PLANAR CHIRAL LEWIS ACIDS AND LEWIS PAIRS

BASED ON FERROCENE

by

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ABSTRACT OF THE DISSERTATION

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Dissertation Advisor: Professor Frieder Jäkle

Organoboranes have been widely used for catalytic transformations, polymerizations, small molecule activation, anion and glycol sensing and construction of electronic materials. These remarkable applications commonly benefit from the electron-deficient nature of tricoordinate boron, i.e., its empty p-orbital can accommodate a lone pair of electrons or participate in conjugation of extended π-systems. Therefore, approaches to enhance the Lewis acidity of the boron center are desirable, and different strategies have been introduced with this aim, including (1) installation of electron withdrawing pendant groups such as pentafluorophenyl groups; (2) generation of cationic borenium species and (3) incorporation of tricoordinate boron into anti-aromatic systems such as borole derivatives. Recently, much effort has been directed to the preparation of the so-called “Frustrated Lewis Pair” (FLP) and the application of their unquenched relativity for catalytic transformations. However, chiral versions of highly Lewis acidic organoboranes remain scarce. On the other hand, planar chiral ferrocenes have proven to provide rigid frameworks for transition metal ligands such as
phosphines and amines, which have been successfully applied to the asymmetric hydrogenation of alkenes, ketones and other processes.

This dissertation describes our efforts towards the stereoselective synthesis of ferrocene-based multifunctional organoboranes with unique geometric features and electrochemical properties: (1) the 1,2-disubstituted ferrocene backbone provides a rigid planar chiral environment; (2) the reversible oxidation of the ferrocene unit can be exploited for redox active Lewis acids, Lewis pairs and ambiphilic ligands. We demonstrate that a series of highly Lewis acidic derivatives can be synthesized via installation of electronic deficient pentafluorophenyl groups and generation of a borenium cation. The planar chiral borenium cation species serves as a catalyst for the asymmetric hydrosilylation of ketones. Next, we concentrated our attention on the construction of planar chiral borane-pyridine systems: the interactions between the borane and pyridine units can be tuned by introduction of different steric and electronic effects. The coordination of a planar chiral diferrocenylphosphaborin ligand to transition metals is also investigated. We discovered that the F\(^-\) binding to the boryl moiety leads to an enhancement of the electron donating properties as a phosphine ligand by monitoring the \(\nu(\text{CO})\) frequency of the corresponding Vaska-type rhodium complex.
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Table of Contents

Abstract of the dissertation ii
Acknowledgements iv
Table of Contents vi
List of Figures ix
List of Schemes xiv
List of Tables xvi

Chapter 1 General Introduction: The Development of Boron-Containing and Ferrocene-Containing Catalysts 1

1.1 General Goals 1
1.2 Borane Lewis Acids as Catalysts 1
  1.2.1 Achiral Borane Lewis Acids 1
  1.2.2 Chiral Borane Lewis Acids 5
1.3 Ferrocenes as Frameworks for Catalyst Support 7
  1.3.1 Achiral Ferrocene Frameworks 8
  1.3.2 Planar Chiral Ferrocene Frameworks 9
1.4 Prior Work on Ferrocene-based Lewis Acids and Lewis Pairs 14
1.5 Notes and References 18

Chapter 2 Characterization of Planar Chiral Lewis Acids Derived from Naphthylferrocenes 21

2.1 Introduction 21
2.2 Results and Discussion 22
2.3 Conclusions 34
2.4  Experimental Section 35
2.5  Supporting Information 43
2.6  Notes and References 50

Chapter 3  Stereoseletive Borylation of Planar Chiral Pyridylferrocenes 53
  3.1  Introduction of Directed Metalation 53
  3.2  Results and Discussion 55
  3.3  Mechanistic Study of Borylation 61
  3.4  Conclusions 67
  3.5  Experimental Section 67
  3.6  Supporting Information 80
  3.7  Notes and References 94

Chapter 4  Synthesis and Characterization of Planar Chiral Lewis Pairs Derived from Pyridylferrocenes 98
  4.1  Introduction 98
  4.2  Synthesis and Characterization 99
  4.3  Conclusions 113
  4.4  Experimental Section 115
  4.5  Supporting Information 126
  4.6  Notes and References 136

Chapter 5  Catalytic Application of Planar Chiral Ferrocenyl Lewis Acids: Studies of Lewis Acidity, Substrate Binding and Asymmetric Process 138
  5.1  Introduction 138
  5.2  Synthesis and Characterization 140
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>Lewis Acidity Determination and Substrate Binding</td>
<td>142</td>
</tr>
<tr>
<td>5.4</td>
<td>Asymmetric Catalytic Process</td>
<td>146</td>
</tr>
<tr>
<td>5.5</td>
<td>Experimental Section</td>
<td>148</td>
</tr>
<tr>
<td>5.6</td>
<td>Supporting Information</td>
<td>153</td>
</tr>
<tr>
<td>5.7</td>
<td>Notes and References</td>
<td>164</td>
</tr>
<tr>
<td>Chapter 6</td>
<td><strong>Planar Chiral Diferrocene Systems</strong></td>
<td>167</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>167</td>
</tr>
<tr>
<td>6.2</td>
<td>Results and Discussions</td>
<td>171</td>
</tr>
<tr>
<td>6.3</td>
<td>Conclusions</td>
<td>191</td>
</tr>
<tr>
<td>6.4</td>
<td>Experimental Section</td>
<td>191</td>
</tr>
<tr>
<td>6.5</td>
<td>Supporting Information</td>
<td>205</td>
</tr>
<tr>
<td>6.6</td>
<td>Notes and References</td>
<td>216</td>
</tr>
<tr>
<td>Overall Conclusion</td>
<td>218</td>
<td></td>
</tr>
<tr>
<td>List of Publications</td>
<td>221</td>
<td></td>
</tr>
<tr>
<td>Curriculum Vitae</td>
<td>222</td>
<td></td>
</tr>
</tbody>
</table>
List of Figures

| Figure 1-1. | Structure of tris(pentafluorophenyl)borane and its applications in hydrosilylation, hydrostannylation and polymerization reactions | 3 |
| Figure 1-2. | Representative chiral boranes for asymmetric transformations | 6 |
| Figure 1-3. | A commercially available Dppf ligand and a monodentate phosphinoferrocene | 8 |
| Figure 1-4. | Assignment of the stereochemistry of enantiomeric 1,2-heterodisubstituted ferrocenes according to Schlögl | 10 |
| Figure 1-5. | Planar chirality determination applying CIP protocol | 11 |
| Figure 1-6. | Definition of different structural parameters in this thesis | 11 |
| Figure 1-7. | Chiral resolution of rac-O by preparative chiral HPLC | 12 |
| Figure 1-8. | Products of direct borylation of ferrocene with different equivalents of BBr₃ | 15 |
| Figure 1-9. | Representative ferrocenes with strong Lewis acid and Lewis base substituents | 16 |
| Figure 2-1. | Examples of enantiomerically pure planar chiral ferrocenylboranes | 22 |
| Figure 2-2. | X-ray crystal structure plots of 1 and 2 | 24 |
| Figure 2-3. | Low temperature $^{19}$F NMR spectrum of 5 | 27 |
| Figure 2-4. | $^{19}$F-$^{19}$F 2D gCOSY NMR spectrum of 5 | 27 |
| Figure 2-5. | Variable temperature $^{19}$F NMR spectra of 5 | 29 |
| Figure 2-6. | Variable temperature $^{19}$F NMR spectra of 4 | 30 |
| Figure 2-7. | X-ray crystal structure plots of 4 and 5 | 32 |
Figure 2-8. UV/Vis absorption spectra of 3, 4 and 5

Figure 2-9. Cyclic voltammogram of compound 5

Figure 2-10. Ortep plot of 1

Figure 2-11. Ortep plot of 2

Figure 2-12. Ortep plot of 4

Figure 2-13. Ortep plots of two independent molecules of 5

Figure 2-14. Supramolecular Structure of 5

Figure 2-15. Intermolecular interactions in 4

Figure 3-1. Examples of ortho-lithiation of chiral ferrocenes and the product of borylation of 1,1′-bis(trimethylstannyl)ferrocene (racemate)

Figure 3-2. Ortep plot of (pS)-2Sn

Figure 3-3. 1H NMR spectra (Cp region) of single crystals of (pR)-3

Figure 3-4. Excerpt of the 1H-1H NOESY NMR spectrum for (pR)-3

Figure 3-5. Ortep plots of (pR)-3 and (pS)-3

Figure 3-6. Proposed reaction pathway in the formation of (pR)-3 from (pS)-2Sn

Figure 3-7. Ortep plot of (pR, S)-1

Figure 3-8. Crystal structure plot of [(pS)-4][Al(OC(CF3)3)4]−

Figure 3-9. Multinuclear NMR spectral data

Figure 3-10. Excerpt of the 2D-NOESY spectrum of compound (pR)-3 in C6D6

Figure 3-11. High resolution MALDI-MS data of [(pS)-4][B(C6F5)3Me]−

Figure 3-12. HPLC trace and corresponding UV-visible spectrum of (pS)-2Sn

Figure 3-13. HPLC traces and corresponding UV-visible spectra of 3

Figure 4-1. Examples of FLPs and planar chiral ferrocenes
Figure 4-2. Ortep plots of (pR)-4-Pf, (pR)-4-Mes, (pS)-5-Pf and (pS)-5-Mes

Figure 4-3. Sections of the $^{19}$F-$^{19}$F EXSY NMR spectrum of 5-Pf and illustration of the equilibrium between ‘closed’ and ‘open’ forms of 5-Pf

Figure 4-4. Ortep plots for the ring-opened products 6 and 7

Figure 4-5. Difference Fourier electron density contour map of compound 7

Figure 4-6. Cyclic voltammograms of compounds 4-Pf, 4-Mes, 5-Pf and 5-Mes

Figure 4-7. Ortep plot for compound 4-Pf$^+$

Figure 4-8. Ortep plot for compound 5-Cl

Figure 4-9. MALDI-MS data of compound 4-Mes

Figure 4-10. Comparison of UV-Vis absorption spectra in CHCl$_3$

Figure 4-11. Chiral HPLC trace and UV-Vis spectrum of 4-Pf (40% ee)

Figure 4-12. Chiral HPLC trace and UV-Vis spectrum of (pR)-4-Pf

Figure 4-13. Chiral HPLC trace and UV-Vis spectrum of (pR)-4-Mes

Figure 4-14. Chiral HPLC trace and UV-Vis spectrum of (pS)-5-Pf

Figure 4-15. Chiral HPLC trace and UV-Vis spectrum of (pS)-5-Mes

Figure 4-16. Chiral HPLC trace and UV-Vis spectrum of (pS)-6

Figure 4-17. Chiral HPLC trace and UV-Vis spectrum of (pS)-7

Figure 4-18. $^{19}$F-$^{19}$F EXSY spectrum of 4-Pf at 80 °C in d$_8$-toluene

Figure 4-19. $^{19}$F-$^{19}$F EXSY spectrum of 5-Pf at 80 °C in d$_8$-toluene

Figure 5-1. Examples of highly Lewis acidic organoboranes

Figure 5-2. Expansion of the Cp region of the $^1$H NMR spectra for a) (pR)-2 (exo and endo-isomers), b) (pR)-2 + B(C$_6$F$_5$)$_3$ and c) (pR)-3$^+$ (CDCl$_3$) and photographs illustrating the associated color change
Figure 5-3. Ortep plot of (pR)-3⁺ 142
Figure 5-4. Competitive binding of (pR)-3⁺ and B(C₆F₅)₃ to Et₃PO examined by $^{31}$P NMR spectroscopy 143
Figure 5-5. Competitive binding of (pR)-3⁺ and B(C₆F₅)₃ to Et₃PO examined by $^{11}$B NMR spectroscopy 144
Figure 5-6. VT $^1$H NMR spectra for a mixture of (pR)-3⁺ and Et₃SiH in CDCl₃ 145
Figure 5-7. Ortep plots of Substrate binding of (pR)-3⁺ with acetone, acetophenone and hydride 146
Figure 5-8. Data corresponding to determination of enantiomeric excess of catalysis products 155
Figure 5-9. Chiral HPLC analysis for compound (pR)-2 155
Figure 5-10. Complete $^1$H NMR spectra of (pR)-2, (pR)-2 + B(C₆F₅)₃, and (pR)-3⁺ in CDCl₃ 156
Figure 5-11. 2D-NOESY spectra of compound (pR)-2 in C₆D₆ 157
Figure 5-12. Comparison of UV-Vis spectra of (pS)-1, (pR)-2 and (pR)-3⁺ 158
Figure 5-13. High-resolution MALDI-MS spectra of compound (pR)-2 159
Figure 5-14. Competitive binding of (pR)-3⁺ and B(C₆F₅)₃ to acetophenone 160
Figure 5-15. Ortep plot of the second independent molecule of (pR)-3⁺ 161
Figure 5-16. Ortep plots of two independent molecules of (pR)-3⁺(acetophenone) 162

Figure 6-1. Representative examples of element-bridged diferrocenes 168
Figure 6-2. Examples of ambiphilic ligands, the different coordination modes and the targeted diferrocenylphosphaborin compound T₂ 171
Figure 6-3. Comparison of NMR data for cycles 2-SnSn, 2-SnSi and 2-BSi 174
Figure 6-4. Ortep plots of 2-SnSi and 2-BSi

Figure 6-5. Cycle voltammetry and square-wave voltammetry data for 2-SnSn, 2-SnSi, 2-BSi

Figure 6-6. Solid state structure of a doubly oxidized species derived from 2-BSi

Figure 6-7. Ortep plots of 3a-SnP and 3b-SnP

Figure 6-8. Ortep plots of 4-BP and 5-BP

Figure 6-9. Square-wave voltammetry data for 3b-SnP, 4-BP and 5-BP

Figure 6-10. \(^1\)H and \(^{31}\)P NMR spectra for complex (5-BP)\(_2\)Rh(CO)Cl

Figure 6-11. Cyclic voltammetry and square-wave voltammetry data for complex (5-BP)\(_2\)Rh(CO)Cl

Figure 6-12. IR spectra for complex (5-BP)\(_2\)Rh(CO)Cl and after addition of F\(^-\)

Figure 6-13. Multinuclear NMR spectral data

Figure 6-14. UV/Vis absorption spectra of cycles 2-SnSn, 2-SnSi and 2-BSi

Figure 6-15. Maldi-MS data of compounds 2-SnSn and 2-SnSi

Figure 6-16. Maldi-MS data of compound 3b-SnP

Figure 6-17. Maldi-MS data of compound 3a-SnP

Figure 6-18. Maldi-MS data of compound 4-BP

Figure 6-19. Ortep plot of 1-Sn

Figure 6-20. Disorder in the solid state of 2-SnSi

Figure 6-21. Chiral HPLC traces and the corresponding UV-Vis spectra of 2-SnSi, 2-BSi, 3a-SnP, 3b-SnP and 4-BP
List of Schemes

Scheme 1-1. The first example of dihydrogen activation by an intramolecular FLP

Scheme 1-2. The interchange between classical Lewis pair and FLP and its reaction with dihydrogen

Scheme 1-3. Activation of carbonyl groups by a Lewis acidic borenium cation intermediate

Scheme 1-4. An example of a planar chiral ferrocene-based Ir catalyst used for the asymmetric hydrogenation of an imine

Scheme 1-5. Synthesis of rac-O

Scheme 1-6. Synthesis of Josiphos ligands and stepwise modification of Kagan’s sulfinate

Scheme 1-7. Reaction between ferrocene and Piers’ borane to give S

Scheme 1-8. Synthesis of rac-W and its chiral resolution by N-methylpseudoephedrine

Scheme 2-1. Synthesis of the enantiomerically pure organometallic naphthylferrocene derivatives 1 and 2

Scheme 2-2. Synthesis of highly Lewis acidic planar chiral ferrocenylboranes

Scheme 3-1. Synthesis of planar chiral pyridylferrocenes (pS)-2Sn and (pS)-2Hg

Scheme 3-2. Synthesis and HPLC traces of planar chiral (pS)-3 and (pR)-3

Scheme 3-3. Reactivity of (pS)-2Sn toward selected Lewis and Brønsted acids

Scheme 3-4. Reaction of FcLu with PhBCl₂
Scheme 4-1. Synthesis of planar chiral \((pS)\)-\textbf{2-Sn} and \((pS)\)-\textbf{3-Hg}


Scheme 4-3. Reactions of \((pS)\)-\textbf{5-Pf} and \((pS)\)-\textbf{5-Mes} with H\textsubscript{2}O

Scheme 4-4. Preparative oxidation of \((pR)\)-\textbf{4-Pf} and \((pS)\)-\textbf{5-Mes}

Scheme 5-1. Synthesis of \((pR)\)-\textbf{3+}

Scheme 5-2. Hydrosilylation of ketones catalyzed by \((pR)\)-\textbf{3+}

Scheme 6-1. Synthesis of planar chiral tin-bridged diferrocene \textbf{1-Sn}

Scheme 6-2. Synthesis of planar chiral cycles \textbf{2-SnSn} and \textbf{2-SnSi}

Scheme 6-3. Synthesis of planar chiral cycle \textbf{2-BSi}

Scheme 6-4. Synthesis of planar chiral cycles \textbf{3a-SnP} and \textbf{3b-SnP}

Scheme 6-5. Synthesis of the ambiphilic ligand \textbf{5-BP}

Scheme 6-6. Synthesis of a Vaska-type rhodium compound
List of Tables

Table 2-1. Line shape analysis and coalescence temperatures for 4 and 5 28
Table 2-2. Details of X-ray crystal structure analyses of complexes 1, 2, 4 and 5 48
Table 2-3. Coalescence temperatures for compounds 4 and 5 49
Table 2-4. Line shape analysis results of compounds 4 and 5 49
Table 3-1. Crystal data and structure refinement details for (pR, S)-1, (pS)-2Sn, (pS)-3, (pR)-3, and [(pS)-4][Al(OC(CF3)3)4]− 80
Table 4-1. Crystal data and structure refinement details for 4-Pf, 5-Pf, 4-Mes, 5-Mes, 4-Pf+, 5-Cl, 6 and 7 126
Table 5-1. Hydrosilylation of different ketones with silanes in the presence of (pR)-3+ as catalyst 147
Table 5-2. Details of X-ray analyses of (pR)-3 and (pR)-3+(acetophenone) 163
Table 6-1. X-ray structural parameters of 2-SnSi and 2-BSi 175
Table 6-2. Redox potentials of 2-SnSn, 2-SnSi and 2-BSi 178
Table 6-3. X-ray structural parameters of 3a-SnP and 3b-SnP 180
Table 6-4. X-ray structural parameters of 4-BP and 5-BP 182
Table 6-5. Redox potentials of 3b-SnP, 4-BP and 5-BP 185
Table 6-6. Redox potentials of (5-BP)2Rh(CO)Cl 188
1.1 General Goals
The general goal of my PhD research was to develop new chiral ferrocene compounds featuring highly Lewis acidic borane moieties. The chirality of these Lewis acids is derived from the rigid ferrocene framework. The research initially focused on the synthesis of highly Lewis acidic organoboranes and was then expanded to the area of planar chiral Lewis pairs bearing both Lewis acid (LA) and Lewis base (LB) moieties. These systems are very interesting due to the diverse modes of LA-LB and boron-iron interactions that could greatly impact the properties and enable applications in a variety of research fields.

