)C(C_6H_5)_3][B(C_6F_5)_4]$ **(3.2)**, $[(4\text{-}EtPy)C(C_6H_5)_3][B(C_6F_5)_4]$ **(3.3)**, and $[(4\text{-}DMAP)C(C_6H_5)_3][B(C_6F_5)_4]$ **(3.4)** were successfully obtained as the only products for each case, and characterized. ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopic analyses showed the absence of any other by-product. The selected NMR data of these compounds are shown in Table 3.2.

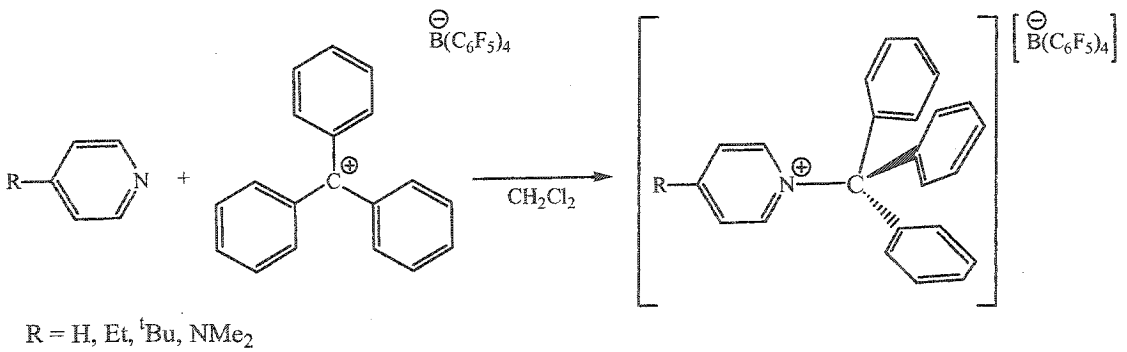


Figure 3.3: Generation of the trityl pyridinium borate salt.

Table 3.2: ^{1}H, $^{11}B\{^{1}H\}$ and ^{19}F NMR chemical shifts found for the pyridine-adducts obtained in CD_2Cl_2 as solvent.

Pyridine	^{1}H NMR δ free 4-RPy	^{1}H NMR δ	$^{11}B\{^{1}H\}$ NMR δ	^{19}F NMR δ
Py (**3.1**)	8.61 (α-H) 7.37 (β-H) 7.74 (γ-H)	8.76 (α-H) 7.99 (β-H) 8.54 (γ-H)	−17.0	−133.39 (*o*-F) −163.82 (*p*-F) −167.72 (*m*-F)
4-^{t}BuPy (**3.2**)	8.51 (α-H) 7.33 (β-H)	8.58 (α-H) 7.90 (β-H)	−17.0	−133.33 (*o*-F) −163.85 (*p*-F) −167.73 (*m*-F)
4-EtPy (**3.3**)	8.47 (α-H) 7.12 (β-H)	8.56 (α-H) 7.75 (β-H)	−17.0	−133.35 (*o*-F) −163.82 (*p*-F) −167.70 (*m*-F)
4-DMAP (**3.4**)	8.20 (α-H) 6.45 (β-H)	7.95 (α-H) 6.67 (β-H)	−16.9	−133.38 (*o*-F) −163.95 (*p*-F) −167.81 (*m*-F)

$^{11}B\{^{1}H\}$ and ^{19}F NMR spectra for each pyridinium borate salt [4-RPy-$C(C_6H_5)_3$][$B(C_6F_5)_4$] (**3.1** to **3.4**) showed practically no difference, indicating that interaction existing between the borate anion with its respective pyridinium cation is minimum in all the salts.

The difference in ^{1}H NMR chemical shifts between the pyridine ring protons of the borate salts [4-RPy-$C(C_6H_5)_3$][$B(C_6F_5)_4$] (R = H, ^{t}Bu, Et, NMe_2) and the ring protons of the free pyridines is significant, particularly for the β-protons. The chemical shifts of the pyridine ring β-protons for the pyridinium compounds are downfield of the free substituted pyridine (Table 3.2) due to electron donation to the trityl fragment. The highest field shift of the pyridine ring protons was observed in **3.1**, while the lowest field shift was observed for **3.4**. This trend follows the ability as a base of the 4-RPy, where the strongest Lewis base **3.4** has a pK_a value of 9.14, the weakest electron donor **3.1** has a pK_a value of 5.14.

In the case of **3.4** the pyridine ring α-protons are shifted upfield with respect to corresponding protons of the free pyridine 4-DMAP. This is the only pyridinium cation

that shows this phenomenon. This is due to the substituent (NMe_2). The nitrogen in the amino group donates electron density to the pyridine ring π-system (unlike ^{t}Bu and Et which also donate electron density, but inductively), promoting a shift upfield for pyridine ring α-protons (Figure 3.4).

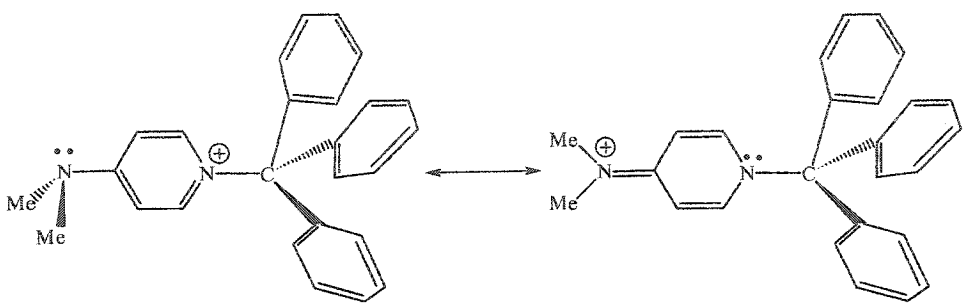


Figure 3.4: Donation of electron density of the amino group (NMe_2) to the pyridine ring through the π-system in **3.4**.

Reactions between pyridines and trityl $[C(C_6H_5)_3]^+$ have previously been reported.[107-109] Briegleb showed the reaction between pyridines and $[C(C_6H_5)_3]^+$ are reversible and dependent on the concentration of the pyridine and solvent.[107] Damico and Broaddus reported the reaction of trityl salts with a variety of tertiary amines, secondary amines and pyridines.[108] Their research showed that as long as there are no aliphatic α- or β-hydrogens in the amine, the reaction will halt with the formation of the ammonium salt. The reaction of trityl $[C(C_6H_5)_3]^+$ with pyridine (Py) in CH_2Cl_2 gave the trityl pyridinium salt $[PyC(C_6H_5)_3]^+$ as the only product. Equivalent results were also observed by Okamoto and Shimakawa.[109]

3.3.2. Reactions Between Substituted Pyridine and *Tris*(pentafluorophenyl)borane

In general, the procedure followed to generate nitrogen-boron adducts consisted on mixing equimolar amounts of the substituted pyridine with $B(C_6F_5)_3$ in CH_2Cl_2 at RT and left to react for 30 minutes (Figure 3.5). The adducts $Py{\cdot}B(C_6F_5)_3$ (**3.5**), 4-^{t}BuPy$\cdot B(C_6F_5)_3$, (**3.6**) 4-EtPy$\cdot B(C_6F_5)_3$ (**3.7**) and 4-DMAP$\cdot B(C_6F_5)_3$ (**3.8**) were successfully synthesized and characterized by ^{1}H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and ^{19}F NMR spectroscopy.

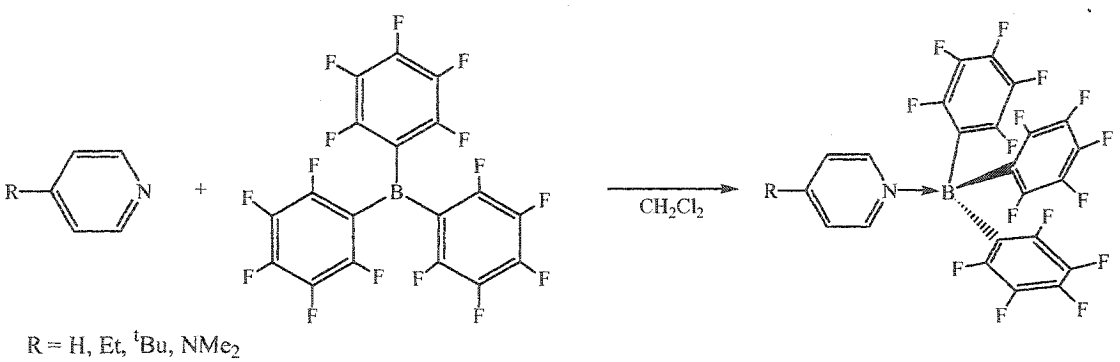


Figure 3.5: Synthetic procedure followed to afford the pyridine-borane adducts.

The substituted pyridine adducts display[102,103] the ^{1}H NMR chemical shifts for α-H further downfield (δ ca. 8.5 - 9.0 ppm) from the free pyridine protons. The formation of these adducts was also followed by $^{11}B\{^1H\}$ NMR analysis, where the chemical shifts observed were upfield from the signal for free $B(C_6F_5)_3$ (δ 0.3 ppm in CD_2Cl_2). The ^{1}H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and ^{19}F NMR spectra obtained for these four compounds were consistent with the proposed structures, where the Lewis acid $B(C_6F_5)_3$ and the Lewis base 4-RPy (R = H, Et. ^{t}Bu, Me_2N) are joined by the N→B dative bond. The ^{19}F NMR resonances of the fluorine atoms in the C_6F_5 moiety of the borate are shifted upfield (Table 3.3) compared to the free borane $B(C_6F_5)_3$ (^{19}F NMR δ −128.5, −143.3, −160.6 ppm in CD_2Cl_2).

The difference in ^{1}H NMR chemical shifts of the protons of 4-RPy (R = H, ^{t}Bu, Et, NMe_2) at the corresponding borane adducts 4-RPy·$B(C_6F_5)_3$ and the protons at the free 4-RPy can be used to probe the electronic effect of the substituted pyridine. The difference in ^{1}H NMR chemical shifts is noticeable for the β-protons. The downfield shift of the pyridine ring β-protons for the adducts can be attributed to the formation of the N→B dative bond (Table 3.3). The highest field shift of the pyridine ring protons was observed in **3.7**, while the lowest field shift was observed for **3.8**. This trend follows the ability as a base of the 4-RPy, where the strongest Lewis base in **3.8** has a pK_a value of 9.14, the weakest electron donor (found in **3.7**) has a pK_a value of 6.02.

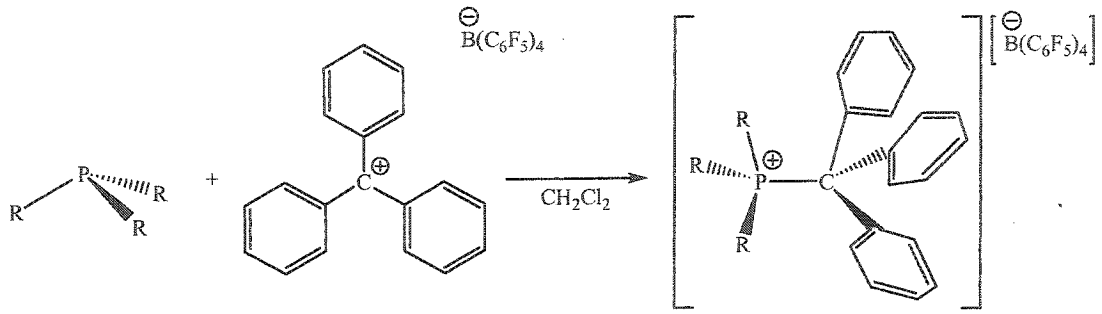
Table 3.3: ^{1}H, $^{11}B\{^1H\}$ and ^{19}F NMR chemical shifts found for the pyridine-borane adducts in CD_2Cl_2 as solvent. * pK_a values of the free pyridine.

Pyridine	**pK_a** * [122]	**^{1}H NMR δ** free 4-RPy	**^{1}H NMR δ**	**$^{11}B\{^1H\}$ NMR δ**	**^{19}F NMR δ**
Py (**3.5**)	5.14	8.61 (α-H) 7.37 (β-H) 7.74 (γ-H)	8.61 (α-H) 7.71 (β-H) 8.21 (γ-H)	−3.88	−132.15 (*o*-F) −157.83 (*p*-F) −164.28 (*m*-F)
4-^{t}BuPy (**3.6**)	5.99	8.51 (α-H) 7.33 (β-H)	8.45 (α-H) 7.63 (β-H)	−4.37	−132.15 (*o*-F) −158.14 (*p*-F) −164.44 (*m*-F)
4-EtPy (**3.7**)	6.02	8.47 (α-H) 7.12 (β-H)	8.43 (α-H) 7.49 (β-H)	−4.29	−132.20 (*o*-F) −158.09 (*p*-F) −164.40 (*m*-F)
4-DMAP (**3.8**)	9.14	8.20 (α-H) 6.45 (β-H)	7.90 (α-H) 6.60 (β-H)	−5.60	−132.89 (*o*-F) −159.16 (*p*-F) −165.02 (*m*-F)

Previous work involving the generation of nitrogen–boron adducts include the work of Massey,[33] Blackwell,[100] Lesley,[103,140] Lucarini[145] and Höpfl.[146] Some of the work include the formation of adducts with pyridine derivatives,[33,103,140] however none of them show a relationship between the electronic effect and the pK_a of the Lewis base in the borane adduct.

3.3.3. Reactivity of Tertiary Phosphines with Trityl Borate

Analogous reactions of $[C(C_6H_5)_3][B(C_6F_5)_4]$ with tertiary phosphines in CH_2Cl_2 formed the phosphonium borate salts (Figure 3.6).



R = Me, ^{n}Bu, *p*-$CH_3C_6H_4$, C_6H_5

Figure 3.6: Reaction between $[C(C_6H_5)_3][B(C_6F_5)_4]$ and PR_3, affording the tritylphosphonium salt.

In this manner the phosphonium salts $[Me_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (**3.9**), $[^nBu_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (**3.10**), $[Ph_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (**3.11**), and $[(p\text{-}CH_3C_6H_4)_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (**3.12**) were synthesized and characterized by NMR spectroscopy. In these cases, the $^{31}P\{^1H\}$ NMR chemical shift is significantly downfield from the chemical shift observed for the free phosphines (Table 3.4). The $^{11}B\{^1H\}$ and ^{19}F NMR spectra for each phosphonium borate salt $[R_3PC(C_6H_5)_3][B(C_6F_5)_4]$ (**3.9** to **3.12**) showed no significant change in the chemical shift between them. It is likely that the interaction existing between the borate anion and its respective phosphonium cation is consistent in all these salts.

Table 3.4: $^{31}P\{^{1}H\}$ NMR data of the reaction products between PR_3 and $[C(C_6H_5)_3][B(C_6F_5)_4]$

Phosphine	$^{31}P\{^{1}H\}$ NMR δ free phosphine	$^{31}P\{^{1}H\}$ NMR δ coordinated phosphine	$\Delta\delta_{(\delta coord - \delta free)}$
P^iPr_3	19.9	40.4	20.5
PCy_3	11.1	29.4	18.3
P^nBu_3	−31.5	42.8	74.3
P^tBu_3	62.9	50.2	−12.7
PMe_3	−62.0	38.1	100.1
$P(o\text{-}C_7H_7)_3$	−29.7	−29.7	0
$P(p\text{-}C_7H_7)_3$	−7.7	24.6	32.3
$P(C_6H_5)_3$	−5.1	24.7	29.8

However, the ^{1}H and $^{13}C\{^{1}H\}$ NMR analyses of the reaction between $[C(C_6H_5)_3][B(C_6F_5)_4]$ and P^iPr_3 did not reflect the generation of the expected phosphonium salt. The ^{1}H NMR spectra (Figure 3.7) showed a signal at δ 5.69 ppm with an integration value of one proton, which was not observed in the previously obtained adducts. In the $^{13}C\{^{1}H\}$ NMR data the signal at δ ca. 67 ppm, which is around where the signal for the quaternary carbon of these salts would be expected is absent. Instead a signal at δ ca. 56.9 ppm was observed. These new signals corresponded to a tertiary carbon (R_3C–H). A closer analysis of all the spectroscopic data collected revealed that the product yielded was the [*p*-benzhydryl-phenyl]tri*iso*propylphosphonium borate salt **3.13** (Figure 3.8). The structural assignment of **3.13** was also confirmed by X-ray crystallographic analysis.