This chapter provides an overview of the prior research on (a) organoboranes as Lewis acids, (b) the use of ferrocene as a framework for chiral catalyst, and (c) ferocene-based Lewis acids and Lewis pairs.

1.2 Borane Lewis Acids as Catalysts

1.2.1 Achiral Borane Lewis Acids
Borane, in the simplest form BH₃, is widely recognized by organic chemists for its extensive applications in reduction of unsaturated C-C, C-N, C-O double bonds, as well as C-C triple bonds.¹ Lewis acidic boron halides (BX₃) are utilized in organo-synthetic applications including dealkylation of ethers, condensation reactions, and as catalysts for Friedel-Crafts-type reactions and other acid-related chemistry.² In most of the cases,
these processes require the use of stoichiometric amounts of Lewis acid to activate the substrates under anhydrous conditions. Recent years have seen a growing interest in the synthesis of more moisture-tolerant boron-based catalysts by installation of sterically bulky and electronically withdrawing substituents such as pentafluorophenyl groups onto the boron center. Quite a number of reactions such as Mukaiyama aldol reactions, Diels-Alder reactions and others proceed smoothly in the presence of catalytic amounts of tris(pentafluorophenyl)borane \([\text{B}(\text{C}_6\text{F}_5)_3, \text{A}]\). Piers and coworkers noted that \(\text{B}(\text{C}_6\text{F}_5)_3\) catalyzes the hydrosilylation reaction of ketones and imines with hydrosilanes through a unique silane activation pathway. Yamamoto and coworkers further explored the hydrostannylation of alkynes, allenes and alkenes by employing the same catalyst. Moreover, \(\text{B}(\text{C}_6\text{F}_5)_3\) also serves as an excellent co-catalyst for Ziegler-Natta type polymerizations. The perfluoroaryl borane is capable of abstracting alkyl or hydride anions, thereby generating activated Ziegler-Natta catalysts based on metallocene and quasimetalloocene frameworks. When compared to other Lewis acidic cocatalysts such as trityl \((\text{Ph}_3\text{C}^+)\) and MAO (methylaluminoxane), the boron species have the advantage that the steric and electronic properties can be tuned by modifying the perfluoroaryl groups to achieve high activities for polymerization (Figure 1-1).
More recently, the area of so-called “Frustrated Lewis Pairs” (FLPs) has developed dramatically since Stephan’s pioneering research. In 2006, Stephan incorporated a bulky phosphine and highly acidic borane into the same molecule (B) and utilized the unquenched reactivity for the heterolytic cleavage of dihydrogen (Scheme 1-1). Sterically demanding Lewis acids (e.g. organoboranes, organoaluminum species, silylium cations) and bulky Lewis bases (e.g. phosphines, amines, pyridines, carbenes) proved to be excellent candidates to compose such types of systems. B(C₆F₅)₃ has been most widely used as the Lewis acid component due to its high Lewis acidity, stability and accessibility.
While initial reports pointed towards the importance of separating Lewis acids and bases by using steric hindrance, more recent studies indicate that there is no strict boundary between conventional Lewis pairs and FLPs. For example, Stephan et al. investigated a system consisting of B(C₆F₅)₃ and 2,6-dimethylpyridine. The Lewis adduct exists in thermal equilibrium with the free Lewis acid and base and is therefore capable of activating small molecules such as dihydrogen or THF (Scheme 1-2).

Scheme 1-1. The first example of dihydrogen activation by an intramolecular FLP.

Scheme 1-2. The interchange between classical Lewis pair and FLP and its reaction with dihydrogen.

In fact, since the first reports of the successful cleavage of dihydrogen by FLPs, a variety of systems have been developed and explored for the activation of alkynes, NO, CO₂, and other small molecules. More recently, much effort has been focused on the design of FLPs for catalytic processes such as hydrogenation, hydrosilylation and hydroboration of ketones, imines and olefins, as well as the polymerization of olefins.
1.2.2 Chiral Borane Lewis Acids

Various chiral organic frameworks containing Lewis acidic borane moieties have been explored as catalysts for asymmetric transformations. Early examples include Brown’s pinene-based organohaloboranes \(^{10}\) \((\text{C})\), Hawkins’ naphthylcyclohexyl-dichloroboranes \(^{11}\) \((\text{D})\) and organoboron-modified binaphthyl species first studied by Kaufmann \((\text{G})\) and later by Yamamoto \((\text{E})\) and Piers \((\text{F})\).\(^{12}\) These and related chiral Lewis acidic organoboranes serve as excellent catalysts for enantioselective Diels Alder reactions.\(^{11,12d,13}\) Although the initial examples showed their high effectiveness for stereoselective transformations, the poor stability remained a drawback. To overcome this disadvantage, the halide substituents were replaced with pentafluorophenyl groups. More recently, Oestreich and coworkers reported the synthesis and Lewis acidity study of a binaphthyl-based cyclic borane \((\text{H})\) and investigated its applications in hydrosilylation and dehydrogenative coupling reactions.\(^{14}\) A further communication by Klankermayer demonstrated that camphor can serve as a suitable structural motif \((\text{I})\). These chiral boranes were tested as catalysts for metal-free hydrogenation of imines and showed good stereoselectivity. Together with bulky Lewis bases, the camphor-derived chiral systems form FLPs that activate dihydrogen and serve as catalysts for asymmetric hydrosilylation of imines (Figure 1-2).\(^{15}\)
Compared to these purely organic systems, main group Lewis acid catalysts supported by metallocene framework are less developed, not to mention that examples for planar chiral versions remain exceedingly rare. One of the reasons is perhaps that the Lewis acid species tend to be susceptible to oxidative degradation when attached to the electron rich metallocene. This could pose a major problem for purification and chiral resolution. One of the successful examples was reported by Fu and coworkers. They synthesized a planar chiral azaborolyl heterocycle (J) which facilitates the asymmetric aldol reaction of silyl ketene acetics with aldehydes with de higher than 95%. Interestingly, the mechanism likely involves a Lewis acidic cationic boron species generated after the dissociation of the tosylate group, which then activates the carbonyl group. However, because of the
high stability of the complexed product, this stereoselective reaction can only proceed with a stoichiometric amount of the Lewis acid (Scheme 1-3).

Scheme 1-3. Activation of carbonyl groups by a Lewis acidic borenium cation intermediate.

1.3 Ferrocenes as Frameworks for Catalyst Support

The exploration of organometallic chemistry was fueled by the discovery of ferrocene by Pauson and Kealy\textsuperscript{17} and the confirmation of its sandwich-type structure by Woodward, Wilkinson and Fischer about 6 decades ago.\textsuperscript{18} This organoiron species exhibits a distinct high stability and aromaticity, owing to a new coordination type—the $\eta^5$ (pentahapto) sandwich structure. Over the past decades, the area of organometallic chemistry has developed dramatically. There are excellent and comprehensive reviews on the topic of ferrocene and its applications in the fields of catalysts, pharmaceuticals, materials chemistry and others.\textsuperscript{19} The following brief summary will focus primarily on the most recent progress with planar chiral ferrocene catalysts, closely related to our research topics but not covered in the previous reviews.
1.3.1 Achiral Ferrocene Frameworks

Ferrocene is a typical aromatic compound, but it exhibits exciting and unique characteristics when compared to other ordinary aromatics such as benzene, mostly resulting from its negative charge on the Cp (cyclopentadienyl) ring and the sandwich type coordination. For instance, it undergoes electrophilic substitution much faster than the benzene analog; the presence of two Cp rings also provides much more diverse coordination modes when ferrocene is used as a ligand backbone. An example is bis(diphenylphosphino)ferrocene (Dppf, L),\textsuperscript{19a, 19c} which is a versatile ligand for transition metal catalyzed reactions (Figure 1-3). The free ligand itself and its transition metal complexes have been commercialized and utilized as catalysts for the formation of C-C bonds. The presence of electron rich Cp rings not only renders the phosphine to be a powerful ligand, but flexible rotation allows for different conformations when coordinated to metal centers.

There are only a few examples of achiral ferrocenes in FLP type chemistry. A 1-di-tert-butylphosphine ferrocene derivative (M) was synthesized by Stephan and co-workers and FLP type behavior in combination with a strong Lewis acid was demonstrated for the activation of dihydrogen (Figure 1-3).\textsuperscript{20}

\[ \text{Dppf} \]

\[ \text{M} \]

\textbf{Figure 1-3.} A commercially available Dppf ligand and a monodentate phosphinoferrocene.
1.3.2 Planar Chiral Ferrocene Frameworks

The three dimensional structure of ferrocene results in planar chirality in the case of 1,2- or 1,3- heterodisubstituted species. These planar chiral ferrocene derivatives have been an important tool for asymmetric transformations in academia as well as industry. Perhaps the most successful example is the Josiphos ligand class. By employing an Ir catalyst with (R,Sp)-Xyliphos (N) as ligand, the asymmetric hydrogenation of an imide to the corresponding chiral amine is accomplished as showed in Scheme 1-4. The latter is an important intermediate for the synthesis of the herbicide (S)-metolachlor. The final product is produced with a volume of 10000 tons per years.21

Scheme 1-4. An example of a planar chiral ferrocene-based Ir catalyst used for the asymmetric hydrogenation of an imine.

The original nomenclature of planar chirality for ferrocene species is somewhat arbitrary but easy to define and follow. The method according to Schlögl22 notes that when a molecule is viewed from the top of the substituted Cp ring, the planar chirality is determined by the order going from the substituent with high priority to that with lower priority. For example, if the order is clockwise the molecule has a “R” configuration otherwise “S”. Stereodescriptors “Rp” and “Sp” are used to denote planar chirality (Figure 1-4). In addition, “RX” and “SX” are used to identify noncarbon chirality centers. Literature known compounds will be named consistently using this method in this thesis to minimize confusion.
However, in order to avoid ambiguity with phosphorus chirality centers, a more sophisticated nomenclature, the Cahn, Ingold and Prelog (CIP) protocol\textsuperscript{23} could be followed. In this method (Figure 1-5), a pilot atom with the highest priority of the atoms needs to be identified. In the example of 1,2-disubstituted ferrocenes (\textit{vide infra}) with a boron and tin substituent, C1 (attached to the heavier Sn) is identified as the pilot atom. Next, C1 is considered to be connected to four atoms as a regular tetrahedral carbon, and the substituents are assigned in order of highest priority if there is a choice (Sn\textsuperscript{a} > Fe\textsuperscript{b} > C\textsuperscript{c} > C\textsuperscript{d}). When viewed from the side of the pilot atom, if the three atoms form a clockwise direction in order of priority, the chirality is assigned as $pR$, otherwise it is assigned as $pS$. This protocol is adopted in our recent publications and also for most of the planar chiral systems described in this thesis.

\textbf{Figure 1-4.} Assignment of the stereochemistry of enantiomeric 1,2-heterodisubstituted ferrocenes according to Schlögl (priority $X > Y$).
In addition, some structural parameters are defined herein with the aim to understand the framework-substituent interactions (Figure 1-6): 1) dip angle $\alpha$ is the bending of the substituent out of the Cp ring, which allows us to investigate the interaction between the iron center and the Lewis acidic pendant group; 2) tilt angle $\beta$ is the angle of two distorted Cp rings under certain degree of steric hindrance or restriction; 3) bridge angle $\gamma$ is the bond angle of $\text{C}_\text{Cp}-\text{X}-\text{C}_\text{Cp}'$, with the bridging atom X.

Planar chiral ferrocene derivatives can be obtained starting either from achiral or chiral precursors. In the first synthetic protocol, the functionalization of the ferrocene framework is generally not stereoselective, and further chiral resolution methods are required for the separation into individual enantiomers. Fu et al. noted that reaction of FeCl$_2$ first with Cp*Li and then with a lithiated DMAP-fused Cp ligand species gives a
racemic mixture of rac-O (Scheme 1-5). This racemate could be resolved by preparative chiral HPLC and the enantiomerically pure product was employed as chiral catalyst for asymmetric transformations (Figure 1-7). More recently, Fu and co-workers introduced planar chiral versions of azaferrocene and DMAP derivatives as enantioselective nucleophilic catalysts and successfully applied them in the addition of alcohols to ketenes, rearrangement of O-acylated enolate and acylation of alcohols by anhydrides.\textsuperscript{24}

\[
\text{FeCl}_2 \overset{1)}{(C_5\text{Me}_5)\text{Li}} \rightarrow \text{rac-}\text{O}
\]

**Scheme 1-5.** Synthesis of rac-O.

**Figure 1-7.** Chiral resolution of rac-O by preparative chiral HPLC.

Chiral resolution of a racemate has the advantage that it does not involve chiral synthesis from the precursor. Moreover, in many cases both of the enantiomers can be utilized, which improves atom economy. However, the limitation of this method is that it
relies heavily on the performance of chiral HPLC columns and the difficulty to find suitable chiral resolving reagents. These problems could be critical if the planar chiral compounds are air and moisture sensitive, which is a common issue with highly Lewis acidic systems. To overcome these drawbacks and develop a more general protocol towards planar chiral ferrocenes, chiral auxillaries were introduced as substituents to one or both Cp rings. They serve as directing groups for diastereoselective ortho-directed lithiation. Among the very first examples, Ugi and co-workers introduced chiral enantiomers of N,N-dimethyl-1-ferrocenylethylamine (Ugi’s amine) as the starting material for diastereoselective ortho-directed metalations, which proved to be a significant breakthrough in ferrocene chemistry. Ugi’s amine itself is resolved by complexation with (R)-(+) -tartaric acid. It can be readily deprotonated by n-BuLi in diethyl ether at 27 °C, quenched by addition of an electrophile to form the products with diastereomeric excess values up to 92%. The diastereomer can be purified by simple column chromatography or crystallization. By using this method, planar chiral ferrocenes were first introduced as ligands for catalysts. In the 1990s, a series of planar chiral diphosphine ferrocenes were developed, namely the Josiphos family of ligands. This family of ligands, featuring the general structure shown in Scheme 1-6, has been applied to a variety of reactions including asymmetric reduction of C= C, C=O and C=N unsaturated double bonds. Alternatively, a chiral sulfinate group can be added as an auxiliary. The latter has the advantage that after derivatization of the ortho position, the sulfinate group itself can be readily replaced by lithiation with tert -butyl lithium or magnesiation with Grignard species and subsequent treatment with electrophiles (Scheme
Throughout the thesis, we will follow Kagan’s synthesis, which provides excellent control for the stepwise introduction of different substituents.

Scheme 1-6. a) Synthesis of Joshiphos ligands from Ugi’s amine as a chiral precursor. b) Stepwise modification of Kagan’s sulfinate for the preparation of bifunctional ferrocenes with a controlled geometry.

1.4 Prior Work on Ferrocene-based Lewis Acids and Lewis Pairs

Different from the ferrocene-based ligands and Lewis base catalysts, ferrocenyl Lewis acids can be obtained by direct electrophilic borylation of ferrocene. Treatment of ferrocene with different amounts of BBr₃ leads to different degree of borylation (Figure 1-8). Ferrocene also reacts readily with HB(C₆F₅)₂ at 80 °C to give (S) after elimination of a dihydrogen molecule (Scheme 1-7).
Figure 1-8. Products of direct borylation of ferrocene with different equivalents of BBr₃.

Scheme 1-7. Reaction between ferrocene and Piers’ borane to give S.

The Lewis acid S was initially reported by Piers in 2001 and a detailed the investigation of the Fe-B interaction was provided. Aldridge et al. showed more recently that (S), combined with tri-tert-butylphosphine, can be used to detect nitrous oxide with dual sensory signal output. The geometry of the boron changed from trigonal to tetrahedral conformation before and after complexation with nitrous oxide, which is accompanied by colorimetric and electrochemical changes of the ferrocenyl unit. A series of related highly Lewis acidic species was achieved by Oestreich and co-workers by incorporation of tricoordinate silylum cations (T). Different substituents, including alkyl and aryl groups, were introduced on the silicon atom to investigate the influence on Lewis acid strength and catalytic performance in Diels Alder reactions.
A more intriguing but less explored direction is to develop systems that bear both Lewis acid and base moieties. One example that was reported by Bourissou is a ferrocene compound with a diphenylphosphino and dimesitylboryl moiety (U). The dimesitylboryl group is moderately Lewis acidic, and unlikely to promote FLPs behavior. Nonetheless, it has been applied as an ambiphilic ligand in a Ru-catalyzed hydroformylation.\textsuperscript{31} Interestingly, Aldridge succeeded in generating the planar chiral version of this Lewis pair (V).\textsuperscript{32} Due to the steric hindrance, the interaction between B and P is absent. To our knowledge, small molecule activation or catalytic applications have not been studied with this class of compounds (Figure 1-9).

![Figure 1-9. Representative ferrocenes with strong Lewis acid and Lewis base substituents.](image)

Another unique example is the synthesis and resolution of a planar chiral bifunctional Lewis acid by Jäkle and co-workers.\textsuperscript{33} Low temperature borylation of 1,1’-bis(trimethylstannyl)ferrocene with BCl\textsubscript{3} leads to 1-stannyl-2-borylferrocene (\textit{rac-W}) as the major product (Scheme 1-8). This result is remarkable, because for other silylated or stannylated aromatics cleavage of the element-carbon bond in an \textit{ipso}-borodemetalation tends to occur much faster than activation of the C-H bond. The unique reactivity is attributed to the directing effect of the stannyl group, the ability of the iron center to
mediate proton transfer, and the presence of a second stannyl moiety that acts as a good leaving group. The reaction, however, produces a racemate that has to be resolved into the individual enantiomers by the introduction of a chiral resolving reagent [(+)-N-methylpseudoephedrine]. This novel class of bifunctional Lewis acids facilitates the conversion of a ketone into the asymmetric allylated alcohol product with good ee values.


The research discussed above provides a good starting point for the investigation of ferrocene-based planar chiral Lewis acids and Lewis pair. The survey of the recent literature reveals that a more general protocol for the synthesis of these chiral compounds is lacking. We envisioned that ferrocene would provide a rigid support for Lewis acids and FLP catalyst. Kagan’s protocol is ideal to access a variety of planar chiral ferrocenes with different features – not only systems with sterically demanding chiral boranes, but also planar chiral Lewis pairs with distinct steric and electronic properties. This dissertation will describe their stereo-selective synthesis, structural investigation, and asymmetric catalytic applications.
1.5 Notes and References


Chapter 2 Synthesis and Characterization of Planar Chiral Lewis Acids

Derived from Naphthylferrocenes

2.1 Introduction

As discussed in Chapter 1, highly Lewis acidic organoboranes play key roles as reagents and catalysts in organic synthesis. Especially important for organic transformation are chiral derivatives. In an effort at enhancing the Lewis acidity of the boron sites, a backbone-perfluorinated binaphthylborane derivative has also been introduced by Piers and co-workers. Soderquist and co-workers prepared enantiomerically pure 9-borabicyclo[3.3.2]decane derivatives and studied their applications in various organic transformations, including asymmetric allyl-, crotyl-, allenyl-, propargyl-, and hydroboration reactions. Finally, highly Lewis acidic organoboranes are of much interest for transition metal-free hydrogenation reactions. Stephan and co-workers first demonstrated that frustrated Lewis pairs consisting of a combination of a strong Lewis acid and sterically hindered Lewis base are capable of activating dihydrogen and other small molecules. Recent studies have been aimed at utilizing this unusual reaction for stereoselective hydrogenation reactions.