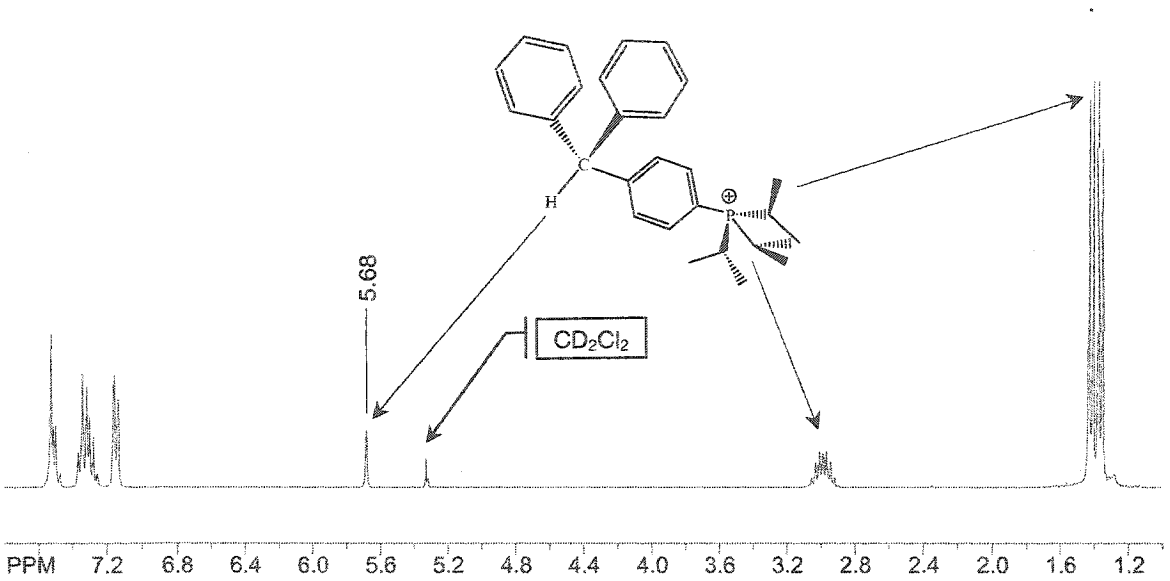


Figure 3.7: ^{1}H NMR spectrum of the product of (p-^{i}Pr$_3$P-C$_6$H$_4$)(C$_6$H$_5$)$_2$CH (**3.13**)

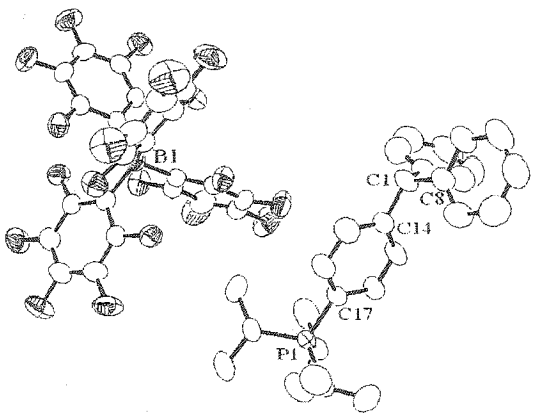
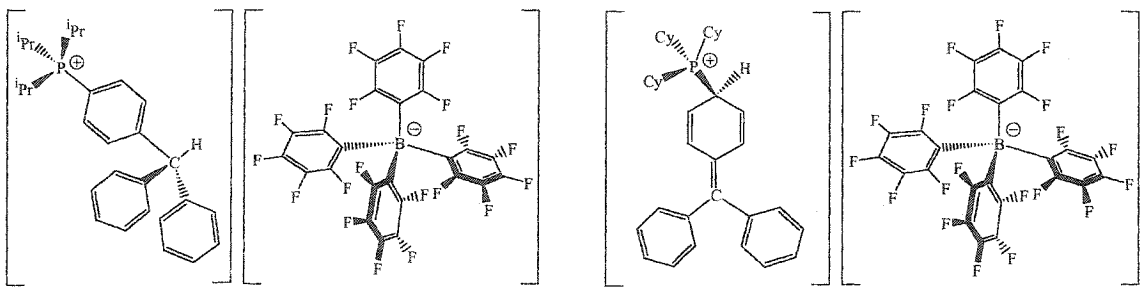


Figure 3.8: ORTEP diagram of (p-^{i}Pr$_3$P-C$_6$H$_4$)(C$_6$H$_5$)$_2$CH (**3.13**) (hydrogen atoms are omitted for clarity; 50% thermal ellipsoids). Selected bond distances (Å): P(1)–C(17) 1.804(4); C(1)–C(14) 1.545(6); C(1)–C(8) 1.548(7); C(1)–C(2) 1.587(7).

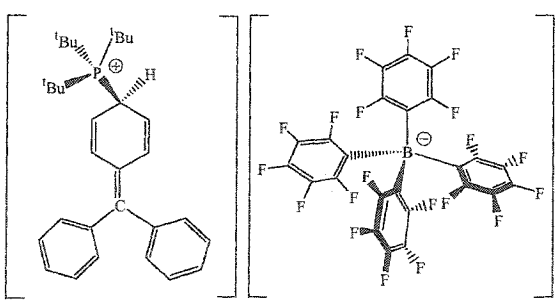
In contrast, the reactions involving PR$_3$ (R = Cy, ^{t}Bu) and [C(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] neither gave the phosphonium salts [R$_3$PC(C$_6$H$_5$)$_3$][B(C$_6$F$_5$)$_4$] nor the salts (p-R$_3$P-C$_6$H$_4$)(C$_6$H$_5$)$_2$CH (analogous to **3.13**). Instead the (4-benzhydrylidene-cyclohexa-2,5-

dienyl)phosphonium salts **3.14** and **3.15** were obtained as the only products (Figure 3.9). For both cases, the ^{1}H NMR spectra showed three sets of doublets at δ ca. 6.80 ppm, δ ca. 6.00 ppm and δ ca. 4.50 ppm; the first two of them integrating to two protons and the last one integrating to one proton (Figure 3.10). The first two doublets correspond to the cyclohexadienyl moiety, whereas the second doublet corresponds to the proton in 4-C in the cyclohexadienyl fragment. For both phosphines the ^{13}C{^{1}H} NMR analyses revealed three resonance signals at δ ca. 134.4 ppm, δ ca. 125.6 ppm and δ ca. 119.7 ppm, which correlate with the resonances observed in the ^{1}H NMR spectra. Furthermore, the ^{13}C{^{1}H} NMR signal corresponding to the carbon atom bearing both phenyl groups, was also observed at δ ca.140.8 ppm.



3.13

3.14



3.15

Figure 3.9: [*p*-benzhydryl-phenyl]phosphonium borate salt **3.13**, and (4-benzhydrylidene-cyclohexadienyl)phosphonium borate salts, **3.14** and **3.15** obtained from the reactions of the phosphines $P^{i}Pr_3$, PCy_3 and $P^{t}Bu_3$ with $[C(C_6H_5)_3][B(C_6F_5)_4]$.

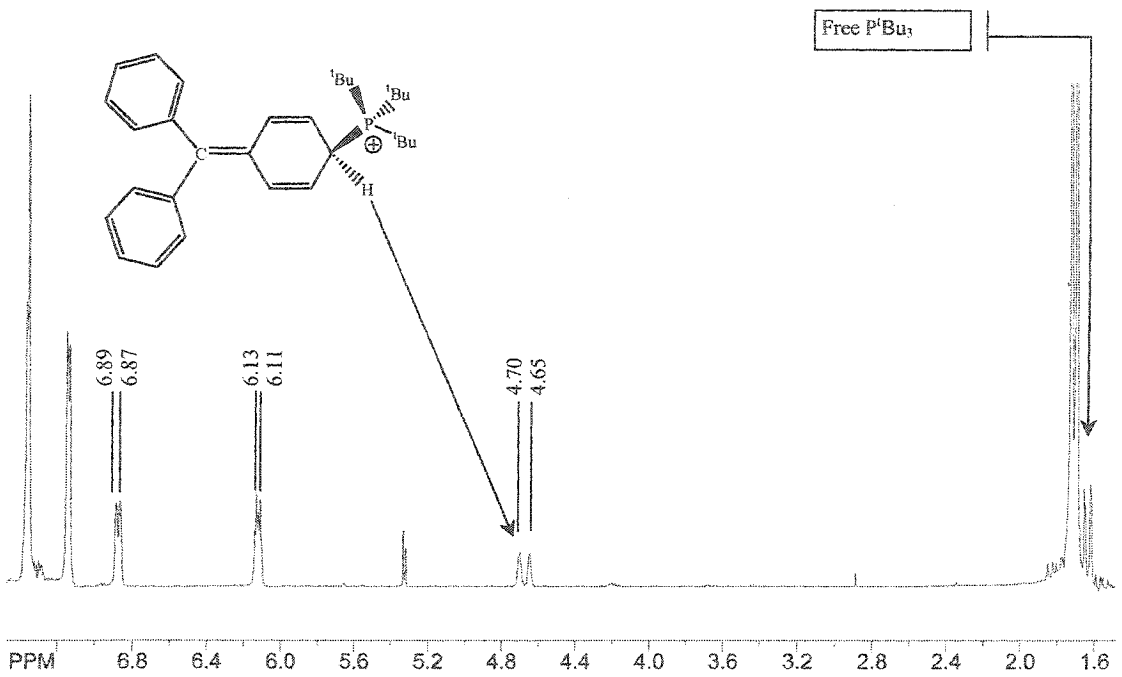


Figure 3.10: ^{1}H NMR spectrum of **3.15**.

Previous research involving phosphines and trityl borate includes the work performed by Lambert and So,[147] where the reactions between secondary phosphines and $[C(C_6H_5)_3][B(C_6F_5)_4]$ produced the respective phosphonium ions. Work performed by Hoffmann and Schellenbeck[112] includes the reaction of a variety of tertiary phosphines possessing different substituents at the phosphorus atom, which give the corresponding trityl phosphonium borate salts as the products. Similarly, Sanders[110] and Fang *et al.*[148] also reported a series of trityl phosphonium salts afforded by analogous reactions. However, it was Bidan and Genies[111] work which pointed out that, depending on the size of the R-groups present in the phosphine (e.g. $P(C_6H_5)(^tBu)(CH_3)$ and $P(C_6H_5)_3$) and the reaction conditions, the [*p*-benzhydryl-phenyl]-phosphonium salt could be obtained as a product instead of the trityl phosphonium salt (Figure 3.11).[111] They proposed a reaction mechanism that seems to explain the formation of the [4-benzhydrylidene-cyclohexadienyl]phosphonium salts and [*p*-benzhydryl-phenyl]-phosphonium salt (Figure 3.12).[111]

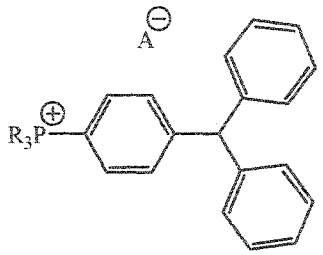


Figure 3.11: Phosphonium salts, the reaction products between tertiary phosphines and trityl salts.

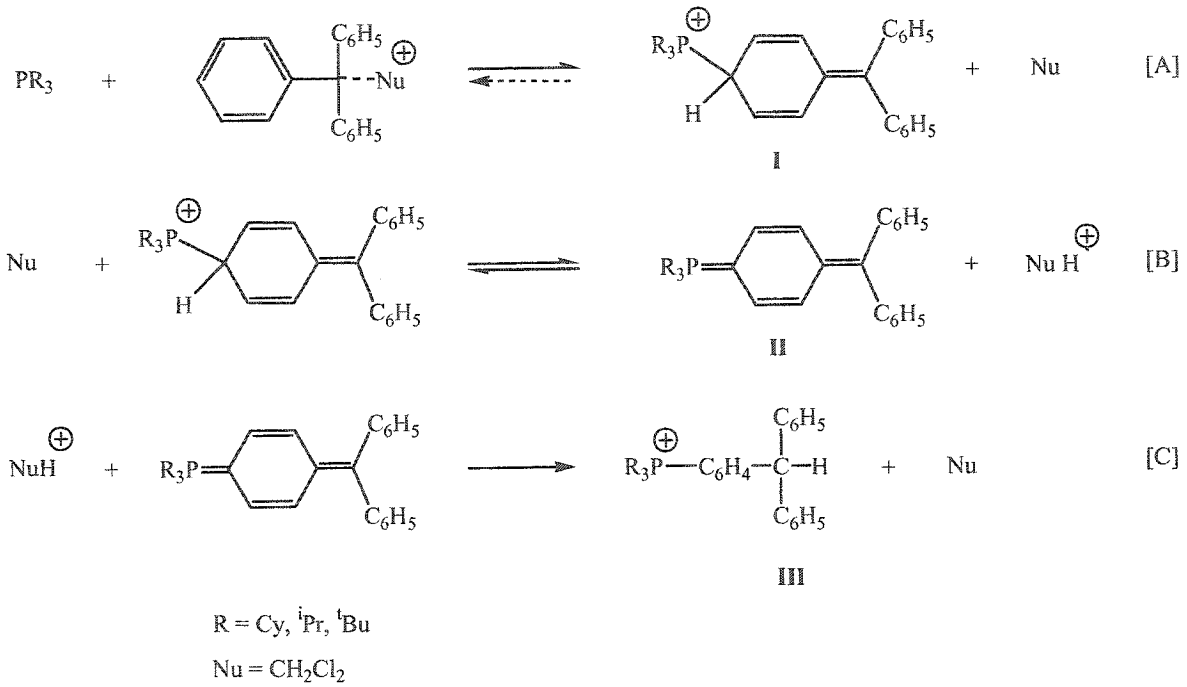


Figure 3.12: Reaction mechanism expressed by [**A**], [**B**] and [**C**] for the formation of the isomers (p-R_3P^+-C_6H_4)(C_6H_5)$_2$CH (**III**).[111]

This mechanism appears to provide an explanation for the results observed in the reactions performed with P^iPr_3, P^tBu_3 and PCy_3. In reaction [**A**] (Figure 3.12), a nucleophilic substitution (S_N2) takes place. Bidan and Genies suggested that a pyridine

could be a suitable nucleophile.[h] In our case, it is possible that the same tertiary phosphine PR_3 (R = ^{i}Pr, Cy, ^{t}Bu) might have served as the nucleophile (Nu). [**B**] and [**C**] represent the reactions that convert **I** into the phosphonium **III**. During the attack of the trisubstituted phosphine molecule (PR_3), the nucleophile should be liberated promoting the formation of an ylide (**II**) which is more stable than the (4-benzhydylidene-cyclohexadienyl)phosphonium **I** precursor.

Bidan and Genies[111] also proposed that the ylide (**II**, Figure 3.12) oxidizes when the phosphonium cation (**I**) is reduced, giving free phosphine and trityl radical species (Figure 3.13). The radical species dismutate, what would consume the available protons that could protonate the ylide by forming triphenylmethane, preventing reaction [**C**] to be reversible.

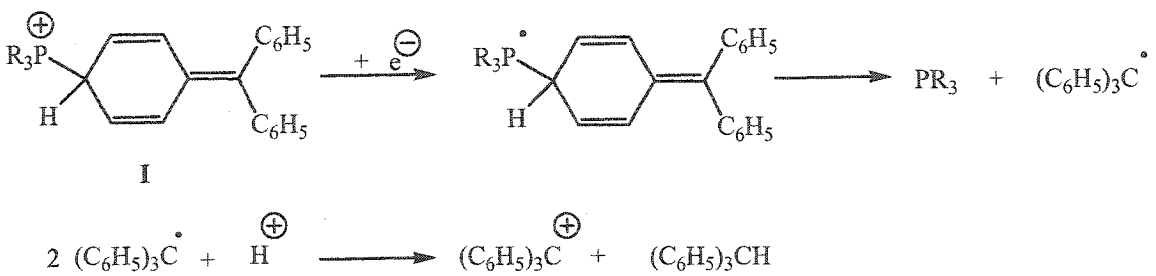


Figure 3.13: Nucleophilic attack to neutral trityl radicals.