We have focused our attention on ferrocenylborane-based Lewis acids. One motivation has been that preparation of planar chiral derivatives could open up a new entry into enantioselective Lewis acid catalysts. Attractive is also that the Lewis acidity of the borane moiety can be tuned through reversible redox chemistry at the metal centers. Prior efforts by our group involved studies on the binding properties of

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*a This chapter is adapted from a journal publication*
heteronuclear bidentate 1-stannyl-2-borylferrocene derivatives, which are obtained in their racemic form via a rearrangement reaction from 1,1'-bis(trimethylstannyl) ferrocene and boron halides RBCl₂ (R = Cl, Ph, C₆F₅). We have demonstrated that the bidentate Lewis acid 1,2-Fc(BClMe)(SnMe₂Cl) (A) can be resolved into its constituent planar chiral enantiomers and subsequently employed them in the enantioselective allylation of ketones. In this context, we would like to also note that Aldridge and co-workers recently obtained compound (B) in enantiomerically pure form via regioselective ortho-metalation and subsequent diastereomer separation by recrystallization.

![Figure 2-1. Examples of enantiomerically pure planar chiral ferrocenylboranes (Mes=2,4,6-trimethylphenyl, Tol=4-methylphenyl).](image)

We describe here a high-yielding enantioselective synthesis route to the planar chiral naphthyl ferrocenylborane 1,2-Fc(Np)(BCl₂), which in turn serves as a versatile precursor to other chiral organoborane Lewis acids through subsequent transmetallation reactions.

### 2.2 Results and Discussion

(Sp)-2-(1-Naphthyl)-1-(trimethylstannyl)ferrocene (I) was prepared in analogy to a literature procedure for the synthesis of (Sp)-2-(1-naphthyl)-1-(tributylstannyl)ferrocene. Reaction of (Sp,S₈)-2-(1-naphthyl)-1-(p-
tolylsulfanyl)ferrocene with \( t \)-butyllithium followed by quenching with Me₃SnCl gave 1 in 60% yield after recrystallization from methanol (Scheme 2-1). The \(^1\)H and \(^{13}\)C NMR spectra of 1 show patterns that are consistent with a 1,2-disubstituted ferrocene derivative, and a signal at \( \delta \approx 7.1 \) in the \(^{119}\)Sn NMR spectrum confirms the attachment of the trimethylstannyl group. The absolute configuration of 1 as the \( S_p \) isomer was assigned from the single crystal X-ray structure, which confirms stereoselective replacement of the sulfinate moiety (Figure 2-2a). Two independent molecules are found in the unit cell. The angle between the Cp and the naphthyl group is 72.27(9)° and 83.22(10)°, respectively, and the orientation of the naphthyl group matches that proposed for related compounds\(^{12c}\) based on NMR studies.

![Scheme 2-1](image)

**Scheme 2-1.** Synthesis of the enantiomerically pure organometallic naphthylferrocene derivatives 1 and 2.

Treatment of aryltin species with HgCl₂ is generally known to lead to highly selective tin-mercury exchange.\(^{7e,13}\) Indeed, reaction of 1 with HgCl₂ in acetone led to facile formation of 2 in 84% isolated yield. The \(^1\)H NMR shows three signals at \( \delta \approx 4.82 \) (dd), 4.64 (psd), and 4.30 (dd), as expected for a 1,2-disubstituted Cp ring, and a singlet at 4.33 for the free Cp ring. Single crystal X-ray analysis confirmed that the \( S_p \) stereochemistry is unchanged relative to that of the Sn precursor (Figure 2-2b). The angle between the Cp
ring and the naphthyl group of 77.1(1)° is similar to that found for 1. The Hg(1)-C(1) (2.024(5) Å) and Hg(1)-Cl(1) distances (2.312(1) Å) are comparable to those found in chloromercury ferrocene and other related organomercury compounds. The C1-Hg1-Cl1 angle of 179.0° indicates an almost perfect linear coordination geometry at Hg. In the solid state, 2 exhibits an interesting supramolecular structure with infinite helical chains that arise from weak intermolecular Hg1···Cl1 contacts (3.298(1) Å) as shown in Figure 2-2c.

**Figure 2-2.** a) X-ray crystal structure plot of 1. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-C1 2.135(3), C2-C11 1.488(4), C1-C2-C11 124.7(3), Sn1-C1-C2 125.6(2). b) X-ray crystal structure plot of 2. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Hg1-C1,
2.024(5), Hg1-C11 2.312(1), C2-C11 1.489(7), C1-Hg1-C11 179.0(1), C1-C2-C11 122.4(4), Hg1-C1-C2 123.0(3). c) Illustration of the extended structure of 2 in the solid state.

We then studied the reactivity of these organometallic naphthylferrocene derivatives towards boron halides. Reaction of 1 with BBr₃ in CDCl₃ at –35 °C resulted in the formation of a mixture of the 1,1’- and 1,3-disubstituted species according to ¹H NMR analysis of the crude product mixture (ratio of 57:43) (see Experimental Section). Presumably, rearrangement occurs through interannular proton transfer, as previously reported for the reaction of 1,1’-bis(trimethylstannyl)ferrocene with boron halides.⁷ In contrast, reaction of 2 with one equiv of BCl₃ at –30 °C in hexanes resulted in clean conversion to the chiral Lewis acid Rₚ-1,2-NpFcBCl₂ (3) in a good yield of 82%. The formation of 3 was confirmed by ¹H, ¹³C and ¹¹B NMR, high resolution MS, and elemental analysis. In the Cp region of the ¹H NMR spectrum of 3 the pattern of a 1,2-disubstituted ferrocene was retained with three signals at 4.63 (dd), 4.57 (br), and 4.38 (br) for the substituted Cp ring and a singlet at 4.02 for the free Cp ring. The ¹¹B NMR resonance at δ 49 is in a similar range as that reported for the achiral analog FcBCl₂ (δ 50.5)¹⁵.

Scheme 2-2. Synthesis of highly Lewis acidic planar chiral ferrocenylboranes.
The novel planar chiral diarylchloroborane $R_{p-1,2}$-$\text{NpFeBCl(C}_6\text{F}_5)$ (4) and triarylborane species $R_{p-1,2}$-$\text{NpFeB(C}_6\text{F}_5)_2$ (5) were obtained by treatment of 3 with 1 and 2 equiv of pentafluorophenyl copper$^{16}$, respectively (Scheme 2-2). Compounds 4 and 5 were isolated as dark red microcrystalline solids in 80 and 84% yield, respectively. Their structures were confirmed by multinuclear NMR, high resolution MALDI-TOF MS or elemental analysis, and single crystal X-ray analysis. The $^{11}$B NMR shifts of 4 (55 ppm) and 5 (54 ppm) are in a similar range as that reported by Piers for the achiral analog FcB($\text{C}_6\text{F}_5)_2$ (53 ppm)$^9$, which is consistent with the presence of a weak Fe$\rightarrow$B interaction (see vide infra).$^{17}$ At room temperature, the $^{19}$F NMR spectrum of 4 shows three slightly broadened resonances at $\delta$–130, –154.1, –162.7. In contrast, 5 shows two sets of strongly broadened $^{19}$F NMR peaks, one of which is attributed to the $\text{C}_6\text{F}_5$ ring (A) adjacent to the naphthyl moiety and the other to the $\text{C}_6\text{F}_5$ ring (B) that is pointing away. The apparent signal broadening suggests hindered rotation about the B-C(Cp) and/or the B-C($\text{C}_6\text{F}_5)$ bonds. We performed variable temperature $^{19}$F NMR studies to further examine the fluxional behavior of compounds 4 and 5.
Figure 2-3. Low temperature $^{19}$F NMR spectrum of 5 (CDCl$_3$, 470.4 MHz, $-60 \, ^\circ C$).

Figure 2-4. $^{19}$F-$^{19}$F 2D gCOSY NMR spectrum of 5 (CDCl$_3$, $-50 \, ^\circ C$).
For compound 5, two distinct sets of resonances of equal intensity were observed for the C₆F₅ moieties at −60 °C (Figure 2-3). They were assigned based on 2D ¹⁹F-¹⁹F NMR spectroscopy (see Figure 2-4). Ring (A) shows five ¹⁹F NMR resonances due to hindered rotation about the C₆F₅ ring (A), which is a result of the presence of the adjacent naphthyl moiety. In contrast, ring (B) shows only one signal for the meta-fluorines and strongly broadened signals for the ortho-fluorines, indicating a much lower barrier of rotation. The energy barriers were determined from both line shape analysis¹⁸ and coalescence temperature methods¹⁹ (see Figure 2-5). Analysis of the temperature dependence of the line shape of the para-F atoms provides information on the B-C(Cp) barrier, while information on the rotational barrier of the C₆F₅ ring (A) can be obtained from line shape analysis for the ortho- or meta-F atoms (Table 2-1). A similar barrier was deduced for exchange of the meta-fluorines of ring A (ΔG₂⁹⁸ = 58.9(1) kJ mol⁻¹) and the para-fluorines of rings A/B (ΔG₂⁹⁸ = 58.3(6) kJ mol⁻¹), which indicates that the rotation of ring (A) and interchange between rings (A) and (B) require about the same energy, while rotation of ring (B) is comparatively much more facile (ΔG₂⁸⁸ = 39.8(6) kJ mol⁻¹ for ring B; cf. ΔG₂⁸⁸ = 55.5(8) kJ mol⁻¹ for ring A).

**Table 2-1.** Results from line shape analysis and coalescence temperatures for 4 and 5.

<table>
<thead>
<tr>
<th>Compd</th>
<th>Probe</th>
<th>ΔH₂⁹⁸[a] [kJ mol⁻¹]</th>
<th>ΔS₂⁹⁸[a] [J mol⁻¹ K⁻¹]</th>
<th>ΔG₂⁹⁸[a] [kJ mol⁻¹]</th>
<th>Tc[b] [K]</th>
<th>dG[Tc][b] [kJ mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 A→B</td>
<td>p-F(A)</td>
<td>37.1(6)</td>
<td>-45.5(8)</td>
<td>50.6(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 B→A</td>
<td>p-F(B)</td>
<td>37.0(3)</td>
<td>-36.9(3)</td>
<td>48.0(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4A</td>
<td>m-F(A)</td>
<td>22.1(6)</td>
<td>-110(3)</td>
<td>55.0(4)</td>
<td>265(3)</td>
<td>50.0(6)</td>
</tr>
<tr>
<td>4B</td>
<td>o-F(B)</td>
<td>33(1)</td>
<td>-41(2)</td>
<td>45.8(8)</td>
<td>248(3)</td>
<td>44.1(6)</td>
</tr>
<tr>
<td>5 A→B</td>
<td>p-F(A)</td>
<td>52.5(7)</td>
<td>-19.4(3)</td>
<td>58.3(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Ring A</td>
<td>m-F(A)</td>
<td>30(1)</td>
<td>-97(4)</td>
<td>58.9(1)</td>
<td>308(3)</td>
<td>58(2)</td>
</tr>
<tr>
<td>----------</td>
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<td>--------</td>
<td>-------</td>
</tr>
<tr>
<td>5 Ring B</td>
<td>o-F(B)</td>
<td>[c]</td>
<td>[c]</td>
<td>[c]</td>
<td>228(3)</td>
<td>39.8(6)</td>
</tr>
</tbody>
</table>

[a] Data from line shape analysis using the fitting program DNMR. [b] Data from coalescence temperature method using the approximation \( \Delta G^\neq = 19.1 \, T_c [9.97 + \log(T_c \Delta \nu^{-1})] \) for estimation of \( \Delta G^\neq \) at \( T_c \). [c] Data were not well resolved.

**Figure 2-5.** Variable temperature \(^{19}\text{F} \) NMR spectra of 5 (CDCl\(_3\), 470.4 MHz).
Compound 4 also shows two sets of $^{19}$F NMR peaks at $-60^\circ C$, but their relative intensity is different (Figure 2-6). Hence, a major and a minor rotational isomer are formed ($4A$ and $4B$). Based on a comparison with the NMR data for 5, we can confidently assign the major isomer to be that with the C$_6$F$_5$ group pointing toward the naphthyl group. The free energy barriers for interconversion of isomer $4A$ into $4B$ and vice versa were calculated to be $\Delta G^e_{298} = 50.6(4)$ and $48.0(3) \text{ kJ mol}^{-1}$, respectively, suggesting that the isomer with the pentafluorophenyl group pointing toward the naphthyl group is energetically favourable by about 2-3 kJ mol$^{-1}$.

The solid state structures were examined by single crystal X-ray diffraction. The X-ray analysis of 5 revealed two independent molecules with similar structural features in the asymmetric unit, while only one molecule of 4 was found (Figure 2-7). For 4, the isomer with the C$_6$F$_5$ moiety pointing toward the naphthyl group crystallized out, which is
consistent with our findings that this isomer is energetically favourable in solution. The boryl moieties are bent away from the plane of the substituted Cp ring of the ferrocenyl unit in both 4 and 5, with interplanar angles of Cp//BC₂Cl = 21.4° for 4 and Cp//BC₃ = 14.8° and 16.0° for the independent molecules of 5, respectively. This tilting of the boryl group toward the iron atom and the comparatively short B-C bond lengths (for 4, B-C₇ = 1.511(3); for 5, B-C₇ = 1.521(6), 1.501(6) Å) indicate a considerable degree of electronic delocalization between the electron rich ferrocene and the electron deficient boron atom. In comparison, the angle in Piers' structure is ca. 16° and those for the two independent molecules in the asymmetric unit of FcBBr₂ are 17.7° and 18.9°. The observation that the tilting of the boryl group is much more pronounced in 4 than in 5 may suggest increased steric strain in the latter due to the additional C₆F₅ group, which is preventing even closer contact between Fe and B. Indeed, considerable strain is evident for both molecules from the Cp//Cp tilt angles, which range from 7.0° to 7.6°. Noteworthy is also an intramolecular π-stacking interaction between the naphthyl moiety and the pentafluorophenyl ring (centroid-centroid distances in 4: 3.792 and 3.579 Å; 5: 3.512 and 3.701 Å). The interplanar angle between the C₆F₅ moiety and the naphthyl ring ranges from 7.6° for 5 to 14.7° for 4. In the solid state, both 4 and 5 reveal an interesting supramolecular 3D network structure as a result of multiple CH⁻⁻⁻π and CF⁻⁻⁻π interactions (see 2.5 Supporting Information, Figures 2-14, 2-15).

We examined the electronic structures of the ferrocenylborane Lewis acids by UV-visible spectroscopy and cyclic voltammetry measurements. The longest wavelength absorption occurs at lowest energy for the bisperfluorophenyl-substituted compound 5 (491 nm, \( \varepsilon = 1680 \)), followed by 4 (475 nm, \( \varepsilon = 1280 \)) and 3 (455 nm, \( \varepsilon = 1120 \)) (Figure 2-8). This band can be attributed to a dd transition of the ferrocene moieties with significant charge transfer character. The particular order may suggest that electronic interactions between the ferrocenyl \( \pi \) orbitals and the empty \( p \)-orbitals on boron are promoted by the electron deficient C_6F_5 groups more effectively than by the electronegative chlorine atoms.
Finally, we explored the possibility of 5 to undergo reversible oxidation. The cyclic voltammogram of 5 shows a reversible redox process at $E_{1/2} = +460$ mV vs the Fc/Fc$^+$ couple (Figure 2-9), which is considerably more anodic than those determined for 1 (+6 mV) and 2 (+127 mV). The higher +ve potential for 5 is in good agreement with data reported by Piers et al. for FcB(C$_6$F$_5$)$_2$ (+450 mV in trifluorotoluene/Bu$_4$N[B(C$_6$F$_5$)$_4$])$^{9b}$ and attributed to the electron withdrawing nature of the B(C$_6$F$_5$)$_2$ moiety. Addition of the Lewis base pyridine, which binds to boron and thus renders the boryl group more electron rich, shifts the redox potential of 5 to +90 mV. The fact that 5 undergoes a reversible electrochemical oxidation clearly suggests the possible use of this new class of compounds as redox-active chiral Lewis acid.
Figure 2-9. Cyclic voltammogram of compound 5 (CH₂Cl₂, 0.05 M Bu₄N[B(C₆F₅)₄], reported versus Fe/Fe⁺, which is taken as +610 mV versus Cp*₂Fe/Cp*₂Fe⁺ (indicated with an asterisk, Cp*=pentamethylyclopentadienyl) as an internal reference). The small peak at approximately +50 mV is due to trace amounts of naphthylferrocene that is formed as a result of the reaction of 5 with traces of water (Inset: plot of current versus square root of scan rate).

2.3 Conclusions

In conclusion, we describe the first examples of highly Lewis acidic planar chiral ferrocenylborane Lewis acids. Compounds 4 and 5 are structurally closely related to the important class of chiral binaphthyl species, which have found abundant use in catalysis applications. Importantly, the ferrocenyl group not only provides a rigid chiral environment, but the redox-active nature of the central iron atom may allow for tuning and further enhancement of the Lewis acidity. Additional studies in this regard and on the
application of compounds 4 and 5, as well as related planar chiral Lewis acids, in stereoselective organic synthesis are in progress. To explore the combination of these chiral Lewis acids with sterically hindered Lewis bases in the context of so-called frustrated Lewis pairs will be also of interesting.

2.4 Experimental Section

Materials and General Methods: BCl₃ (1M in hexanes), t-butyl lithium (1.7M in hexanes), and mercuric chloride were purchased from Acros. BBr₃ (99+%) was obtained from Aldrich and distilled prior to use. Caution! BBr₃ is toxic and highly corrosive and should be handled appropriately with great care. Fluorinated grease was used for ground glass joints in all reactions involving boron tribromide. (S₈,S₈)-2-(1-naphthyl)-1-(p-tolylsulfinyl)ferrocene¹², pentafluorophenyl copper²¹, and (C₆F₅)₂BCl²² were prepared according to literature procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (MBraun). THF was distilled from sodium/benzophenone. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently degassed via several freeze-pump-thaw cycles. Deuterated chloroform (CDCl₃ >99.7%) was obtained from Cambridge Isotope Laboratories (CIL). The solvent was stirred for several days over anhydrous CaH₂, then degassed via several freeze pump thaw cycles and stored over 3Å molecular sieves. All 499.9 MHz ¹H NMR, 125.7 MHz ¹³C NMR, 470.4 MHz ¹⁹F NMR, 160.4 MHz ¹¹B NMR, and 186.4 MHz ¹¹⁹Sn NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a 5 mm dual broadband gradient
probe (Nalorac, Varian Inc., Martinez, CA). Solution $^1$H and $^{13}$C NMR spectra were referenced internally to the solvent signals. $^{19}$F NMR spectra were referenced externally to $\alpha,\alpha',\alpha''$-trifluorotoluene (0.05% in C$_6$D$_6$; $\delta = -63.73$), $^{11}$B NMR spectra to BF$_3$·OEt$_2$ ($\delta = 0$) in C$_6$D$_6$, and $^{119}$Sn NMR spectra to SnMe$_4$ ($\delta = 0$) in C$_6$D$_6$. The abbreviation Np is used for 1-naphthyl; splittings of NMR signals are abbreviated as pst (pseudo-triplet), nr (not resolved), br (broad).

GC-MS spectra were acquired on a Hewlett Packard HP 6890 Series GC system equipped with a series 5973 mass selective detector and a series 7683 injector. MALDI-TOF measurements were performed either on an Applied Biosystems 4700 Proteomics Analyzer in reflectron (+) mode with delayed extraction or an Apex Ultra 7.0 Hybrid FT-MS (Bruker Daltonics). Benzo[a]pyrene was used as the matrix (10 mg/mL in toluene). Samples were prepared in toluene (10 mg/mL), a drop of pyridine or picoline was added, the resulting solution was mixed with the matrix in a 1:10 ratio, and then spotted on the wells of a sample plate inside a glove box. UV-visible absorption data were acquired on a Varian Cary 500 UV-vis/NIR spectrophotometer. Solutions were prepared using a microbalance (±0.1 mg) and volumetric glassware and then charged into quartz cuvettes with sealing screw caps (Starna) inside the glovebox. Optical rotation analysis was performed on an Autopol III polarimeter, Rudolph Research Analytical, using a tungsten-halogen light source operating at $\lambda = 589$ nm. Cyclic voltammetry measurements were carried out on a BAS CV-50W analyzer. The three-electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode, and a Ag wire as the pseudo-reference electrode. The voltammograms of 1 and 2 were recorded in CH$_2$Cl$_2$ containing [Bu$_4$N]PF$_6$ (0.1 M) as the supporting electrolyte and that of 5 in CH$_2$Cl$_2$ containing
[Bu₄N][B(C₆F₅)₄]) (0.05 M). Data were acquired with decamethylferrocene as an internal reference and are reported relative to the ferrocene/ferrocenium couple (+560 mV with 0.1M [Bu₄N]PF₆ in CH₂Cl₂ and +610 mV with 0.05 M [Bu₄N][B(C₆F₅)₄]) in CH₂Cl₂ vs. decamethylferrocene/decamethylferrocenium couple). Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Yellow needle-like crystals of 1 and yellow rod-like crystals of 2 were obtained from methanol and dichloromethane, respectively; dark red plate-like crystals of 4 and 5 were grown from hexanes at −37 °C. X-ray data for 1, 2, 4 and 5 were collected on a Bruker SMART APEX CCD Diffractometer using Cu-Kα (1.54178 Å) radiation. Details of X-ray diffraction experiments and crystal structure refinements are provided in Table 2-2. Numerical absorption correction was applied to 4 and 5, and SADABS⁴ absorption correction was applied to 1 and 2. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least squares procedures on F². All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL program package.⁵ For 5, the program Squeeze in Platon was used to remove highly disordered hexanes molecules (8 molecules per unit cell). The Squeeze method found a total electron count of 172.0 and 171.3 in a volume of 799.3 and 799.2 Å³ in the solvent regions of the unit cell, respectively. The calculated electron count for four hexanes is about 200, which is slightly larger than the experimental values. However, integration of the ¹H NMR spectrum shows that the ratio of 5 to solvent is ca. 14:10,
which indicates that some of the hexanes in the crystal lattice evaporated under high vacuum.

Crystallographic data for the structures of 1, 2, 4, and 5 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 765783-765786. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Synthesis of (S_p)-2-(1-Naphthyl)-1-(trimethylstannyl)ferrocene (1). A solution of t-BuLi (2.45 mL of 1.7M solution in hexanes, 4.17 mmol) was added dropwise via a syringe to a stirred solution of (S_p,S_p)-2-(1-naphthyl)-1-(p-tolylsulfinyl)ferrocene (1.71 g, 3.80 mmol) in freshly distilled THF (50 mL) at –78 °C. The solution was stirred for 5 minutes before adding Me_3SnCl (0.91 g, 4.57 mmol) in THF (30 mL). The solution was stirred at the same temperature for 1 h and subsequently quenched with a small amount of distilled water. Standard workup and flash column chromatography on silica gel with hexanes as the eluent gave a mixture of (S_p)-2-(1-naphthyl)-1-(trimethylstannyl)ferrocene and 1-naphthylferrocene. Recrystallization from methanol gave spectroscopically pure (S_p)-2-(1-naphthyl)-1-(trimethylstannyl)ferrocene. Yield: 1.09 g (60%). \([\alpha]_{20}^D (c 0.93, \text{CH}_2\text{Cl}_2) = –126°.\) ¹H NMR (499.9 MHz, CDCl_3, 25 °C) \(\delta 8.04 (d, J = 7.5 \text{ Hz}, 1\text{H}, \text{Np}), 7.84 (d, J = 8.0 \text{ Hz}, 2\text{H}, \text{Np}), 7.80 (d, J = 8.5 \text{ Hz}, 1\text{H}, \text{Np}), 7.49 (pst, J = 7.5 \text{ Hz}, 1\text{H}, \text{Np}), 7.44 (pst, J = 7.0 \text{ Hz}, 1\text{H}, \text{Np}), 7.37 (pst, J = 7.5 Hz, 1\text{H}, \text{Np}), 4.61 (dd, \(^3J = 2.5, 1.0 \text{ Hz}, \(^4J(117/119\text{Sn},H) = 7.0 \text{ Hz}, 1\text{H}, \text{Cp-3}), 4.57 (pst, \(^3J = 2.5 \text{ Hz}, 1\text{H}, \(^4J(117/119\text{Sn},H) = 6.0 \text{ Hz}, \text{Cp-4}), 4.30 (dd, \(^3J = 2.5, 1.0 \text{ Hz}, \(^3J(117/119\text{Sn},H) = 10.0 \text{ Hz}, 1\text{H}, \text{Cp-5}), 4.29 (s, 5\text{H}, \text{Cp-4}).\)
\( \text{C}_5\text{H}_5 \), \(-0.07 \text{ s/d} \), \( ^2J(117/119\text{Sn,H}) = 53/55 \text{ Hz} \), \( 9\text{H}, \text{SnMe}_3 \); \(^{13}\text{C}\) NMR (125.7 MHz, CDCl\(_3\), 25 \(^\circ\)C) \( \delta \) 137.0, 133.8, 133.4, 129.4, 128.2, 127.4, 126.7, 125.7, 125.7, 125.1 (Np), 96.0 (ipso-CpNp), 74.4 (s/d, \(^2J(117/119\text{Sn,C}) = 50 \text{ Hz} \), Cp-5), 74.3 (s/d, \(^3J(117/119\text{Sn,C}) = 35 \text{ Hz} \), Cp-4), 73.0 (ipso-CpSn), 70.4 (s/d, \(^3J(117/119\text{Sn,C}) = 40 \text{ Hz} \), Cp-3), 69.4 (C\(_5\text{H}_5\)), \(-8.0 \text{ s/d} \), \(^1J(117/119\text{Sn,C}) = 343/360 \text{ Hz} \), \( \text{SnMe}_3 \); \(^{119}\text{Sn}\) NMR (186.4 MHz, CDCl\(_3\), 25 \(^\circ\)C) \( \delta \) \(-7.1 \); GC-MS (m/z, (%)): 476 [M\(^+\)] (76), 461 [M\(^+\)–Me] (100), 431 [M\(^+\)–3Me] (71). UV-Vis (CH\(_2\)Cl\(_2\), \(2.35 \times 10^{-3} \text{ M}\)): \( \lambda_{\text{max}} = 448 \text{ nm} \) (\( \varepsilon = 255 \))CV (CH\(_2\)Cl\(_2\), \(1.0 \times 10^{-3} \text{ M}\)): \( E_{1/2} = 6 \) mV (\( \Delta E_p = 142 \text{ mV} \)). Elemental analysis for C\(_{23}\)H\(_{24}\)FeSn, calcd. C 58.16, H 5.09, found C 58.04, H 5.05%.

**Synthesis of (S\(_p\))-2-(1-Naphthyl)-1-(chloromercurio)ferrocene (2).** A solution of (S\(_p\))-2-(1-naphthyl)-1-(trimethylstannyl)ferrocene (175 mg, 0.368 mmol) in acetone (10 mL) was added dropwise to a solution of HgCl\(_2\) (100 mg, 0.368 mmol) in acetone (15 mL). The mixture was stirred for 30 minutes before adding it to water. A yellow solid precipitated, which was collected on a frit and washed first with water and then with hexanes. The product was dried under high vacuum at 60 \(^\circ\)C for 6 h. Yield: 169 mg (84%). \([\alpha]^{20}_D\) (\(c 0.93, \text{CH}_2\text{Cl}_2\)) = \(-103^\circ\). \(^1\text{H}\) NMR (499.9 MHz, CDCl\(_3\), 25 \(^\circ\)C) \( \delta \) 8.06-8.04 (m, 2H, Np), 7.87 (d, \( J = 7.5 \text{ Hz} \), 1H, Np), 7.83 (d, \( J = 8.5 \text{ Hz} \), 1H, Np), 7.52 (pst, \( J = 7.5 \text{ Hz} \), 1H, Np), 7.47 (pst, \( J = 7.5 \text{ Hz} \), 1H, Np), 7.43 (pst, \( J = 7.5 \text{ Hz} \), 1H, Np), 4.82 (dd, \( J = 2.5, 1.0 \text{ Hz} \), 1H, Cp-3), 4.64 (pst, \( J = 2.5 \text{ Hz} \), 1H, Cp-4), 4.33 (s, 5H, C\(_5\text{H}_5\)), 4.30 (dd, \( J = 2.5, 1.0 \text{ Hz} \), 1H, Cp-5). \(^{13}\text{C}\) NMR (125.7 MHz, CDCl\(_3\), 25 \(^\circ\)C) \( \delta \) 136.7, 133.8, 133.0, 128.8, 128.6, 128.1, 126.3, 126.2, 125.7, 125.6 (Np), 92.4 (ipso-Cp), 90.6 (ipso-Cp), 73.1 (Cp), 72.7 (Cp), 70.6 (Cp), 70.2 (C\(_5\text{H}_5\)). UV-Vis (CH\(_2\)Cl\(_2\), \(2.27 \times 10^{-3} \text{ M}\)): \( \lambda_{\text{max}} \)
$= 451 \text{ nm} (\varepsilon = 294)$. CV (CH$_2$Cl$_2$, $1.0 \times 10^{-3}$ M): $E_{1/2} = 127$ mV ($\Delta E_p = 153$ mV).
Elemental analysis for C$_{20}$H$_{15}$FeHgCl, calcd. C 43.90, H 2.76, found C 44.19, H 2.65%.

**NMR Scale Reaction of 1 with BBr$_3$.** To a solution of 1 (10.2 mg, 21.5 µmol) in CDCl$_3$ (0.8 mL) was added a solution of BBr$_3$ (5.4 mg, 21.6 µmol) in CDCl$_3$ (0.2 mL) at $-35 \degree C$. The mixture was stirred for 30 minutes. The ratio of the 1,1’- to 1,3-isomers was determined according to $^1$H NMR integration of the Cp resonances to ca. 57:43. NMR data for the mixture: $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C) Np region: $\delta$ 8.44 (d, $J = 7.5$ Hz, Np), 8.35 (d, $J = 7.0$ Hz, Np), 8.1-7.8 (m, Np), 7.6-7.4 (m, Np), 0.78 (s, Me$_3$SnBr); Cp region of 1,1’-isomer $\delta$ 4.86 (pst, $J = 1.8$ Hz, 2H, Cp-H), 4.76 (pst, $J = 1.8$ Hz, 2H, Cp-H), 4.62 (pst, $J = 1.8$ Hz, 2H, Cp-H), 4.49 (pst, $J = 1.8$ Hz, 2H, Cp-H); Cp region of 1,3-isomer: $\delta$ 5.42 (dd, $J = 2.5$, 1.5 Hz, 1H, Cp-H4/5), 5.05 (pst, $J = 1.5$ Hz, 1H, Cp-H2), 4.79 (dd, $J = 2.5$, 1.5 Hz, 1H, Cp-H4/5), 4.28 (s, 5H, C$_3$H$_5$). $^{11}$B NMR (160.4 MHz, C$_6$D$_6$, 25 °C) $\delta$ 47.2.

**Synthesis of 3:** To a suspension of (S$_p$)-2-(1-naphthyl)-1-(chloromercurio)ferrocene (2) (0.56 g, 0.118 mmol) in hexane (30 mL) at $-30 \degree C$ was added BCl$_3$ (1.24 mL, 1 M solution in hexane) inside a glove box. The reaction mixture was stirred for 2 h. The color of the solution turned orange and a grey solid formed, which was removed by filtration. The filtrate was kept at $-37 \degree C$ for two days to give an orange crystalline solid. The product was recrystallized once more from warm hexane. A second fraction was obtained upon concentration of the combined mother liquors. Isolated yield: 380 mg (82 %); $^1$H NMR (499.9 MHz, C$_6$D$_6$, 25 °C): $\delta$=7.94 (br d, $J=7.0$ Hz, 1 H; Np), 7.74 (br d, $J=6.5$ Hz, 1 H; Np), 7.69–7.65 (m, 2 H; Np), 7.37 (br pst, $J=6.5$ Hz, 1 H; Np), 7.21 (br pst, $J=8.0$ Hz, 1 H; Np), 7.14 (br s, 1 H; Np), 4.63 (dd, $J=2.5$, 1.0 Hz, 1 H; Cp-3/5), 4.57 (br s, 1 H;
Cp-3/5), 4.38 (br pst, 1 H; Cp-4), 4.02 ppm (s, 5 H; free Cp); $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta$=135.2, 134.1, 133.3, 128.4, 128.3, 128.0, 126.2, 125.9 (2 signals), 125.2 (Np), 97.9, 82.9, 77.3, 75.4, (substituted Cp), 72.6 ppm (C$_5$H$_5$) (the ipso-Cp-B signal was not observed); $^{11}$B NMR (160.4 MHz, C$_6$D$_6$, 25 °C): $\delta$=49.4 ppm ($\nu$$_{1/2}$=350 Hz); UV/Vis (CH$_2$Cl$_2$, 1.00×10$^{-3}$ M): $\lambda$$_{max}$=455 nm ($\varepsilon$=1120); MALDI-TOF (+ reflector mode, benzopyrene/pyridine) m/z: calcd for C$_{20}$H$_{15}$BCl$_2$Fe: 391.9993; found: 392.0023; elemental analysis calcd (%) for C$_{20}$H$_{15}$BCl$_2$Fe: C 61.14, H 3.85; found C 61.30, H 3.49.

Synthesis of 4: A precooled solution of [C$_6$F$_5$Cu]$_4$ (18 mg, 20 μmol) in toluene (3 mL, −37 °C) was added dropwise to a precooled solution of 3 (31 mg, 79 μmol) in toluene (5 mL, −37 °C) under stirring. The reaction mixture was stirred for 3 h at RT and then filtered. All volatile components were removed under high vacuum. The crude product was purified by recrystallization from hexane at −37 °C to give a dark red microcrystalline solid. Isolated yield: 39 mg (80 %); $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta$=7.71 (d, $J$=8.5 Hz, 1 H; Np), 7.66 (d, $J$=8.5 Hz, 2 H; Np), 7.47 (br s, 1 H; Np), 7.39 (t, $J$=7.1 Hz, 1 H; Np), 7.31 (m, $J$=7.5 Hz, 2 H; Np), 5.15 (pst, $J$=2.5 Hz, 1 H; Cp), 5.02 (br, 1 H; Cp), 4.9 (br, 1 H; Cp), 4.53 ppm (s, 5 H; free Cp); $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta$=150–130 (ortho-, meta-, para-C$_6$F$_5$ signals are broad and not resolved), 115.1 (br, ipso-C$_6$F$_5$), 132.5, 129.1, 127.6, 127.5, 125.8, 125.7, 124.2, 98.1 (ipso-Cp-B), 77.7 (Cp), 81.5 (Cp), 75.9 (br, Cp), 71.7 ppm (C$_5$H$_5$); $^{11}$B NMR (160.4 MHz, C$_6$D$_6$, 25 °C): $\delta$=55.3 ppm ($\nu$$_{1/2}$=500 Hz); $^{19}$F NMR (470.4 MHz, CDCl$_3$, 25 °C): $\delta$=−130 (2 F; ortho-F), −154.1 (1 F; para-F), −162.7 ppm (2 F; meta-F); UV/Vis (CH$_2$Cl$_2$, 1.00×10$^{-3}$ M): $\lambda$$_{max}$=475 nm ($\varepsilon$=1280); elemental analysis calcd (%) for C$_{26}$H$_{15}$BClF$_5$Fe: C 59.54, H 2.88; found C 59.41, H 2.88.
**Synthesis of 5:** A solution of $\left[\text{C}_6\text{F}_5\text{Cu}\right]_4$ (117 mg, 127 μmol) in toluene (5 mL) was added dropwise at RT to a solution of 3 (100 mg, 255 μmol) in toluene (5 mL) under stirring. The mixture was stirred for 3 h at 80 °C and then cooled to RT and filtered. All volatile components were removed under high vacuum. The crude product was purified by repeated recrystallization from hot hexane to give a dark red microcrystalline solid.