In the case of **3.14** and **3.15**, the reaction stops at [**A**], since (4-benzhydrylidene-cyclohexa-2,5-dienyl)-phosphonium salts **I** are the only species present, as it was confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopic analyses. For **3.13**, the reaction yields the [*p*-benzhydryl-phenyl]-phosphonium species **III**. The possibility that the reaction might undergo this reaction mechanism is supported by the formation of **3.14** and **3.15**. For both cases, the ^{1}H and ^{13}C{^{1}H} NMR spectra and a DEPT experiment confirm the presence of the cyclohexadienyl group (Figure 3.10, p. 108).

[h] A nucleophile (or nucleophilic reagent) is a reagent that forms a bond to its reaction partner (the electrophile) by donating both bonding electrons. Lewis bases are nucleophilic reagents.

The trend observed is that if the ability of the phosphines to act as electron donors (Lewis bases) increases it is likely that the reaction will follow the mechanism proposed. This phenomenon could also be attributed to the increase of size of the phosphine substituents. The reaction mechanism (Figure 3.12, p. 107) was proposed by Bidan and Genies[111] to explain the reaction product $[(p\text{-}P(C_6H_5)_3\text{-}C_6H_4)(C_6H_5)_2CH][B(C_6F_5)_4]$ (Figure 3.14) generated by $P(C_6H_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$. $P(C_6H_5)_3$ is a poor electron donor compared P^iPr_3, PCy_3 and P^tBu_3; but it is considerably sterically bulky (as are P^iPr_3, PCy_3 and P^tBu_3). These tertiary phosphines (weak Lewis bases and strong Lewis bases) can form such products not mattering their electron donating ability. What they have in common is that all have a big cone angle (Table 3.5). It can only be speculated that the mechanism and final products depend on the size of the phosphine and not necessarily in its electron donating ability.

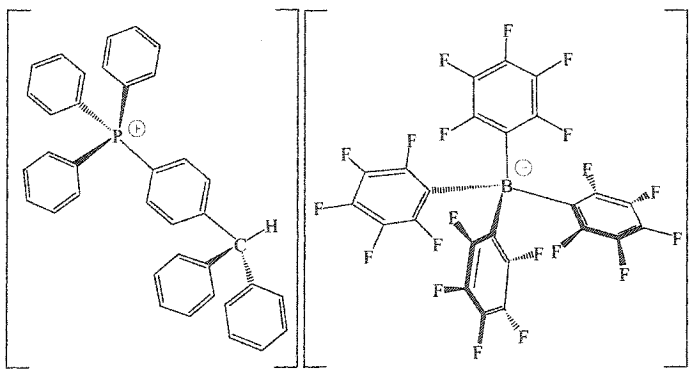
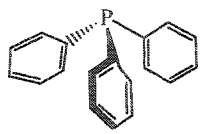
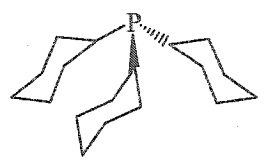
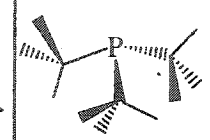


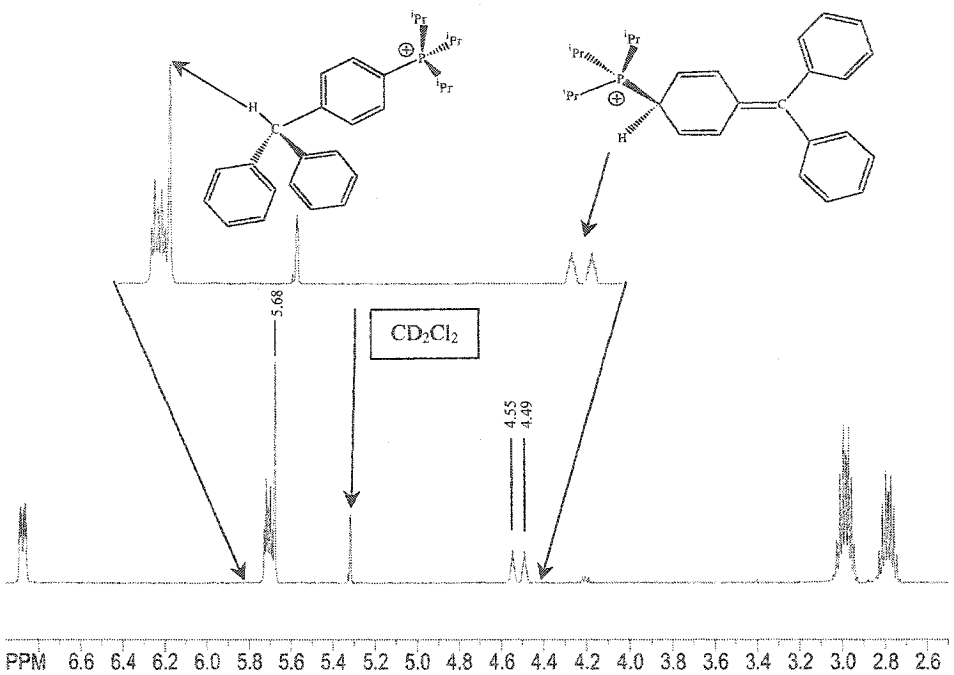
Figure 3.14: Compound $[(p\text{-}P(C_6H_5)_3\text{-}C_6H_4)(C_6H_5)_2CH][B(C_6F_5)_4]$ is generated by the reaction between $P(C_6H_5)_3$ and $[C(C_6H_5)_3][B(C_6F_5)_4]$.

Table 3.5: List of sterically bulky tertiary phosphines in increasing order of basicity with respect to their pK_a value.

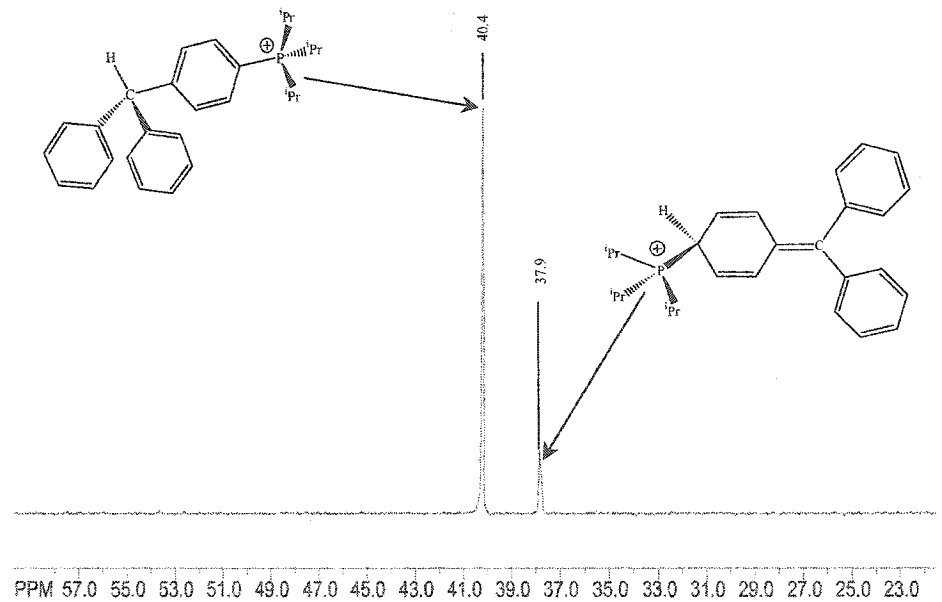
PHOSPHINE	$P(C_6H_5)_3$ 	P^iPr_3 	PCy_3 	P^tBu_3 
pK_a[14,15]	2.73	9.3	9.7	11.4
Tolman Cone Angle [14,15]	145°	160°	170°	182°

In order to know if the source of the proton bound to the tertiary carbon was the *p*-carbon in the phenyl group or CH_2Cl_2 solvent, the reaction between P^iPr_3 and $[C(C_6H_5)_3][B(C_6F_5)_4]$ was performed again, using CD_2Cl_2 as the solvent. When the reaction was finished, a ^1H NMR analysis revealed a signal at δ 5.67 ppm, indicative of a sp^3 carbon forming a C–H bond and not a C–D bond. The reaction was again performed with CD_2Cl_2 as solvent. This time, the ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired immediately after the addition of P^iPr_3 to the $[C(C_6H_5)_3][B(C_6F_5)_4]$. Both spectra showed the intermediate (4-benzhydrylidene-cyclohexadienyl)tri*iso*propyl phosphonium borate and **3.13** present in the same solution (Figure 3.15), suggesting that the reaction follows the mechanism proposed by Bidan and Genies.

$P(o\text{-}CH_3C_6H_4)_3$ showed no reactivity with $[C(C_6H_5)_3][B(C_6F_5)_4]$ after 30 minutes or even after 24 hours, as stated previously by Fang,[148] which can be interpretated in terms of steric interactions between the phosphine and trityl borate. $P(C_6H_5)_3$ and $P(p\text{-}CH_3C_6H_4)_3$ do react with trityl borate, and both tertiary phosphines have a pK_a value (3.84 and 2.73 respectively) close to the one that $P(o\text{-}CH_3C_6H_4)_3$ has (pK_a = 3.08). However, in this case, no reaction occurs. The cone angle of $P(o\text{-}CH_3C_6H_4)_3$ (θ = 194°) differs greatly to the one that $P(C_6H_5)_3$ and $P(p\text{-}CH_3C_6H_4)_3$ have (θ= 145° in both cases), which is the main difference between the three phosphines. This difference in the size of the phosphines can be the reason why no reaction was observed.



^{1}H NMR spectrum



$^{31}P\{^{1}H\}$ NMR spectrum

Figure 3.15: ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of the reaction between $P^{i}Pr_3$ and $[C(C_6H_5)][B(C_6F_5)_4]$ in CD_2Cl_2, showing both species, intermediate and final product **3.13.**

3.3.4. Reaction of Tertiary Phosphines and *Tris*(pentafluorophenyl)borane

The products of the reactions performed between tertiary phosphines and *tris*(pentafluorophenyl)borane were obtained following the same procedure. The synthetic method to achieve such adducts, consisted of first preparing a solution of $B(C_6F_5)_3$ in CH_2Cl_2. Subsequently an equimolar amount of phosphine was added to the borane solution at RT and left to stir for 30 minutes (Figure 3.16). Previously published procedures differ from the procedure followed in this thesis in the choice of solvent, where it has been reported the use of toluene or pentane instead of CH_2Cl_2.[104,106,143]

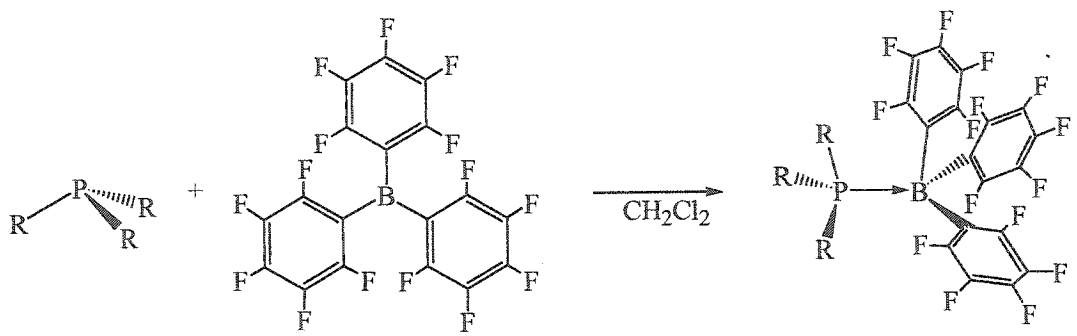


Figure 3.16: Synthetic procedure followed to afford the phosphine-borane adducts.

The reaction of $B(C_6F_5)_3$ with PMe_3 gave the adduct $Me_3P{\cdot}B(C_6F_5)_3$ (**3.16**) as an insoluble white solid. Similar reactions with $P(C_6H_5)_3$ and $P(p\text{-}CH_3C_6H_4)_3$ yielded what are thought to be the adducts as white solids (**3.17** and **3.18** respectively), which were partially soluble in CH_2Cl_2. Benzene was also tried as a solvent, but even after heating the solution, no evidence of even partial solubility was witnessed. NMR spectroscopic analysis did not detect the presence in solution of either adduct. However, elemental analysis of the obtained solids was in agreement with the theoretical calculations.

In contrast, the reaction involving P^nBu_3 gave as a single product the adduct $^nBu_3P{\cdot}B(C_6F_5)_3$ **3.19**, which was characterized by NMR spectroscopy (Table 3.6). The $^{31}P\{^1H\}$ NMR spectrum showed a chemical shift downfield at δ 0.56 ppm compared to the free phosphine. $^{11}B\{^1H\}$ NMR spectrum showed a chemical shift upfield from the

borane starting material (CD_2Cl_2, δ 0.3 ppm) at δ −15.6 ppm. The ^{19}F NMR spectrum showed that the fluoride substituents were upfield shifted (δ −129.85 ppm *o*-F, −157.58 ppm *p*-F and −164.44 ppm *m*-F) compared to the resonances of the free Lewis acid $B(C_6F_5)_3$ (δ −128.5 ppm *o*-F, −143.3 ppm *p*-F and −160.6 ppm *m*-F in CD_2Cl_2).

Reactions involving the more basic phosphines P^iPr_3 and PCy_3 did not give the expected adduct, but instead they formed the isomeric structures **3.20** and **3.21** shown in Figure 3.17, which were characterized by NMR spectroscopy (**3.20** was confirmed by X-ray analysis, Figure 3.18). Both structures are analogous to the phosphonium salt **3.13**. Table 3.5 shows the $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and ^{19}F NMR data for the compounds obtained from these reactions between the tertiary phosphines P^iPr_3 and PCy_3 and borane $B(C_6F_5)_3$.

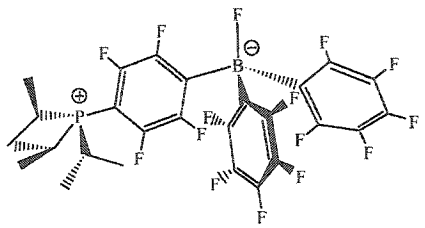
Table 3.6: ^{31}P, $^{11}B\{^1H\}$ and ^{19}F NMR chemical shifts found for (*p*-R_3P–$(C_6F_4)(C_6F_5)_2BF$ (R = ^{i}Pr, Cy) adducts obtained at 30 °C in CD_2Cl_2 as solvent. [a] Signals corresponding to the tetrafluorophenyl group.

Phosphine	$^{31}P\{^1H\}$ NMR δ free phosphine	$^{31}P\{^1H\}$ NMR δ coordinated phosphine	$^{11}B\{^1H\}$ NMR	^{19}F NMR
P^nBu_3 (**3.19**)	−31.5	−0.56	−15.6	−129.85 (*o*-F) −157.58 (*p*-F) −164.44 (*m*-F)
P^iPr_3 (**3.20**)	19.9	53.2	−0.89	−124.84 (*o*-F)[a] −127.71 (*m*-F)[a] −132.14 (*o*-F) −158.11 (*p*-F) −163.07 (*m*-F) −189.37 (F–B)
PCy_3 (**3.21**)	11.1	41.6	−0.70	−128.76 (*o*-F)[a] −132.03 (*m*-F)[a] −135.81 (*o*-F) −161.92 (*p*-F) −166.83 (*m*-F) −193.11 (F–B)

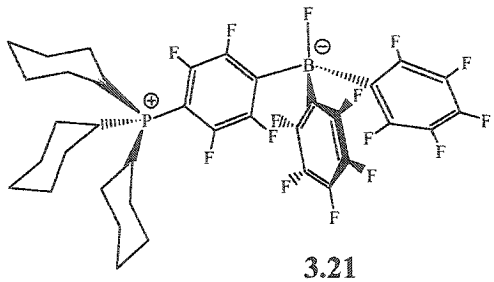
The $^{31}P\{^1H\}$ NMR data for **3.20** and **3.21** showed a different chemical shift from the free phosphine, indicating that the starting material was no longer present. The

$\Delta\delta$ values ($\delta_{adduct} - \delta_{free\ base}$) is *ca.* 30 for both compounds, which could be due to the P–C bond formation.