Isolated yield: 140 mg (84 %); $[\alpha]_D^{26}$ (c=0.072, hexane)=$-132^\circ$; $^1$H NMR (499.9 MHz, CDCl3, 25 °C): δ=7.71 (d, $J=6.5$ Hz, 1 H; Np), 7.62 (m, 2 H; Np), 7.53 (d, $J=8.5$ Hz, 1 H; Np), 7.40–7.25 (m, 3 H; Np), 5.28 (pst, $J=2.5$ Hz, 1 H; Cp-4), 5.26 (dd, $J=2.5$, 1.0 Hz, 1 H; Cp-5), 4.61 (s, 5 H; free Cp), 4.17 (br s, 1 H; Cp-3), 2.0–0.8 ppm (ca. 10 H; hexane); $^{13}$C NMR (125.69 MHz, CDCl3, 25 °C): δ=150–130 (ortho-, meta-, para-C$_6$F$_5$ signals are broad and not resolved), 115.1 (br, ipso-C$_6$F$_5$), 133.4, 133.3, 132.4, 129.4, 127.8, 127.4, 126.1, 126.0, 125.8, 124.6 (Np), 100.0 (ipso-CpC), 83.3 (ipso-Cp-B), 77.7 (Cp), 77.5 (Cp), 75.8 (br, Cp), 71.6 ppm (C$_3$H$_5$); $^{11}$B NMR (160.4 MHz, C$_6$D$_6$, 25 °C): δ=54 ppm ($w_{1/2}=900$ Hz); $^{19}$F NMR (470.4 MHz, CDCl3, 25 °C): δ=$-127.5$ (br, 1 F; ortho-F$_{A2}$), $-132.8$ (br, 1 F; ortho-F$_{A6}$), $-128.7$ (br, 2 F; ortho-F$_{B3,5}$), $-151.8$ (br, 1 F; para-F$_{A4}$), $-156.5$ (br, 1 F, para-F$_{B4}$), $-161.5$ (br, 2 F; meta-F$_{B3,5}$), $-163.3$ (pst, 1 F; meta-F$_{A3}$), $-163.8$ ppm (pst, 1 F; meta-F$_{A3}$). $^{19}$F NMR (470.4 MHz, CDCl3, -60 °C): δ=$-128.0$ (d, $J$(F,F)=23 Hz, 1 F; ortho-F$_{A2}$), $-133.1$ (d, $J$(F,F)=24 Hz, 1 F; ortho-F$_{A6}$), $-126.7$, $-130.1$ (very br, ortho-F$_{B3,5}$), $-150.9$ (t, $J$(F,F)=18 Hz, 1 F; para-F$_{B4}$), $-156.4$ (t, $J$(F,F)=21 Hz, 1 F; para-F$_{A4}$), $-160.7$ (br, 2 F; meta-F$_{B3,5}$), $-162.9$ (pst, 1 F; meta-F$_{A5}$), $-163.8$ ppm (pst, 1 F; meta-F$_{A3}$); UV/Vis (CH$_2$Cl$_2$, $1.00\times10^{-3}$ M): $\lambda_{max}=491$ nm ($\varepsilon=1680$); CV (CH$_2$Cl$_2$, 1.9$\times10^{-3}$ M): $E_{1/2}=460$ mV ($\Delta E_p=214$ mV); CV of complex with pyridine (CH$_2$Cl$_2$,
1.9 × 10^{-3} \text{ M}): E_{1/2}=93 \text{ mV} \ (\Delta E_p=98 \text{ mV}); \text{ high-resolution MALDI-TOF (+ mode, benzopyrene/picoline) m/z: calcd for C}_{32}\text{H}_{15}\text{BF}_{10}\text{Fe: 656.0457; found: 656.0455.}

2.5 Supporting Information

**Figure 2-10.** Ortep plot of 1 with thermal ellipsoids at the 50\% probability level; hydrogen atoms are omitted for clarity.

**Molecule 1:** Sn(1)-C(1) 2.135(3), Sn(1)-C(21) 2.144(3), Sn(1)-C(22) 2.138(4), Sn(1)-C(23) 2.148(4), C(2)-C(11) 1.488(4), C(1)-Sn(1)-C(22) 106.51(15), C(1)-Sn(1)-C(21) 109.07(13), C(22)-Sn(1)-C(21) 111.67(19), C(1)-Sn(1)-C(23) 113.37(14), C(22)-Sn(1)-C(23) 110.92(18), C(21)-Sn(1)-C(23) 105.39(15).

**Molecule 2:** Sn(2)-C(24) 2.136(3), Sn(2)-C(44) 2.151(4), Sn(2)-C(45) 2.140(4), Sn(2)-C(46) 2.139(4), C(25)-Sn(2)-C(46) 110.26(15), C(24)-Sn(2)-C(45) 108.56(13), C(46)-Sn(2)-C(45) 108.74(17), C(24)-Sn(2)-C(44) 109.77(16), C(46)-Sn(2)-C(44) 109.8(2), C(45)-Sn(2)-C(44) 109.67(19).
Figure 2-11. Ortep plot of 2 with thermal ellipsoids at the 50% probability level, hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Hg(1)-C(1), 2.024(5), Hg(1)-Cl(1) 2.3120(12), C(2)-C(11) 1.489(7), C(1)-Hg(1)-Cl(1) 179.02(14).

Figure 2-12. Ortep plot of 4 with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): B(1)-C(1) 1.511(3), B(1)-C(11) 1.587(4), B(1)-Cl(1) 1.787(3), C(1)-B(1)-C(11) 123.9(2), C(1)-B(1)-Cl(1) 119.5(2), C(11)-B(1)-Cl(1) 115.95(18); Cp//Cp 7.0, Cp//Np 59.2, C₆F₅//Np 14.7.
Figure 2-13. Ortep plots of two independent molecules of 5 with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°):

Molecule 1: B(1)-C(2) 1.521(6), B(1)-C(21) 1.598(7), B(1)-C(27) 1.578(7), C(1)-C(2) 1.468(6), C(2)-B(1)-C(27) 123.0(4), C(2)-B(1)-C(21) 122.2(4), C(27)-B(1)-C(21) 114.3(4); Cp//Cp 7.6, Cp//Np 65.1, C₆F₅//Np 7.6. Molecule 2: B(2)-C(34) 1.501(6), B(2)-C(53) 1.595(6), B(2)-C(59) 1.581(6), C(33)-C(34) 1.484(6), C(34)-B(2)-C(59) 121.5(4), C(34)-B(2)-C(53) 122.2(4), C(59)-B(2)-C(53) 115.6(4); Cp//Cp 7.8, Cp//Np 62.4, C₆F₅//Np 12.3.
Figure 2-14. Supramolecular Structure of 5.

Two crystallographically independent molecules in the asymmetric unit of 5 generate two different 1D helical chains via intermolecular C-H---π (C17-H17---π_{Cp} = 2.968 Å and C49-H49---π_{Cp} = 2.880 Å) interactions between the ferrocene and naphthyl moieties. Further, an intermolecular C-H---π interaction (C9-H9---π_{Np} = 2.994 Å and C39-H39---π_{Np} = 2.673 Å) between the aforementioned chains leads to a double helical structure. Each double helical chain interacts with two neighbouring chains via intermolecular C-F---π interaction (C15-F15---π_{Pr} = 3.298 Å and C5-F5---π_{Pr} = 3.205 Å). These interactions generate an interesting supramolecular “diboracyclophane” and the propagation of these interactions leads to the formation of a 2D helical layer structure. The C-H---F interactions between the adjacent layers generate a 3D structure.
Figure 2-15. Intermolecular Interactions in 4.
A similar supramolecular structure is found as described above for compounds 5.
### Table 2-2. Details of X-ray crystal structure analyses of complexes 1, 2, 4 and 5.

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<td>C_{26}H_{15}BClF_{5}Fe</td>
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<td>8.43570(10)</td>
<td>11.7701(14)</td>
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<td>11.5784(2)</td>
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<td>10.90310(10)</td>
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<td>1060.94(2)</td>
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<td>4</td>
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<td>8</td>
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<td>2.189</td>
<td>1.642</td>
<td>1.335</td>
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</tr>
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<td>independent reflns</td>
<td>6222 [R(int) = 0.0318]</td>
<td>2741 [R(int) = 0.0291]</td>
<td>3146 [R(int) = 0.0415]</td>
<td>11627 [R(int) = 0.1206]</td>
</tr>
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<td>SADABS</td>
<td>Numerical</td>
<td>Numerical</td>
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<td>( R_1 = 0.0179 )</td>
<td>( R_1 = 0.0285 )</td>
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<tr>
<td>[ I &gt; 2( \sigma(I) ) ] a</td>
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<td>( wR_2 = 0.0382 )</td>
<td>( wR_2 = 0.0678 )</td>
<td>( wR_2 = 0.1264 )</td>
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<td>( R_1 = 0.0191 )</td>
<td>( R_1 = 0.0315 )</td>
<td>( R_1 = 0.0774 )</td>
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<td>( wR_2 = 0.0486 )</td>
<td>( wR_2 = 0.0386 )</td>
<td>( wR_2 = 0.0695 )</td>
<td>( wR_2 = 0.1430 )</td>
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<td>0.019(4)</td>
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[a] \( R_1 = \sum |F_o| - |F_c| / \sum |F_o|; \quad wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2] \}^{1/2}. \)
Table 2-3. Coalescence temperatures from analysis of VT NMR data for compounds 4 and 5.

<table>
<thead>
<tr>
<th>NpFcBC1Pf (4)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>o-F</td>
<td>m-F</td>
<td>G°</td>
</tr>
<tr>
<td>Major (4A)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T_c (K)</td>
<td>(ppm)</td>
<td>G° (kJ/mol)</td>
<td>T_c (K)</td>
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<tr>
<td>257</td>
<td>0.38</td>
<td>49.7±0.7</td>
<td>265</td>
</tr>
<tr>
<td>Minor (4B)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>T_c (K)</td>
<td>(ppm)</td>
<td>G° (kJ/mol)</td>
<td>T_c (K)</td>
</tr>
<tr>
<td>248</td>
<td>2.5</td>
<td>44.1±0.6</td>
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<table>
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<th>NpFcBPf2 (5)</th>
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<td></td>
<td>o-F</td>
<td>m-F</td>
<td>G°</td>
</tr>
<tr>
<td>(ring B)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>T_c (K)</td>
<td>(ppm)</td>
<td>G° (kJ/mol)</td>
<td>T_c (K)</td>
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<tr>
<td>228</td>
<td>3.34</td>
<td>39.8±0.6</td>
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</table>

The approximation \( \Delta G^\neq = 19.1 T_c [9.97 + \lg(T_c \Delta v^{-1})] \) for estimation of \( \Delta G^\neq \) at \( T_c \) was used; see: M. Hesse, H. Meier, B. Zeeh, Spectroscopic Methods in Organic Chemistry, Thieme, Stuttgart, 1997.

Table 2-4. Line shape analysis results from VT NMR data of compounds 4 and 5.^[a]^

<table>
<thead>
<tr>
<th>NpFcBC1Pf (4)</th>
<th>4A</th>
<th>4B</th>
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<th>Isomer 4B</th>
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<td></td>
<td>m-F</td>
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<td>H° (kJ/mol)</td>
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<td>37.0(3)</td>
<td>22.1(6)</td>
<td>34(1)</td>
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<tr>
<td>S° (J/mol*K)</td>
<td>-45.5(8)</td>
<td>-36.9(3)</td>
<td>-110(3)</td>
<td>-41(2)</td>
</tr>
<tr>
<td>( G_{298}^\neq ) (kJ/mol)</td>
<td>50.6(4)</td>
<td>48.0(3)</td>
<td>55.0(4)</td>
<td>45.9(8)</td>
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<table>
<thead>
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<th>Ring A</th>
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<td>m-F</td>
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<tr>
<td>H° (kJ/mol)</td>
<td>52.5(7)</td>
<td>47.7(13)</td>
<td>30(1)</td>
</tr>
<tr>
<td>S° (J/mol*K)</td>
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<td>-33.4(10)</td>
<td>-97(4)</td>
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<tr>
<td>( G_{298}^\neq ) (kJ/mol)</td>
<td>58.3(6)</td>
<td>57.6(10)</td>
<td>58.9(1)</td>
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<tr>
<td>( G_{222}^\neq ) (kJ/mol)</td>
<td>56.9(5)</td>
<td>55.3(8)</td>
<td>52.2(1)</td>
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</table>
[a] Data from line shape analysis using the program DNMR. Error calculations for $\Delta G^\circ$ are based on the covariance relationship between $\Delta H^\circ$ and $\Delta S^\circ$ (see J. Sandström, Dynamic NMR Spectroscopy, Academic Press, New York, 1982, p 118).

2.6 Notes and References


Chapter 3 Stereoseletive Borylation of Planar Chiral Pyridylferrocenes

3.1 Introduction of Directed Metalation

Directed metalation of aromatic compounds has developed into a powerful synthetic tool over the past two decades. While early studies have primarily focused on lithiations, a variety of other metals (e.g. Mg, Zn, Cd, Mn) have been successfully utilized more recently. Much progress has also been achieved when using mixed metal systems. The ortho-metalation of ferrocenes is of particular importance, because it provides an opportunity for stereoselective synthesis of planar chiral derivatives. Planar chiral ferrocenes continue to be critically important ligands in transition metal-catalyzed processes. Typically a chiral substituent on one or both Cp rings is utilized as a directing group. Alternatively, a chiral base can be added as an auxiliary. Early examples include Ugi’s chiral aminomethylferrocene derivatives (A) and Kagan’s p-tolylsulfinylferrocene (B). The latter has the advantage that after derivatization of the ortho-position, the sulfinate group itself can be readily replaced by lithiation with tert-butyl lithium or magnesiation with Grignard species and subsequent treatment with electrophiles.

Figure 3-1. Examples of ortho-lithiation of chiral ferrocenes and the product of borylation of 1,1′-bis(trimethylstannyl)ferrocene (racemate)

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a This chapter is adapted from a journal publication
The borylation of ferrocenes serves as an important tool in the synthesis of redox-active Lewis acids for anion recognition and Lewis acid catalysis,\textsuperscript{11-15} the preparation of redox-active ligands,\textsuperscript{6} and the development of new boron-containing electroactive materials\textsuperscript{7}. Moreover, ferrocenylboronic acids are interesting building blocks for supramolecular materials\textsuperscript{8} and desirable precursors to other ferrocene derivatives by means of Suzuki-Miyaura coupling procedures.\textsuperscript{9} Two methods have primarily been used for their synthesis; the direct borylation of ferrocenes with BBr\textsubscript{3} and the metathesis of metalated ferrocenes (FcM, M = Li, Mg, HgX, SnR\textsubscript{3}) with borane species BX\textsubscript{3} (X = F, Cl, Br, OR).

While the direct borylation of parent ferrocene is a facile process and multiply borylated species can be obtained with good regioselectivity,\textsuperscript{10} the need for use of highly reactive boranes limits the functional group tolerance; moreover, ortho-borylation products are very rare due to both steric and electronic deactivation effects. A notable exception is the low temperature borylation of 1,1’-bis(trimethylstannyl)ferrocene with BCl\textsubscript{3}, which leads to 1-stannyl-2-borylferrocene (C) as the major product.\textsuperscript{11} This result is remarkable, because for other silylated or stannylated aromatics cleavage of the element-carbon bond in an ipso-borodemetalation tends to occur much faster than activation of the C-H bond.\textsuperscript{12, 13} The unique reactivity is attributed to the directing effect of the stannyl group, the ability of the iron center to mediate proton transfer, and the presence of a second stannyl moiety that acts as a good leaving group.\textsuperscript{14} The reaction, however, produces a racemate that has to be resolved into the individual enantiomers.\textsuperscript{15}

To develop stereoselective borylation procedures for planar chiral ferrocenes remains a challenging task.\textsuperscript{16} Here we demonstrate the selective ortho-borylation of planar chiral stannylnated and mercurated pyridylferrocenes. We discovered that from a single
enantiomerically pure 2-pyridyl-1-(p-tolylsulfinyl)ferrocene precursor, both (pR)- and (pS)-2-boryl-1-pyridylferrocene can be generated individually with high stereoselectivity.

3.2 Results and Discussion

Synthesis and Characterization of 2-Pyridyl-1-stannylferrocene (pS)-2Sn and 2-Pyridyl-1-mercurioferrocene (pS)-2Hg. The enantiomerically pure planar chiral precursor (pR, Ss)-2-(3,5-dimethylpyrid-2-yl)-1-(p-tolylsulfinyl)ferrocene ((pR, Ss)-1) was prepared by Negishi coupling of the corresponding zincated ferrocene species and 2-iodo-3,5-dimethylpyridine in analogy to the synthesis of other 2-aryl-1-sulfinylferrocenes (Scheme 3-1).9a, 19 The X-ray structure of 1 is displayed in (see 3.6 Supporting Information, Figure 3-7) and confirms the stereochemical assignments. Subsequent reaction of 1 with tert-butyl lithium followed by treatment with Me3SnCl gave (pS)-2-(3,5-dimethylpyrid-2-yl)-1-(trimethylstannyl)ferrocene ((pS)-2Sn) in 69% yield after crystallization from methanol. The corresponding 1-mercurio-2-pyridylferrocene derivative (pS)-2Hg, was obtained in essentially quantitative yield by treatment of (pS)-2Sn with one equivalent of HgCl2 in acetone. The 1H and 13C NMR spectra of (pS)-2Sn and (pS)-2Hg show the characteristic pattern of 1,2-disubstituted ferrocenes. The 119Sn NMR signal for (pS)-2Sn at $\delta = -39.9$ ppm is strongly upfield shifted compared to other stannylferrocenes (e.g. 1-trimethylstannyl-2-(1-naphthyl)ferrocene19c $\delta = 7.1$ ppm), which suggests an increase of electron density at the Sn center due to coordination of the adjacent pyridyl group. This is consistent with the X-ray crystal structure of (pS)-2Sn (Figure 3-2), which reveals a Sn1···N1 distance of 2.805(3) Å that is significantly shorter than the sum of the van der Waal’s radii of Sn and
N (3.61 Å²). Consequently, the geometry at Sn is distorted toward a trigonal bipyramidal structure as reflected in a large equatorial C1-Sn1-C19 angle of 116.83(18)° (moving towards 120°) and a small C1-Sn1-C20 angle of 102.8(2)° (moving towards 90°). Moreover, the Sn1-C20 bond of 2.165(5) Å is elongated compared to the other Sn-C bonds (2.122(4) - 2.129(5) Å), which is a result of Lewis base binding in the trans-position of the Sn center. The pyridyl group is positioned almost co-planar with the substituted Cp ring (Py/Cp = 10°); the slight deviation is likely due to steric repulsion of one of the methyl groups on pyridine and the Cp proton (H3) adjacent to the pyridyl group.

The absolute configuration of (pS)-2Sn based on the X-ray crystal structure is consistent with the stannyl group assuming the position of the sulfinate moiety in (pR)-1 as shown in Scheme 3-1. Only a single isomer was detected by chiral HPLC analysis and a specific rotation value of [α]²⁰ = –20° was determined. The formation of (pS)-2Hg proceeds with retention of stereochemistry based on a comparison of the optical rotation ([α]²⁰ = –107°) with that of similar compounds that were crystallographically characterized. This is consistent with an ipso-mercuriodestannylation, which is the generally accepted mechanism for these types of reaction.

Scheme 3-1. Synthesis of planar chiral pyridylferrocenes (pS)-2Sn and (pS)-2Hg.
Figure 3-2. Ortep plot of (pS)-2Sn (50% thermal displacement ellipsoids). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Sn1···N1 2.805(3), Sn1-C1 2.122(4), Sn1-C18 2.126(5), Sn1-C19 2.129(5), Sn1-C20 2.165(5), C1-Sn1-C18 109.98(17), C1-Sn1-C19 116.83(18), C1-Sn1-C20 102.8(2), C18-Sn1-C19 113.5(2), C18-Sn1-C20 107.3(2), C19-Sn1-C20 105.2(2), N1···Sn1-C1 66.65, N1···Sn1-C18 81.27, N1···Sn1-C19 77.20, N1···Sn1-C20 168.6.

Conversion of (pS)-2Sn and (pS)-2Hg to the Boracycles (pR)-3 and (pS)-3. The reaction of planar chiral ferrocenyltin species with boron halides generally tends to be unselective because multiple sites on the Cp rings are prone to attack by the electrophile, commonly yielding a mixture of 1,2-, 1,3-, and 1,1’-disubstituted products. In contrast, transmetalation from Hg to B generally proceeds with high selectivity via cleavage of the (weak) Hg-C bond. We investigated the borylation of both the organotin species (pS)-2Sn and the organomercury derivative (pS)-2Hg. (pS)-2Sn was reacted with an excess of PhBCl₂ in a mixture of toluene and hexanes at –37 °C, while (pS)-2Hg was treated with one equivalent of PhBCl₂ in toluene at –37 °C. For both reactions the color changed immediately from orange to dark red. The products were isolated in moderate yields as red solids by recrystallization from a mixture of toluene and hexanes at –37 °C. In both cases, the selective formation of a single product with identical NMR spectral data was observed. However, surprisingly, the optical rotation for the product derived
from the mercury precursor (pS)-2Hg ((pS)-3; [α]_{20}^{D} (c = 0.10, CH₂Cl₂) = −2060°) proved to be almost exactly opposite to that derived from the organotin species (pS)-2Sn ((pR)-3; [α]_{20}^{D} (c = 0.10, CH₂Cl₂) = +2110°). Considering also the NMR spectroscopic and X-crystallography results (vide infra) we assign the two products to be the enantiomers (pR)-3 and (pS)-3 (Scheme 3-2). Using chiral HPLC, we estimated the enantiomeric excess (ee) to be 99% for (pR)-3 and 90% for (pS)-3, respectively. The isomer (pS)-3 corresponds to retention of planar chirality, which implies that it is formed as expected through an ipso-borodemercuration reaction (boron attacks at C-Hg). In contrast, the observation of (pR)-3 in the reaction of (pS)-2Sn with PhBCl₂ is highly unusual and indicates an entirely different mechanistic pathway (vide infra).

Scheme 3-2. Synthesis of planar chiral 2-boryl-1-pyridylferrocenes (pS)-3 and (pR)-3 (only the B-chiral isomers with the Ph group the exo position are shown) and corresponding chiral HPLC traces.

As enantiomers, (pR)-3 and (pS)-3 show identical NMR spectra, so they are discussed together. An 11B NMR signal at 6.0 ppm is indicative of a tetracoordinate environment at boron and consistent with formation of the proposed heterocyclic structure due to B-N adduct formation. Upon dissolution of 3 in C₆D₆, initially one set of signals was
observed, but over time a second set gradually started to appear (see Figure 3-3). Equilibration occurred over a period of about 2 days and the final ratio of the (initial) major to the (new) minor component was estimated to about 3.2:1 in C₆D₆. In CDCl₃ or CD₂Cl₂ equilibration was almost instantaneous and the ratios were slightly lower (2.5:1 and 2.1:1). Coalescence was not observed even at elevated temperature (70 °C), which is consistent with an isomerization that is very slow on the NMR time scale. We attribute the two sets of signals to the formation of two distinct B-chiral isomers, one of which features the phenyl group in the exo position and the other in the endo position (Figure 3-4). The resonances of the substituted Cp ring for the minor and the major isomer appear at similar chemical shifts. However, the signal for the free Cp ring in the minor isomer (3.59 ppm) is strongly upfield shifted, because of the shielding effect of the phenyl group in endo-position. Consistent is that the minor isomer is less energetically favorable and thus less abundant due to steric effects between the Ph group and the free Cp ring. The assignments were further confirmed by a 2D NOESY experiment, which clearly revealed an NOE peak between the o-Ph protons and the free Cp ring of the minor isomer, but not the major isomer (Figure 3-3). Noteworthy is also that the exo Ph isomer is the only species present in the solid state (vide infra), hence it is dominant upon initial dissolution.
Figure 3-3. $^1$H NMR spectra (Cp region) of single crystals of (pR)-3 in C$_6$D$_6$ after different time intervals.

Figure 3- 4. Excerpt of the $^1$H-$^1$H NOESY NMR spectrum for (pR)-3 and structures of the two different B-chiral isomers observed in C$_6$D$_6$ solution.

Single crystal X-ray diffraction analyses were performed on both (pR)-3 and (pS)-3, which proved to be essentially isostructural and gave almost identical unit cell dimensions (Table 3-1). Refinement of the Flack parameter provided the correct stereochemical assignment. In agreement with our NMR analysis, in each case only the major B-chiral isomer with the Ph group in the exo position was observed in the solid
state (Figure 3-5). The B-N bond length of 1.629(3) Å for \((pR)-3\) [1.618(4) Å for \((pS)-3\)] is similar to that in \(\text{Py-B(C}_6\text{F}_5)_3\) (1.628(2) Å)\(^2\) and related pyridine-borane adducts. The B-Cl bond length of 1.882(3) Å [1.880(4) Å] is similar to the ones reported for a chlorodibenzoborole-pyridine adduct (1.898(2) and 1.902(2) Å)\(^2\) and significantly longer than in tricoordinate chloroboranes.

**Figure 3-5.** Ortep plots of a) \((pR)-3\) and b) \((pS)-3\) with 50% thermal displacement ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): \((pR)-3\) [(pS)-3]: B1-N1 1.629(3) [1.618(4)], B1-C11 1.882(3) [1.880(4)], B1-C2 1.603(4) [1.593(5)], B1-C18 1.601(4) [1.613(5)], C2-C1-C11 111.0(2) [110.8(3)], C1-C2-B1 109.16(19) [108.9(2)], C2-B1-N1 96.86(18) [97.5(2)], N1-C11-C1 109.0(2) [109.1(3)].

### 3.3 Mechanistic Study of Borylation

The inversion of stereochemistry in the formation of \((pR)-3\) from \((pS)-2\text{Sn}\) is a very interesting discovery that warrants further discussion. Given the high regio- and stereoselectivity of the process, the Lewis basic pyridyl group in \((pS)-2\text{Sn}\) appears to act as an ortho-directing group that facilitates selective borane attack at the C-H position next to the pyridyl group, followed by a protiodestannylation. A detailed summary of the proposed mechanistic steps is provided in Figure 3-6. Depending on the reaction
conditions, initially, a Me group on Sn may be replaced with a chloro-substituent as indicated by the need for two equivalents of PhBCl₂. The first step of the rearrangement mechanism then entails binding of the borane to the Lewis basic pyridyl moiety, followed by electrophilic attack at the ortho-carbon in 3-position. In the final step the proton (H₃) must be transferred to the carbon atom C1 with subsequent release of Me₃SnCl or Me₂SnCl₂. An intramolecular process is likely considering that the reaction is fast even at low temperature; proton transfer could be mediated by protonation of the pyridine ring or a protonated iron species as indicated in Figure 3-6. Even an intermediate in which the proton adopts a bridging position between Fe and N is conceivable. To gain further insight into the individual mechanistic steps and to more generally explore the reactivity of the tin species (pS)-2Sn, we performed a series of NMR scale experiments with Lewis and Bronsted acids (Scheme 3-3).

![Proposed reaction pathway](image)

**Figure 3-6.** Proposed reaction pathway in the formation of (pR)-3 from (pS)-2Sn (X = Me, Cl)

**Step 1: Lewis Acid-Base Adduct Formation and Possible Involvement of a Borenium-Type Intermediate.** The high regio- and stereoselectivity of the borylation process is a strong indication for a directing effect of the pyridyl substituent, which
would require formation of a Lewis acid-base adduct. It is also conceivable that steric strain upon adduct formation with PhBCl₂ is released by chloride abstraction with formation of a borenium cation, a process that could be facilitated by the presence of excess PhBCl₂ as a chloride acceptor. Importantly, these types of borenium cations have been shown previously by others²⁹ to be highly effective intermediates in both intramolecular and intermolecular electrophilic borylation reactions.

Attempts at the direct detection of a Lewis acid-base adduct or a borenium-type species by multinuclear NMR spectroscopy proved unsuccessful because of fast conversion to the final product even at –70 °C. To gather other evidence for such a complex, (pS)-2Sn was reacted with B(C₆F₅)₃ as a Lewis acids that was not expected to lead to follow-up reactions with expulsion of the stannyl group as in the case of chloroboranes.³⁰ Addition of one equivalent of B(C₆F₅)₃ led to a new species with three separate Me signals (1.16, 0.90, 0.56 ppm) of equal integration. The ¹¹B NMR shifted from ca. 60 ppm for B(C₆F₅)₃ to –15.0 ppm, and the ¹⁹F NMR signal for the para-fluorines from –148.6 ppm to –164.1 ppm. These observations suggest that (partial) methyl group abstraction occurred rather than B-N bond formation, with generation of the [MeB(C₆F₅)₃]⁻ anion (Scheme 3-3). The presence of the pyridyl-stabilized stannylium cation [(pS)-4]⁺ and the anion [MeB(C₆F₅)₃]⁻ was further established by high resolution MALDI-MS analysis in positive and negative mode, respectively.

We note that a similar Me group cleavage reaction also occurred when (pS)-2Sn was reacted with one equivalent of PhBCl₂ in hexanes; the chlorostannylferrocene (pS)-4Cl precipitated from the reaction mixture and was isolated as the major product (>95%). We attribute the facile cleavage of the Sn-Me bond to the presence of the pyridyl group in the
trans position, which leads to an elongation of the corresponding Sn-C bond as mentioned earlier in the context of the X-ray structure discussion of (pS)-2Sn. Indeed treatment of (pS)-2Sn with iodine also resulted in clean conversion to the iodo derivative (pS)-4I. Iodide abstraction from (pS)-4I with Krossing’s salt gave [(pS)-4][Al(OC(CF₃)₃)_4] (Scheme 3-3). The latter was fully characterized by multinuclear NMR and a single crystal X-ray structure (see 3.6 Supporting Information, Figure 3-8) established the connectivity. The compound also served to further confirm the identity of the cation in [(pS)-4][MeB(C₆F₅)_3].

Scheme 3-3. Reactivity of (pS)-2Sn toward selected Lewis and Brønsted acids.
(i) B(C₆F₅)₃. (ii) X = Cl: PhBCl₂ in hexanes or Me₂S·BH₃ in CDCl₃; X = I: I₂. (iii) [H(Et₂O)₂][B(C₆F₅)₄]. (iv) [X]⁻ = [Al(OC(CF₃)₃)_4]: (pS)-4I + Li[Al(OC(CF₃)₃)_4].

We reasoned that the presence of the trimethylstannyl group in (pS)-2Sn as a good leaving group facilitated the low temperature borylation and led to side reactions such as methyl abstraction, which prevented us from observing a Lewis acid-base adduct and/or a
borenium type intermediate. To stabilize the possible intermediates, we decided to use the parent lutidylferrocene (FcLu) as a model compound for our mechanistic studies. As expected, an immediate color change to dark red was observed upon mixing of FcLu and B(C₆F₅)₃ in CDCl₃. The $^{11}$B NMR spectrum revealed a peak at −2.1 ppm, suggesting the formation of a tetracoordinate Lewis acid-base adduct. When we reacted FcLu with 1 equivalent of PhBCl₂ (Scheme 3-4) two major products were observed and identified as rac-3 and the protonated lutidylferrocene $[\text{FcLuH}]^+\text{[PhBCl}_3^-]$ (as a result of HCl release in the formation of rac-3). To observe a possible intermediate we carried out an NMR scale reaction of FcLu and PhBCl₂ at −70 °C. Upon addition of 1 equiv of PhBCl₂ at −70 °C formation of a Lewis acid-base adduct was evident from an $^{11}$B NMR resonance at 11.7 ppm. As the reaction mixture was allowed to warm up, the adduct converted to the product rac-3 (ca. 50%), while the other 50% of the starting material was protonated to give $[\text{FcLuH}]^+\text{[PhBCl}_3^-]$. When FcLu, EtN(iPr)₂ and 2 equivs of PhBCl₂ were mixed at −70 °C, we similarly observed adduct formation along with some product rac-3. Within a few hours the adduct completely converted to the product even at −70 °C.

Although no evidence of borenium cation formation could be detected based on $^1$H and $^{11}$B NMR analysis, it is a likely short-lived intermediate giving the fact that the reaction proceeds even at −70 °C in the presence of base and excess PhBCl₂. By comparison, borylation of unsubstituted ferrocene with PhBCl₂ is very slow under ambient condition. Noteworthy is also that according to recent literature reports borenium ion-mediated borylation of phenylpyridine occurs only when an excess of BBr₃ is applied in the presence of a bulky base to capture the HBr by-product. In our case, the electron-rich
character of the ferrocene unit allows for reaction even with relatively weakly Lewis acidic compounds such as PhBCl₂.

**Scheme 3-4.** Reaction of FcLu with PhBCl₂.

**Step 2: Proton Migration.** The second step in the proposed mechanism involves proton migration of Cp-H₃ to the C-Sn position, possibly again mediated by the pyridyl group or by the Fe center. To further examine this step, (p₅)-2Sn was treated with one equivalent of Jutzi’s acid,\(^{31}\) \([\text{H(Et}_2\text{O)}_2]^+\text{[B(C}_6\text{F}_5)_4]^-\). Rapid protonation with formation of the corresponding pyridinium species was observed. The latter exhibits a characteristic triplet at 12.2 ppm with a coupling constant of \(J(\text{¹⁴N,H}) = 50\) Hz and a chemical shift that is very different from that reported for protonated ferrocene\(^{28b}\) (\(δ = -1.5\)). The corresponding experiment in which the boracycle (p₅)-3 was treated with Jutzi’s acid led to a spectrum that contains two major species. A quadrupole-broadened signal is clearly observed at 11.5 ppm, which is indicative of protonation of the pyridyl nitrogen. Based on a comparison of the spectral data with those of an independently prepared sample we identified this species as FcLuH\(^+\), which arises from protonolysis of both the B-N and the B-C bond. Based on MALDI-MS evidence, the second species is tentatively assigned to
protonolysis of the dative B-N bond, which would results in a boronium cation that is stabilized by Et$_2$O coordination, $[\text{FcLu}(\text{B(Ph)(OEt}_2)_2)\cdot\text{HCl}]^+$. The observed protonation of the pyridine nitrogen (but not the Fe center) suggests the possible involvement of the pyridine base also in the proton migration step of the rearrangement mechanism.

### 3.4 Conclusions

We have introduced a new stereoselective borylation procedure for the synthesis of planar chiral ferrocenes. The ability to prepare both enantiomers of 3 individually, starting from just one enantiomer of the precursor is very appealing. The inversion of stereochemistry in the formation of (pR)-3 from (pS)-2Sn is a particularly interesting discovery. Given the high regio- and stereoselectivity of the process, the Lewis basic pyridyl group in (pS)-2Sn must act as an ortho-directing group that facilitates selective borane attack at the C-H position next to the pyridyl group. This ultimately implies that cleavage of the Cp-H3 bond in (pS)-2Sn is more facile than the direct cleavage of the Cp-Sn bond. We further propose that formation of a highly reactive borenium cation intermediate enables this unusual reactivity pattern.

The pyridylferrocenylborane heterocycles prepared in here are promising as precursors to new planar chiral borane Lewis acids. We also expect these types of compounds to prove useful as intermediates in the synthesis of chiral pyridylferrocene ligands, by taking advantage of Suzuki-type cross-coupling procedures.$^9$

### 3.5 Experimental Section

**Reagents and general methods.** tert-Butyl lithium (1.7 M in hexanes), $n$-butyl lithium (1.6 M in hexanes), 2,2,6,6-tetramethylpiperidine, EtN(iPr)$_2$, Me$_3$SnCl, PhBCl$_2$, .
Me₂S·BH₃ (1.0 M in CH₂Cl₂), tris(dibenzylideneacetone)dipalladium(0) and tri-tert-butylphosphine were purchased from Aldrich and used without further purification. 2,2,6,6-Tetramethylpiperidine and EtN(iPr)₂ were purchased from Aldrich and distilled from CaH₂ prior to use. 2-Iodo-3,5-dimethylpyridine,³² (S₅)-p-tolylsulfinylferrocene,³³ [H(Et₂O)₂][B(C₆F₅)₄]⁻³¹, Li[Al(OC(CF₃)₃)₄]³⁴ were prepared according to literature procedures. 3,5-Dimethylpyrid-2-ylferrocene (FcLu) was prepared from tributylstannylferrocene by treatment with n-BuLi, followed by addition of ZnBr₂ and subsequent Negishi coupling with tris(dibenzylideneacetone)dipalladium(0) / tri-tert-butylphosphine as the catalyst system. LiTMP was freshly prepared by addition of n-butyl lithium (1.6 M in hexanes) to a THF solution of 2,2,6,6-tetramethylpiperidine at 0 °C. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (MBraun). 499.9 MHz ¹H, 125.7 MHz ¹³C, 160.4 MHz ¹¹B, 470.4 MHz ¹⁹F, and 186.4 MHz ¹¹⁹Sn NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ¹H and ¹³C NMR spectra were referenced internally to solvent signals. ¹¹B NMR spectra were acquired with boron-free quartz NMR tubes and referenced externally to BF₃ · Et₂O (δ = 0) and ¹¹⁹Sn NMR data to SnMe₄ (δ = 0). The following abbreviations are used for signal assignments: Lu = 3,5-dimethylpyrid-2-yl, Fc = ferrocenyl, Cp = cyclopentadienyl. High resolution MALDI-MS (benzo[α]pyrene matrix) or ESI-MS (1 µM in toluene) data were obtained on an Apex Ultra 7.0 Hybrid FTMS (Bruker Daltonics). UV/Vis absorption data were acquired on a Varian Cary 500 UV/Vis/NIR spectrophotometer. Optical rotation analyses were
performed on an Autopol III polarimeter, Rudolph Research Analytical, using a tungsten-
halogen light source operating at $\lambda = 589$ nm. Chiral HPLC analyses were performed on a
Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC
pump, and a 2998 photodiode array detector; a CHIRALPAK® IA-3 column was used
for separation. Elemental analyses were performed by Intertek Pharmaceutical Services,
Whitehouse, NJ.

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD
Diffractometer using CuK$\alpha$ (1.54178 Å) radiation at 100 K. The structures were refined
by full-matrix least squares based on $F^2$ with all reflections (SHELXTL V5.10; G.
Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with
anisotropic displacement coefficients, and hydrogen atoms were treated as idealized
contribution. SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens Area
Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption
correction was applied. Crystallographic data for the structures of (p$R$, $S_s$)-1, (p$S$)-2Sn,
(p$R$)-3, (p$S$)-3 and [(p$S$)-4]$^+\text{[Al(OC(CF$_3$)$_3$)$_4$]}^-$ have been deposited with the Cambridge
Crystallographic Data Center as supplementary publications CCDC 907176 – 907179,
and 938810. Copies of the data can be obtained free of charge on application to CCDC,
12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Synthesis of (p$R$)-2-(3,5-Dimethylpyrid-2-yl)-1-(p-tolysulfynyl)ferrocene (p$R$, $S_s$)-1.
To a pre-cooled ($\sim$78 °C) solution of ($S_s$)-p-tolisulfynylferrocene (3.00 g, 9.26 mmol)
in THF (30 mL) was added a solution of LiTMP (0.5 M in THF, 22.2 mL, 11.1 mmol,
1.20 equiv) dropwise and the mixture was kept stirring for 1 hour. A solution of ZnCl₂ (1.39 g, 10.2 mmol, 1.10 equiv) in THF (20 mL) was then added. After 1 hour at –78 °C the mixture was allowed to warm up and then stirred for 1 hour at 25 °C. Tris(dibenzylideneacetone)dipalladium(0) (0.847 g, 0.926 mmol, 0.10 equiv), tri-tert-butylphosphine (0.374 g, 1.85 mmol, 0.20 equiv) and 2-iodo-3,5-dimethylpyridine (4.31 g, 18.5 mmol, 2.00 equiv) were dissolved in a separate flask in THF (20 mL); after stirring for 5 min the solution was added to the pre-made zinc reagent by syringe. The mixture was stirred for 2 days at room temperature. After addition of saturated NH₄Cl solution (50 mL), the mixture was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were washed with brine and then water, dried over sodium sulfate and concentrated. The residue was chromatographed on alumina gel with ethyl acetate/hexanes (1:2) as the eluent, followed by recrystallization from acetone. Yield: 2.4 g (61%). [α]²₀_D (c = 0.20, CH₂Cl₂) = –222°. ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 8.44 (s, 1H; Lu), 7.86 (d, J = 6.0 Hz, 2H; Tol), 7.37 (d, J = 6.0 Hz, 2H; Tol), 7.25 (s, 1H; Lu), 4.68 (br, 1H; Cp), 4.35 (br, 1H; Cp), 4.13 (s, 5H; free Cp), 4.01 (br, 1H; Cp), 2.47 (s, 3H; Lu-Me), 2.33 (s, 3H; Me), 2.27 (s, 3H; Lu-Me). ¹³C NMR (125.69 MHz, CDCl₃, 25 °C): δ = 151.0, 146.9, 141.4, 141.0, 138.4, 131.6, 131.0, 129.1, 125.8 (Lu and Tol), 95.9 (i-Cp-S), 88.8 (i-Cp-C), 71.6 (Cp), 71.1 (free Cp), 68.5 (Cp), 67.7 (Cp), 21.4, 20.2, 18.0 (Me). High-resolution ESI-MS (pos. mode): m/z 881.1659 ([2M+Na]^+, 100%, calcd for C₄₈H₃₈N₂O₂S₂Fe₂ 881.1592). Elemental analysis for C₂₄H₂₃FeNOS, calcd C 67.13, H 5.40, N 3.26, found C 66.96, H 5.47, N 2.99%.