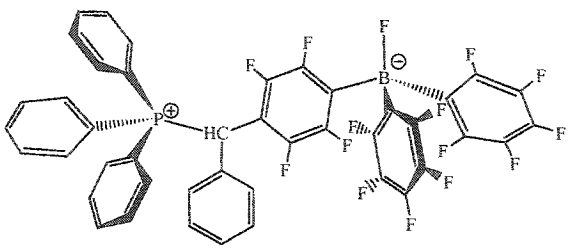
$^{11}B\{^1H\}$ NMR analyses showed a small chemical shift upfield in comparison with the Lewis acid $B(C_6F_5)_3$ starting material, at δ – 0.89 ppm for **3.20** and at δ – 0.70 ppm for **3.21**. The coupling constant ($^1J_{F\text{-}B}$) found for both species is *ca.* 60 Hz. The ^{19}F NMR analyses were very informative. For the compounds **3.20** and **3.21** it was observed that the fluoride substituents are upfield shifted compared to the free $B(C_6F_5)_3$ signals (δ −128.5 ppm *o*-F, −143.3 ppm *p*-F and −160.6 ppm *m*-F in CD_2Cl_2). For both compounds, the new signals were around δ −134.0 ppm *o*-F, δ −160.0 ppm *p*-F and δ −165 ppm *m*-F. ^{19}F NMR spectra also showed that the *ortho*- and *meta*-F of the tetra(fluoro)phenyl group were found downfield from the *ortho*- and *meta*-F at the penta(fluoro)phenyl substituents at the boron atom. The highest field shift was observed for the fluoride coordinated to the boron atom at δ ca. −191 ppm. The ^1H and $^{13}C\{^1H\}$ NMR spectra acquired were also consistent with the proposed structures.



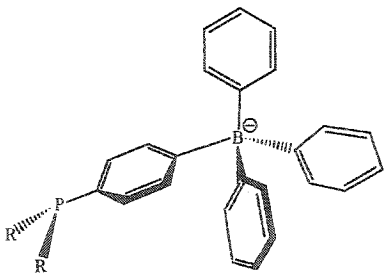
3.20



3.21



a



b

Figure 3.17: Compounds **3.20** and **3.21** and similar compounds **a**[143] and **b**[149] (R = C_6H_5, ^iPr) that have been reported.

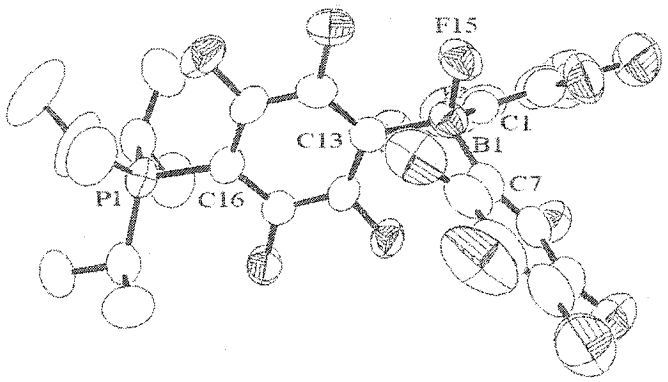


Figure 3.18: ORTEP diagram of (p-$^{i}Pr_3P$-C_6F_4)(C_6F_5)$_2$BF (**3.20**) (hydrogens are omitted for clarity; 50% thermal ellipsoids). Selected bond distances (Å): P(1)–C(16) = 1.826(3); B(1)–C(13) 1.643(4); B(1)–F(15) 1.427(3); B(1)–C(1) 1.658(4); B(1)–C(7) 1.660(4).

Similar structures have been previously reported. The reaction of methylene benzilidene triphenylphosphorane with *tris*(pentafluorophenyl) borane yielded **a**[143] (Figure 3.17) in toluene and at high temperatures. The synthesis of the (phosphino)tetraphenyl borate **b** has also been previously described.[149]

$P^{t}Bu_3$ showed no reactivity with $B(C_6F_5)_3$ after 30 minutes, therefore reaction time was increased for another 2 hours. $^{31}P\{^{1}H\}$ NMR analysis showed two minor signals in addition to the free phosphine. The $^{11}B\{^{1}H\}$ NMR spectrum revealed three different signals. The reaction was left for 24 hours, with the purpose to identify the major product. Interestingly, additional products were observed by NMR spectroscopy, and after 48 hours there was a change in intensity, without being possible to identify any of the products generated. The reaction was performed again, this time at 40 °C for 24 hours, but no significant difference was observed from the previous reaction. Numerous signals were found in ^{19}F, $^{11}B\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra.

Suspecting that PCy_3 and $P^{i}Pr_3$ could behave in a similar fashion to $P^{t}Bu_3$ in the reaction previously described, a set of reactions with PCy_3 and $P^{i}Pr_3$ were left for 48 hours, while another set of reactions with both phosphines were carried out at 40 °C. The only reaction products formed in these reactions were the isomeric products **3.20** and **3.19**.

The syntheses of the products **3.20** and **3.21** could be explained by using a similar reaction mechanism to the one proposed by Bidan and Genies,[111] where the isostructural and isoelectronic analog *tris*(pentafluorophenyl)borane plays a role similar to the one of the triphenyl methyl cation (Figure 3.19). The tertiary phosphine present in the reaction mixture could serve as a nucleophile, coordinating to the boron center and promoting an S_N2 nucleophilic substitution of another phosphine molecule [**A**] (Figure 3.19). As represented in reaction [**B**], the fluorine at the *para* position is displaced. The exact mechanism followed is not clear, but probably the boron atom of another borane, with an empty 2p-orbital, could react with the *p*-F at the cyclohexadienyl group by accepting the electrons from the electron donor F^-, promoting the formation of **3.20** and **3.21** [**B**]. Fluorine-boron bonds are known to be stable and it is possible that, because of the nature of such interaction the reaction is irreversible.

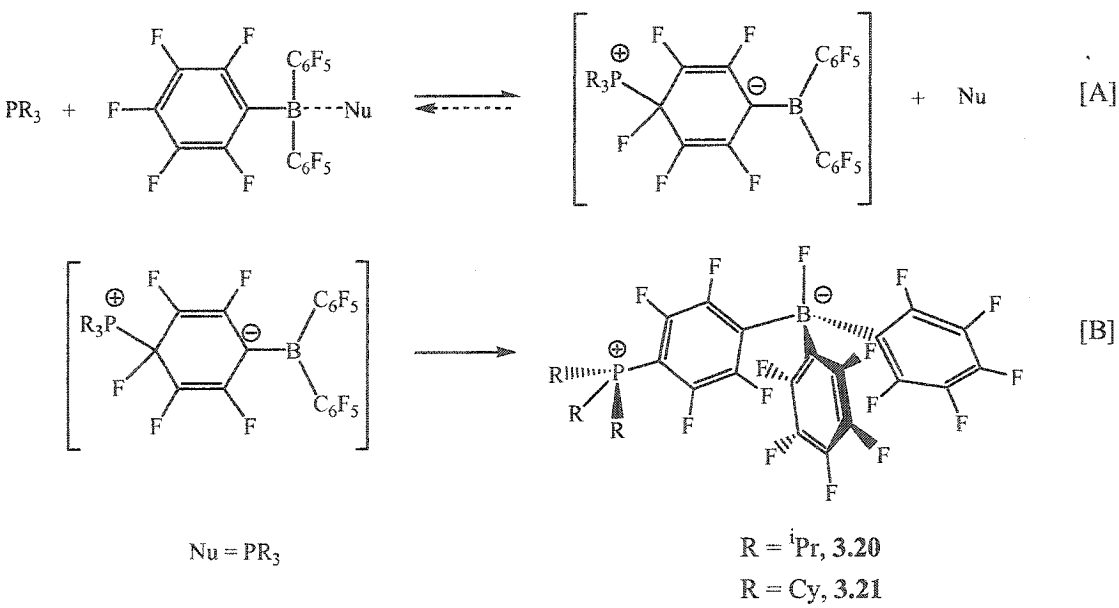


Figure 3.19: Reaction mechanism proposed for the formation of the isomeric structures **3.20** and **3.21**.