**Synthesis of (pS)-2Sn.** To a solution of (pR, S₁)-1 (1.20 g, 2.80 mmol) in THF (30 mL) that was cooled to –78 °C was added t-butyl lithium (1.7 M in hexanes, 2.24 mL, 3.08
mmol, 1.10 equiv) dropwise under stirring. The reaction mixture was kept stirring for 10 min at the same temperature before a solution of Me₂SnCl (0.67 g, 3.36 mmol, 1.2 equiv) in THF (5 mL) was added via syringe. The resulting solution was stirred for 1 h and the temperature was slowly raised to 25 °C. After addition of water the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with brine solution followed by water, dried over sodium sulfate and concentrated. The residue was subjected to column chromatography on silica gel with hexanes-triethylamine mixture (100:1) as the eluent. The fractions containing the product were concentrated and the residue was taken back up in hot MeOH. Crystallization at −37 °C gave red crystals that proved to be suitable for X-ray diffraction analysis. Yield: 0.87 g (69%). [α]²⁰D (c = 0.115, CHCl₃) = −20°. 

\[ \frac{1}{2} \text{H NMR (499.9 MHz, CDCl₃, 25 °C): } \delta = 8.03 \text{ (s, 1H; Lu), 7.22 (s, 1H; Lu), 4.90 (nr, 1H; Cp), 4.55 (nr, 1H; Cp), 4.35 (nr, 1H; Cp), 4.05 (s, 5H; free Cp), 2.59 (s, 3H; Lu-Me), 2.26 (s, 3H; Lu-Me), 0.21 (s/d, J(117/119\text{Sn},H) = 45 Hz, 9H; SnMe₂).} \]

\[ ^{13}\text{C NMR (125.69 MHz, CDCl₃, 25 °C): } \delta = 153.9, 145.2, 139.7, 129.5 \text{ (Lu), 88.7 (i-Cp-C), 75.5 (Cp), 73.0 (i-Cp-Sn), 72.6 (s/d, J(117/119\text{Sn},C) = 50 Hz; Cp), 71.0 (s/d, J(117/119\text{Sn},C) = 38 Hz; Cp), 68.9 (free Cp), 21.1 (Lu-Me), 17.8 (Lu-Me), −5.8 (s/d, J(117/119\text{Sn},C) = 362/382 Hz, SnMe₃).} \]

\[ ^{119}\text{Sn NMR (186.4 MHz, CDCl₃, 25 °C): } \delta = −39.9. \]

UV-Vis (CHCl₃): \( \lambda_{\text{max}} = 454 \text{ (e = 570 M}^{-1} \text{ cm}^{-1}) \). High-resolution MALDI-MS (pos. mode, benzo[\text{α}]pyrene): m/z 440.0124 ([\text{M-Me}]⁺, 100%, caled for \(^{12}\text{C}_{19}\text{H}_{22}\text{N}^{56}\text{Fe}^{119}\text{Sn} 440.0122\)). Elemental analysis for \( \text{C}_{20}\text{H}_{25}\text{NFeSn} \), calcd C 52.89, H 5.55, N 3.09, found C 52.68, H 5.08, N 3.14%.

**Synthesis of (pS)-2\text{Hg}**. A solution of (pS)-2\text{Sn} (30 mg, 0.066 mmol) in acetone (5 mL) was added dropwise to a solution of HgCl₂ (20 mg, 0.076 mmol, 1.1 equiv) in acetone (5
mL) under stirring. The mixture was allowed to stir for 1 hour and then the solvent was removed under high vacuum. The product, (pS)-2Hg, was dried under high vacuum for 2 hours at 60 °C and used without further purification. \([\alpha]^{20}_D\) (c = 0.597, CHCl₃) = −107°.

\(^1\)H NMR of (pS)-2Hg (499.9 MHz, CDCl₃, 25 °C): \(\delta = 8.19\) (s, 1H; Lu), 7.28 (s, 1H; Lu), 5.05 (d, \(J = 2.5\) Hz, 1H; Cp), 4.60 (pst, \(J = 2.5\) Hz, 1H; Cp), 4.36 (d, \(J = 2.5\) Hz, 1H; Cp), 4.07 (s, 5H; free Cp), 2.53 (s, 3H; Lu-Me), 2.28 (s, 3H; Lu-Me). \(^1\)C NMR (125.69 MHz, CDCl₃, 25 °C): \(\delta = 153.0, 145.7, 140.7, 130.6, 130.0\) (Lu), 87.2 (i-Cp-Hg), 85.4 (i-Cp-C), 74.6 (Cp), 73.0 (Cp), 70.2 (Cp), 69.7 (free Cp), 21.3 (Lu-Me), 17.8 (Lu-Me). Elemental analysis for C₁₇H₁₆ClFeHgN, calcd C 38.78, H 3.07, N 2.48, found C 39.20, H 3.07, N 2.48%.

**Synthesis of (pR)-3.** A solution of (pS)-2Sn (100 mg, 0.22 mmol) in a 1:1 mixture of hexanes and toluene (20 mL) was cooled down to −37 °C and then a solution of PhBCl₂ (70 mg, 0.44 mmol, 2.0 equiv) in toluene (2 mL) was added dropwise under stirring. The mixture was stirred over night at room temperature and then the solvents were removed under high vacuum. The residue was taken back up in a mixture of hot hexanes/toluene (1:1). When stored at −37 °C crystals were obtained that contain half an equivalent of toluene; they proved to be suitable for X-ray diffraction analysis. Yield: 55 mg (55%). \([\alpha]^{20}_D\) (c = 0.10, CH₂Cl₂) = +2110°. \(^1\)H NMR (499.9 MHz, CDCl₃, 25 °C): Ratio Major : Minor Isomer = 2.5 : 1; \(\delta = 8.23\) (s, 1H, Lu; Minor), 8.13 (s, 1H; Lu, Major), 7.58 (s, 1H; Lu, Minor), 7.53 (d, \(J = 7\) Hz, 2H; o-Ph, Minor), 7.48 (s, 1H; Lu, Major), 7.37 (pst, \(J = 7\) Hz, 2H; m-Ph, Minor), 7.32 (d, \(J = 7\) Hz, 2H; o-Ph, Major), 7.26 (nr, 1H, p-Ph, Minor), 7.16 (pst, \(J = 7\) Hz, 2H; m-Ph, Major), 7.13 (m, 1H, p-Ph, Major), 4.77 (dd, \(J = 2.5\) Hz, 1 Hz, 1H; Cp, Major), 4.71 (overlapped, 2H; Cp, Minor), 4.62 (dd, \(J = 2.5\) Hz, 1 Hz, 1H;
Cp, Major), 4.58 (m, 2H; Cp, Major + Minor), 4.22 (s, 5H; free Cp, Major), 3.65 (s, 5H; free Cp, Minor), 2.52 (s, 3H; Lu-Me, Major), 2.51 (s, 3H; Lu-Me, Minor), 2.38 (s, 3H; Lu-Me, Minor), 2.30 (s, 3H; Lu-Me, Major). $^1$H NMR (499.9 MHz, C$_6$D$_6$, 25 °C): Ratio Major : Minor Isomer = 3.2 : 1; $\delta$ = 8.03 (overlapped s, 1H, Lu-H6, Major and s, 1H; Lu-H6, Minor), 7.85 (d, $J = 7$ Hz, 2H; o-Ph, Minor), 7.82 (d, $J = 7$ Hz, 2H; o-Ph, Major), 7.43 (ps, $J = 7$ Hz, 2H; m-Ph, Minor), 7.27 (overlapped, 1H, p-Ph, Minor), 7.27 (ps, $J = 7$ Hz, 2H; m-Ph, Major), 7.14 (t, $J = 7$ Hz, p-Ph, Major), 6.47 (s, 1H; Lu-H4, Minor), 6.43 (s, 1H; Lu-H4, Major), 4.77 (nr, 1H; Cp-H3, Minor), 4.64 (nr; Cp-H3, Major), 4.43 (nr, 1H; Cp-H5, Major), 4.33 (nr, 1H; Cp-H4, Major), 4.31 (nr, 1H; Cp-H4, Minor), 4.22 (s, 5H; free Cp, Major), 4.22 (overlapped, 1H; Cp-H5, Minor), 3.59 (s, 5H; free Cp, Minor), 1.87 (s, 3H; Lu-Me-3, Major), 1.80 (s, 3H; Lu-Me-3, Minor), 1.45 (s, 3H; Lu-Me-5, Minor), 1.34 (s, 3H; Lu-Me-5, Major). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 6.0 ($\nu_{1/2} = 210$ Hz). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C) $\delta$ = 158.3, 157.3, 143.3, 142.8, 142.4, 141.5, 131.5, 131.5, 130.4, 130.3, 129.5, 128.9, 127.3, 127.3, 126.4, 126.2 (Lu + Ph), i-Ph-B not observed, 84.0 (i-Cp-C, Major), 82.5 (i-Cp-C, Minor), 74.7 (Cp, Minor), 74.4 (Cp, Major), 70.3 (i-Cp-B, Major), 70.2 (i-Cp-B, Minor), 70.1 (free Cp, Major), 69.8 (free Cp, Minor), 64.6 (Cp, Minor), 64.5 (Cp, Major), 18.3 (Lu-Me, Major), 18.3 (Lu-Me, Minor), 18.2 (Lu-Me, Minor), 18.1 (Lu-Me, Major). UV-Vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 413 ($\varepsilon$ = 1900 M$^{-1}$ cm$^{-1}$), 503 ($\varepsilon$ = 2700 M$^{-1}$ cm$^{-1}$). High-resolution MALDI-MS (pos. mode, benzo[α]pyrene): m/z 413.0828 ([M]$^+$, 40%, calcd for $^{12}$C$_{23}$$^1$H$_{21}$$^{11}$B$^{14}$N$^{35}$Cl$^{56}$Fe 413.0804); m/z 378.1137 ([M-Cl]$^+$, 100%, calcd for $^{12}$C$_{23}$$^1$H$_{21}$$^{11}$B$^{14}$N$^{35}$Fe 378.1115). Elemental analysis for (C$_{23}$H$_{21}$BClFeN)(C$_7$H$_8$)$_{0.2}$, calcd C 67.85, H 5.27, N 3.24, found C
67.99, H 5.27, N 3.15%; the presence of co-crystallized toluene was confirmed by $^1$H NMR and single crystal X-ray diffraction analysis.

**Synthesis of (pS)-3.** (pS)-2Hg (prepared from 30 mg of (pS)-2Sn as described above) was dissolved in toluene (5 mL) and a solution of PhBCl$_2$ (12 mg, 0.076 mmol, 1.1 equiv) in toluene (2 mL) was added at $-37 \, ^\circ$C. Upon addition the color of the mixture turned dark red. After stirring over night at room temperature the solvent was removed under high vacuum. The residue was re-dissolved in a mixture of hot hexanes and toluene (1:1) and a small amount of a black solid was filtered off. The filtrate was kept at $-37 \, ^\circ$C; after repeated filtration to remove small amounts of insoluble impurities, the product formed X-ray quality crystals that contained half an equivalent of toluene. Yield: 11 mg (37%). $\alpha^{20}_D (c = 0.10, \text{CH}_2\text{Cl}_2) = -2060^\circ$.

**Reaction of (pS)-2Sn with one equiv of PhBCl$_2$. Synthesis of (pS)-4Cl.** A solution of (pS)-2Sn (10 mg, 0.022 mmol) in hexanes (2 mL) was cooled down to $-37 \, ^\circ$C and then a solution of PhBCl$_2$ (3.5 mg, 0.022 mmol, 1.0 equiv) in hexanes (1 mL) was added dropwise under stirring. An orange precipitate formed that redissolved upon addition of toluene. The mixture was stirred over night at room temperature and then the solvents were removed under high vacuum. The $^1$H NMR spectrum of the residue revealed the formation of (pS)-4Cl (>95%). $^1$H NMR (499.9 MHz, CDCl$_3$, 25 $^\circ$C): $\delta = 7.82$ (s, 1H; Lu), 7.39 (s, 1H; Lu), 5.03 (d, $J = 2.0 \, Hz$, 1H; Cp), 4.92 (dd, $J = 2.0 \, Hz$, 1H; Cp), 4.70 (pst, $J = 2.0 \, Hz$, 1H; Cp), 4.13 (s, 5H; free Cp), 2.56 (s, 3H; Lu-Me), 2.31 (s, 3H; Lu-Me), 0.92 (s/d, $J^{(117/119}\text{Sn},H) = 70 \, Hz$, 3H; SnMe), 0.69 (s/d, $J^{(117/119}\text{Sn},H) = 68 \, Hz$, 3H; SnMe). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 $^\circ$C): $\delta = 154.7$, 143.4, 142.0, 131.1, 130.5 (Lu), 85.4 (i-Cp-C), 76.4 (s/d, $J^{(117/119}\text{Sn},C) = 68 \, Hz$, Cp), 75.0 (i-Cp-Sn), 74.6 (s/d,
J(^{117/119}\text{Sn,C}) = 67 \text{ Hz, Cp}), 70.8 (s/d, J(^{117/119}\text{Sn,C}) = 48 \text{ Hz, Cp}), 69.5 (\text{free Cp}), 20.9 (\text{Lu-Me}), 17.8 (\text{Lu-Me}), 3.3 (\text{nr, SnMe}) 1.6 (\text{nr, SnMe}). ^{119}\text{Sn} \text{NMR (186.4 MHz, CDCl}_3, 25 \degree \text{C}): \delta = -67.2. \text{High-resolution MALDI-MS (pos. mode, benzo[\alpha]pyrene): m/z 474.9817 ([M]^+, 3\%, calcd for }^{12}\text{C}_{19}\text{H}_{22}\text{H}_{14}\text{N}_{35}\text{Cl}_{56}\text{Fe}^{119}\text{Sn 474.9804}, 459.9589 ([\text{M-Me}]^+, 20\%, calcd for }^{12}\text{C}_{18}\text{H}_{19}\text{H}_{14}\text{N}_{35}\text{Cl}_{56}\text{Fe}^{119}\text{Sn 459.9572}, \text{m/z 440.0134 ([M-Cl]^+, 100\%, calcd for }^{12}\text{C}_{19}\text{H}_{22}\text{H}_{14}\text{N}_{56}\text{Fe}^{119}\text{Sn 440.0122}).

**Reaction of (pS)-2Sn with one equiv of I}_2. \text{Synthesis of (pS)-4I. To a solution of (pS)-2Sn (60 mg, 0.132 mmol) in 10 mL of CH}_2\text{Cl}_2 \text{was added a solution of I}_2 (34 mg, 0.132 mmol) in 5 mL of CH}_2\text{Cl}_2 \text{at -37 \degree \text{C}. After stirring at room temperature for 0.5 hours the solvent was removed under high vacuum. The residue was washed with cold hexanes and then recrystallized from hot hexanes. Yield: 55 mg (73\%). \text{^1H NMR (499.9 MHz, CDCl}_3, 25 \degree \text{C}): \delta = 7.84 (s, 1H; Lu), 7.40 (s, 1H; Lu), 5.07 (nr, 1H; Cp), 5.00 (nr, 1H; Cp), 4.70 (nr, 1H; Cp), 4.15 (s, 5H; free Cp), 2.57 (s, 3H; Lu-Me), 2.32 (s, 3H; Lu-Me), 1.19 (s/d, J(^{117/119}\text{Sn,H}) = 68 \text{ Hz, 3H; SnMe}), 0.95 (s/d, J(^{117/119}\text{Sn,H}) = 66 \text{ Hz, 3H; SnMe}). \text{^13C NMR (125.69 MHz, CDCl}_3, 25 \degree \text{C>): \delta = 154.7, 143.3, 142.2, 131.0, 130.7 (Lu), 85.0 (i-Cp-C), 77.7 (s/d, J(^{117/119}\text{Sn,C}) = 67 \text{ Hz; Cp}), 74.0 (s/d, J(^{117/119}\text{Sn,C}) = 66 \text{ Hz, Cp}), 73.9 (i-Cp-Sn), 71.1 (s/d, J(^{117/119}\text{Sn,C}) = 45 \text{ Hz; Cp}), 69.5 (\text{free Cp}), 21.0 (\text{Lu-Me}), 17.9 (\text{Lu-Me}), 6.5 (s/d, J(^{117/119}\text{Sn,C}) = 483/503 \text{ Hz; SnMe}), 4.1 (s/d, J(^{117/119}\text{Sn,C}) = 543/561 \text{ Hz; SnMe}). \text{^119Sn NMR (186.4 MHz, CDCl}_3, 25 \degree \text{C): \delta = -115.5. High-resolution MALDI-MS (pos. mode, benzo[\alpha]pyrene): m/z 551.8916 ([M-Me]^+, 30\%, calcd for }^{12}\text{C}_{18}\text{H}_{19}\text{H}_{14}\text{N}_{56}\text{Fe}^{119}\text{Sn}_{127}\text{I 551.8932}, \text{m/z 440.0118 ([M-I]^+, 100\%, calcd for }^{12}\text{C}_{19}\text{H}_{22}\text{H}_{14}\text{N}_{56}\text{Fe}^{119}\text{Sn 440.0122}). \text{Elemental analysis for C}_{19}\text{H}_{22}\text{Fe}_{119}\text{Sn, calcd C 40.31, H 3.93, N 2.48, found C 40.42, H 3.93, N 2.40\%.}
Reaction of (pS)-4I with Krossing’s Salt. Synthesis of the Organotin Cation [(pS)-4I][Al(OC(CF3)3)4]. To a sample of Li[Al(OC(CF3)3)4] (13.7 mg, 14 µmol) in a 20 mL vial was added a solution of (pS)-4I; 8.0 mg, 14 µmol) in CDCl3 (1 mL) under vigorous stirring. The mixture was stirred for 0.5 hours and then filtered. 1H NMR analysis showed complete conversion to the product. X-ray quality single crystals were obtained from CHCl3 at –37 °C. 1H NMR (499.9 MHz, CDCl3, 25 °C): δ = 7.82 (s, 1H; Lu), 7.76 (s, 1H; Lu), 5.28 (nr, 1H; Cp), 5.00 (nr, 1H; Cp), 4.79 (nr, 1H; Cp), 4.22 (s, 5H; free Cp), 2.64 (s, 3H; Lu-Me), 2.40 (s, 3H; Lu-Me), 1.32 (s/d, J(117/119Sn,H) = 60 Hz, 3H; SnMe), 1.06 (s/d, J(117/119Sn,H) = 59 Hz, 3H; SnMe). 13C NMR (125.69 MHz, CDCl3, 25 °C): δ = 157.2, 146.5, 143.1, 134.3, 133.5 (Lu), 121.2 (q, J(C,F) = 291 Hz, CF3), 85.5 (i-Cp-C), 77.5 (Cp), 75.4 (s/d, J(117/119Sn,C) = 80 Hz, Cp), 72.2 (s/d, J(117/119Sn,C) = 40 Hz, Cp), 71.3 (i-Cp-Sn), 70.6 (free Cp), 20.8 (Lu-Me), 17.5 (Lu-Me), 0.4 (br, SnMe) 0.0 (br, SnMe). 19F NMR (470.4 MHz, CDCl3, 25 °C): δ = –75.4. 119Sn NMR (470.4 MHz, CDCl3, 25 °C): δ = +171 (br). High-resolution MALDI-MS (pos. mode, benzo[a]pyrene): m/z 440.0120 ([M]⁺, 100%, calcd for 12C19¹H22¹4N56Fe¹¹9Sn 440.0122), 409.9656 ([M-2Me]⁺, 35%, calcd for 12C17¹H16¹4N56Fe¹¹9Sn 409.9652).