Borane-phosphine adducts have been reported previously by other research groups. However, the work involves mainly reactions between primary phosphines[105] ($PH_2{}^tBu$) and secondary phosphines[104] ($PHCy_2$, $PHPh_2$). From these studies the trend

found was that the larger the phosphine ligand the longer the P–B bond. Tertiary phosphine adducts such as $(C_6H_5)_3P{\cdot}B(C_6F_5)_3$ also showed such behavior.[101]

As reported by Jacobsen *et al.*,[101] it is possible that the size of the tertiary phosphine had not allowed the formation of the phosphine-borane adduct. P^iPr_3 and PCy_3 have cone angles of 160° and 170° respectively. The steric bulk of both phosphines might have prevented the formation of the P–B bond.

3.4. Summary

The reactions between trityl borate and 4-RPy (R = H, Et, ^{t}Bu, NMe_2) were performed, allowing the generation of the trityl pyridinium borate salts $[(4\text{-}RPy)C(C_6H_5)_3][B(C_6F_5)_4]$ (**3.1**, **3.1**, **3.3** and **3.4**). Analogous reactions were performed between $B(C_6F_5)_3$ and 4-RPy (R = H, Et, ^{t}Bu, NMe_2). From these reactions the adducts $4\text{-}RPy{\cdot}B(C_6F_5)_3$ (**3.5**, **3.6**, **3.7** and **3.8**) were obtained as well.

The reactions between the Lewis acid $[C(C_6H_5)_3][B(C_6F_5)_4]$ and tertiary phosphines showed to be dependent on the size of the phosphine substituents and solvent. For PMe_3, P^nBu_3, $P(C_6H_5)_3$, and $P(p\text{-}CH_3C_6H_4)_3$ the respective phosphonium salts **3.9**, **3.10**, **3.11** and **3.12** were obtained. Reactions with PCy_3 and P^tBu_3 yielded the (4-benzhydrylidene-cyclohexa-2,5-dienyl)-phosphonium salts **3.14** and **3.15**. The final product of the reaction involving P^iPr_3 was [*p*-benzhydryl-phenyl]phosphonium borate salt **3.13**.

The reactions of *tris*(pentafluorophenyl)borane $B(C_6F_5)_3$ with tertiary phosphines showed a similar dependency to the reactions involving trityl borate. PMe_3 and P^nBu_3 generated the adducts **3.16** and **3.17**. Reactions involving the more sterically hindered phosphines P^iPr_3 and PCy_3 did not afford the adducts, but the zwitterionic structures **3.20** and **3.21**.

Results obtained from the data collected for each experiment reveal that not only the electron donating abilities of phosphines are important, but sterics play a major role in the reactivity.

4. Summary

The active species $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ and $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ were stabilized using a series of substituted pyridines and tertiary phosphines as Lewis bases, generating the ion pairs $[Cp(NP^tBu_3)TiMe{\cdot}4\text{-}RPy][R'B(C_6F_5)_3]$ (R = H, Et, ^{t}Bu, NMe_2; R' = Me, C_6F_5) and $[Cp(NP^tBu_3)TiMe{\cdot}PR''_3][R'B(C_6F_5)_3]$ (R'' = Me, ^{n}Bu, C_6H_5, p-$CH_3C_6H_4$; R' = Me, C_6F_5).

Pyridines stabilized the active species $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ and $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ by complexation. The reactions of the metal complex with tertiary phosphines PR_3 (R = Me, Bu, C_6H_5, p-$CH_3C_6H_4$) of various basicities and cone angles showed a strong dependence on the steric properties of the phosphine. Such effect was reflected in the Cp ligand of the metal complex. For the tertiary phosphines PR''_3 (R'' = ^{i}Pr, Cy, ^{t}Bu), the reaction with $Cp(NP^tBu_3)TiMe(\mu\text{-}MeB(C_6F_5)_3)$ or $[Cp(NP^tBu_3)TiMe][B(C_6F_5)_4]$ in CH_2Cl_2 gave multiple products along with the unexpected chlorophosphonium species $[R''_3PCl][R'B(C_6F_5)_3]$ (R' = Me, C_6F_5). The mechanism of the reaction is not clear, but the results suggest CH_2Cl_2 is probably activated by the metal complex.

Depending on the solvent employed and the stoichiometric ratio used the species $[\{Cp(NP^tBu_3)TiMe\}_2(\mu\text{-}Cl)][R'B(C_6F_5)_3]$ (R' = Me, C_6F_5) (**2.18**), $[\{Cp(NPtBu3)Ti(\mu\text{-}Cl)\}_2][R'B(C_6F_5)_3]_2$ (R' = Me, C_6F_5) (**2.21**) and $[\{Cp(NP^tBu_3)Ti\text{-}Me\}_2(\mu\text{-}Me)][R'B(C_6F_5)_3]$ (R' = Me, C_6F_5) (**2.23**) are generated.

The titanium active species of the $Cp(NP^tBu_3)TiMe_2$ complex proved to be highly electrophilic, having the tendency to react with any nucleophile present in the media, either solvent, Lewis base or the same neutral complex. The reaction products observed in the experimental work showed that when the Lewis base used is bulky, the reaction will follow diverse mechanisms in order to stabilize the cationic moiety.

The reactions between $[C(C_6H_5)_3][B(C_6F_5)_4]$ and substituted pyridines were performed. The trityl pyridinium borate salts $[(4\text{-}RPy)C(C_6H_5)_3][B(C_6F_5)_4]$ (R = H, Et, ^{t}Bu, NMe_2) were successfully obtained. Analogous reactions were performed between $B(C_6F_5)_3$ and 4-RPy (R = H, Et, ^{t}Bu, NMe_2), forming the adducts $4\text{-}RPy{\cdot}B(C_6F_5)_3$.

The reactions between the activators $[C(C_6H_5)_3][B(C_6F_5)_4]$ and tertiary phosphines appear to be dependent on the size of the phosphine substituents and reaction solvent. For PMe_3, P^nBu_3, $P(C_6H_5)_3$, and $P(p\text{-}CH_3C_6H_4)_3$ the respective phosphonium salts $[(R_3P)C(C_6H_5)_3][B(C_6F_5)_4]$ (R = Me, ^{n}Bu, C_6H_5, p-$CH_3C_6H_4$) were obtained. Reactions of PCy_3 and P^tBu_3 afforded the (4-benzhydrylidene-cyclohexa-2,5-dienyl)-phosphonium salts $[(4\text{-}Cy_3P\text{-}C_6H_5)C(C_6H_5)_2][B(C_6F_5)_4]$ (**3.14**) and $[(4\text{-}^tBu_3P\text{-}C_6H_5)C(C_6H_5)_2][B(C_6F_5)_4]$ (**3.15**). The product of the reaction involving P^iPr_3 was the [p-benzhydryl-phenyl]phosphonium borate salt $[(p\text{-}^iP_3P\text{-}C_6H_4)(C_6H_5)_2CH][B(C_6F_5)_4]$ (**3.13**). The reaction of $B(C_6F_5)_3$ with tertiary phosphines showed a similar dependency to the reactions involving trityl borate. The reactions involving P^iPr_3 and PCy_3 did not give the phosphine-borane adducts, but instead the compounds $(p\text{-}^iPr_3P\text{-}C_6F_4)(C_6F_5)_2BF$ (**3.20**) and $(p\text{-}Cy_3P\text{-}C_6F_4)(C_6F_5)_2BF$ (**3.21**) were obtained.

The relationship between the reactivity of phosphine and its steric properties has been previously reported. However, the behavior observed with $B(C_6F_5)_3$ as the Lewis acid has no precedence. Such zwitterionic compounds have the potential to act as counterions for active catalyst. Further research is being developed in this particular area in an effort to better understand mechanism followed by this reaction in order to manipulate its properties.

In conclusion the products obtained from the reactions discussed were dependent on the conditions employed. The steric properties of the Lewis base, order of addition of the reagents and choice of solvent, all played a role. Further research is being done in this particular area.

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