NMR scale reactions of (pS)-2Sn with Lewis and Brønsted acids. Compound (pS)-2Sn (ca. 10 mg) was dissolved in 0.7 mL of CDCl3 (or CD2Cl2) in a J. Young’s NMR tube and the solution was cooled to –37 °C. The selected acid was added either neat or as a solution (Me2S·BH3). NMR data were acquired at room temperature right after mixing the components.

(a) Reaction of (pS)-2Sn with Me2S·BH3. A ca. 5-fold excess of Me2S·BH3 (1M in CH2Cl2) was added to a solution of (pS)-2Sn in CDCl3. Analysis by 1H and 11B NMR
spectroscopy revealed the adduct \((pS)\)-2·BH\(_3\) (ca. 20\%) in equilibrium with the starting components. For \((pS)\)-2Sn•BH\(_3\): \(^1\)H NMR (499.9 MHz, CDCl\(_3\), 25 °C): \(\delta = 8.49\) (s, 1H; Lu), 7.56 (s, 1H; Lu), 4.69 (br, 1H; Cp), 4.57 (br, 1H; Cp), 4.44 (br, 1H; Cp), 4.20 (s, 5H; free Cp), 3.06 (s, 3H; Lu-Me), 2.32 (s, 3H; Lu-Me), 0.08 (s/d, \(J^{(117/119)\text{Sn},H} = 63\) Hz, 9H; SnMe\(_3\)). \(^{11}\)B NMR (160.4 MHz, CDCl\(_3\), 25 °C) \(\delta = -11.0\) (m). Over a period of 48 h \((pS)\)-2 converted to the chlorostannyl derivative \((pS)\)-4Cl as confirmed by comparison of \(^1\)H NMR and high resolution MALDI-MS data with those of an authentic sample prepared from \((pS)\)-2Sn and PhBCl\(_2\) as described above.

(b) Reaction of \((pS)\)-2Sn with B(C\(_6\)F\(_5\))\(_3\). B(C\(_6\)F\(_5\))\(_3\) was added as a solid to a solution of \((pS)\)-2Sn in CDCl\(_3\). The color of the mixture turned slightly darker. \(^1\)H, \(^{11}\)B, and \(^{19}\)F NMR data and MALDI-MS analysis indicated (partial) methyl group abstraction from Sn with formation of the ionic species \([(pS)\]-4\][B(C\(_6\)F\(_5\))\(_3\)Me\]-. \(^1\)H NMR (499.9 MHz, CDCl\(_3\), 25 °C): \(\delta = 7.81\) (s, 1H; Lu), 7.66 (s, 1H; Lu), 5.19 (br, 1H; Cp), 4.90 (br, 1H; Cp), 4.67 (br, 1H; Cp), 4.17 (s, 5H; free Cp), 2.59 (s, 3H; Lu-Me), 2.32 (s, 3H; Lu-Me), 1.16 (br, 3H; SnMe), 0.90 (br, 3H; SnMe), 0.56 (s, 3H; BMe). \(^{11}\)B NMR (160.4 MHz, CDCl\(_3\), 25 °C) \(\delta = -15.0\) (\(w_{1/2} = 70\) Hz). \(^{19}\)F NMR (470.4 MHz, CDCl\(_3\), 25 °C): \(\delta = -132.6\) (d, \(J(F,F) = 22\) Hz, 6F; ortho-F), -164.1 (t, \(J(F,F) = 20\) Hz, 3F; para-F), -166.8 (pst, \(J(F,F) = 20\) Hz, 6F; meta-F). \(^{119}\)Sn NMR (470.4 MHz, CDCl\(_3\), 25 °C): \(\delta = +119.2\) (br). After addition of another equivalent of B(C\(_6\)F\(_5\))\(_3\) the \(^{119}\)Sn NMR shifted to \(\delta = +155.1\) (br), suggesting that an equilibrium is established between free acid and product and shifted toward product in the presence of an excess of the Lewis acid. High-resolution MALDI-MS (pos. mode, benzo[\(\alpha\)]pyrene): m/z 440.0134 ([M]\(^+\), 100\%, calcd for \(^{12}\)C\(_{19}\)H\(_{22}\)\(^{14}\)N\(_{56}\)Fe\(^{119}\)Sn 440.0120). High-resolution MALDI-MS (neg. mode,
benzo[α]pyrene): m/z 527.0061 ([M]+, 100%, calcd for $^{12}$C$_{19}$H$_3^{11}$B$_{19}$F$_{15}$ 527.0083). The identity of [(pS)-4]$^+$$[\text{B(C}_6\text{F}_5)_3\text{Me}]^-$ was further confirmed by comparison of the NMR and MS data with those of an isolated sample of [(pS)-4]$^+$$[\text{Al(OC(F}_3)_3\text{)}_4]$.

(c) Reaction of (pS)-2Sn with [H(Et$_2$O)$_2$]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$. [H(Et$_2$O)$_2$]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ was added to (pS)-2Sn in CD$_2$Cl$_2$. The color of the mixture turned slightly darker. $^1$H NMR data were acquired immediately, indicating formation of the protonated product [(pS)-2Sn-H]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$. However, partial decomposition was observed after a few minutes, preventing isolation. $^1$H NMR (499.9 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = 12.23 (t, $^2$$J$($^{14}$N,H) = 50 Hz, 1H, Lu-H$^+$), 8.23 (d, $^3$$J$(H,H) = 6.5 Hz, 1H; o-Lu), 8.13 (s, 1H; p-Lu), 4.86 (br, 1H; Cp), 4.68 (br, 1H; Cp), 4.59 (br, 1H; Cp), 4.43 (br, 5H; free Cp), 3.50 (br, 8H; ether), 2.59 (s, 3H; Lu-Me), 2.35 (s, 3H; Lu-Me), 1.19 (t, $J$ = 7.0 Hz, 12H; ether), 0.16 (s/d, $J$($^{177/119}$Sn,H) = 55 Hz, 9H; SnMe$_3$).

**NMR scale reactions of FcLu with Lewis and Brønsted acids.**

(a) Reaction of FcLu with [H(Et$_2$O)$_2$]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$. An equimolar amount of [H(Et$_2$O)$_2$]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ was added to a solution of FcLu in CD$_2$Cl$_2$. The color of the mixture turned darker red. $^1$H NMR data were acquired immediately, indicating formation of the protonated product [FcLuH]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$. $^1$H NMR (499.9 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = 11.49 (br, 1H; Lu-H$^+$), 7.99 (s, 1H; Lu), 7.96 (s, 1H; Lu), 4.85 (nr, 2H; Cp), 4.68 (nr, 2H; Cp), 4.29 (s, 5H; free Cp), 3.49 (br, 8H; ether), 2.72 (s, 3H; Lu-Me), 2.45 (s, 3H; Lu-Me), 1.19 (br, 12H; ether). High-resolution MALDI-MS (pos. mode, benzo[α]pyrene): m/z 292.0769 ([M]$^+$, 100%, calcd for $^{12}$C$_{17}$H$_{18}^{14}$N$_{56}$Fe 292.0783). High-resolution MALDI-MS (neg. mode, benzo[α]pyrene): m/z 678.9781 ([M]$^-$, 100%, calcd for $^{12}$C$_{24}^{11}$B$_{19}$F$_{20}$ 678.9768).
(b) Reaction of FcLu with B(C₆F₅)₃. An equimolar amount of B(C₆F₅)₃ was added to a solution of FcLu in CDCl₃. The color of the mixture turned darker red. $^1$H, $^{11}$B, $^{19}$F NMR data were acquired immediately, indicating formation of the adduct FcLu-B(C₆F₅)₃. $^1$H NMR (499.9 MHz, CDCl₃, 25 °C): $\delta$ = 8.42 (br, 1H; Lu), 7.66 (br, 1H; Lu), 4.46 (br, 2H; Cp), 4.29 (nr, 2H; Cp), 4.12 (s, 5H; free Cp), 3.06 (br, 3H; Lu-Me), 2.33 (s, 3H; Lu-Me).

$^{11}$B NMR (160.4 MHz, CDCl₃, 25 °C) $\delta$ = –2.1 ($w_{1/2}$ = 800 Hz). $^{19}$F NMR (470.4 MHz, CDCl₃, 25 °C): $\delta$ = –129.9 (br, 6F; ortho-F), –157.3 (br, 3F; para-F), –164.2 (br, 6F; meta-F).

(c) Low temperature reaction of FcLu with PhBCl₂. A boron-free NMR tube was immersed in a liquid nitrogen bath and charged first with a solution of PhBCl₂ and then a solution of FcLu (1:1) in CD₂Cl₂. The tube was warmed up to –100 °C to let the solid melt and mix. The resulting solution was placed in the NMR spectrometer that was preset to –70 °C. Data were required at –70 °C and then at different temperatures upon warming to RT. The NMR data showed evidence of $[\text{FcLuH}]^+[\text{PhBCl}_3]^-$ and another species that is assigned as the Lewis acid-base adduct. $^1$H NMR for FcLu•PhBCl₂ (499.9 MHz, CD₂Cl₂, –70 °C): $\delta$ = 9.30 (br, 1H; Lu), 7.70 (s, 1H; Lu), 7.00 (br, 2H; Ph), 6.89 (br, 3H; Ph), 4.53 (br, 2H; Cp), 4.01 (nr, 2H; Cp), 3.93 (s, 5H; free Cp), 2.88 (s, 3H; Lu-Me), 2.46 (s, 3H; Lu-Me). $^{11}$B NMR (160.4 MHz, CD₂Cl₂, –70 °C) $\delta$ = 11.7 ($w_{1/2}$ = 900 Hz).

(d) Low temperature reaction of FcLu with 2 equiv PhBCl₂ in the presence of EtN(iPr)₂. A boron-free NMR tube was immersed in a liquid nitrogen bath and charged first with a solution of FcLu, then 1 equiv EtN(iPr)₂ and finally 2 equivs of PhBCl₂ in CD₂Cl₂. The tube was warmed up to –100 °C to let the solid melt and mix. The resulting solution was placed in the NMR spectrometer that was preset to –70 °C and data were
required. Initially compound 3 and the Lewis acid-base adduct were observed as the major species. Signals for the latter gradually disappeared over time giving rise to *rac*-3 as the major product.

NMR scale reaction of *(pR)-3* with *[H(Et₂O)₂]⁺[B(C₆F₅)₄]⁻. *[H(Et₂O)₂]⁺[B(C₆F₅)₄]⁻ was added to a solution of *(pR)-3* in CD₂Cl₂. The color of the mixture turned dark purple.

³¹H NMR (Figure 3-9i), 2D COSY and NOESY data were acquired, which revealed formation of the protonated species [FcLu-H]⁺ and one additional ferrocene-containing compound.

### 3.6 Supporting Information

**Table 3-1.** Crystal data and structure refinement details for *(pR, S₅)-1, (pS)-2Sn, (pS)-3, (pR)-3, and [(pS)-4]⁺[X]⁻ ([X]⁻ = [Al(OC(CF₃)₃)₄]).

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<td>final ( R ) indices ([ I &gt; 2\sigma(I) )]^{[a]}</td>
<td>( R_1 = 0.025 )</td>
<td>( R_1 = 0.027 )</td>
<td>( R_1 = 0.028 )</td>
<td>( R_1 = 0.038 )</td>
<td>( R_1 = 0.065 )</td>
</tr>
<tr>
<td>( wR^2 ) ([ \text{ all data} )]^{[a]}</td>
<td>( wR_2 = 0.061 )</td>
<td>( wR_2 = 0.065 )</td>
<td>( wR_2 = 0.059 )</td>
<td>( wR_2 = 0.075 )</td>
<td>( wR_2 = 0.164 )</td>
</tr>
<tr>
<td>peak_{max}/hole_{min} ((e \text{ Å}^{-3}))</td>
<td>0.23 / -0.24</td>
<td>1.14 / -0.61</td>
<td>0.33 / -0.17</td>
<td>0.33 / -0.40</td>
<td>1.96 / -1.96</td>
</tr>
<tr>
<td>absolute structure parameter</td>
<td>0.016(3)</td>
<td>0.044(7)</td>
<td>0.011(3)</td>
<td>0.021(4)</td>
<td>0.091(9)</td>
</tr>
</tbody>
</table>

\([a] R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)]^2) \}^{1/2} \)
Figure 3-7. Ortep plot of (pR, Ss)-1 (50% thermal displacement ellipsoids). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): N1···S1 2.852, S1-O1 1.49678(18), S1-C1 1.797(2), S1-C18 1.808(3), O1-S1-C1 107.05(11), O1-S1-C18 103.94(11), C1-S1-C18 97.14 (11), Cp//Lu 15.03.

Figure 3-8. Crystal structure plot of [[(pS)-4][Al(OC(CF_3)_3)_4]]. (50% thermal displacement ellipsoids for the cation). Hydrogen and solvent are omitted for clarity. Due to the disorder of the Krossing anion, which is commonly observed in the solid state, two of the carbon atoms in the anion are found ‘Non Positive Definite’, and some of the carbon and fluorine atoms display a high ADP max/min ratio. We used ISOR, DELU, and SADI to try to compensate, they still remain disordered. Fortunately, the cation [(pS)-4]^+ could be refined anisotropically without any problem. Selected distances (Å) and angles (°): Sn1-C1 2.097(8), Sn1-C18 2.130(9), Sn1-C19 2.105(10), Sn1-N1 2.202(7), Sn1···F12A 3.063, C1-Sn1-C18 116.5(3), C19-Sn1-C18 118.7(4), C1-Sn1-N1 80.2(3), C19-Sn1-N1 106.4(3), C18-Sn1-N1 102.4(3), N1-Sn1···F12A 155.7.
**NMR scale Experiments:** (Figure 3-9a – Figure 3-9i)

*Figure 3-9a.* $^1$H (top), $^{19}$F (bottom left), and $^{11}$B (bottom right) NMR spectra of the reaction mixture from treatment of (pS)-2Sn with B(C$_6$F$_5$)$_3$ in CDCl$_3$. 
Figure 3-9b. $^1$H NMR spectrum of the reaction mixture from treatment of (p$S$)-2Sn with $[\text{H(Et}_2\text{O)}_2]^+[\text{B(C}_6\text{F}_5)_4]^-$ in CD$_2$Cl$_2$. 

# : (p$S$)-2Sn

*: MeS·BH$_3$

*: (p$S$)-2Sn·BH$_3$
Figure 3-9c. $^1$H NMR spectra of the reaction mixture from treatment of (pS)-2Sn with an excess of Me$_2$S·BH$_3$ in CDCl$_3$ (top) after 5 min; (bottom) after 48 h.
Figure 3-9d. $^1$H NMR spectrum of the product from treatment of (pS)-2Sn with an excess of Me$_2$S·BH$_3$ in CDCl$_3$ for 48 h, followed by removal of all volatile components.

Figure 3-9e. $^{11}$B NMR spectrum of the reaction mixture from treatment of (pS)-2Sn with an excess of Me$_2$S·BH$_3$ in CDCl$_3$ after 5 min. After removal of all volatile components no $^{11}$B NMR signal was observed.
Figure 3-9f. $^1$H NMR spectra of the reaction mixtures from treatment of FcLu with (top) $[\text{H(Et}_2\text{O)}_2][\text{B(C}_6\text{F}_5)_4]^{-}$ in CD$_2$Cl$_2$ and (bottom) B(C$_6$F$_5$)$_3$ in CDCl$_3$. 
Figure 3-9g. $^1$H and $^{11}$B NMR spectra of the reaction mixture from treatment of FcLu with 2 equivs of PhBCl$_2$ and 1 equiv of EtN($i$Pr)$_2$ in CD$_2$Cl$_2$ at RT.
Figure 3-9h. $^1$H and $^{11}$B NMR spectra of the reaction mixture from treatment of FcLu with 2 equivs of PhBCl$_2$ and 1 equiv of EtN(iPr)$_2$ in CD$_2$Cl$_2$ at $-70$ °C.
Figure 3-9i. $^1$H NMR spectra of the reaction mixture from treatment of (p$^R$)-3 with $[\text{H(Et}_2\text{O)}_2]^+[\text{B(C}_6\text{F}_5)_4]$ in CD$_2$Cl$_2$. 
Figure 3-10. Excerpt of the 2D-NOESY spectrum of compound (pR)-3 in C₆D₆.
Figure 3-11a. High resolution MALDI-MS data of [(pS)-4]^+ [B(C6F5)3Me]^- (left, pos. mode; right, neg. mode)
Figure 3-11b. High resolution (pos. mode) MALDI-MS data of (top) (pS)-4Cl and (bottom) (pS)-4I.

Figure 3-12. HPLC trace (hexanes) and corresponding UV-visible spectrum of (pS)-2Sn.
Figure 3-13. (top) HPLC traces of (pR)-3 and (pS)-3 (hexanes/THF: 93/7). (bottom) HPLC trace and the corresponding UV-visible spectra of racemic 3 (hexanes/THF: 93/7).

3.7 Notes and References


17. The IUPAC-recommended Cahn–Ingold–Prelog (CIP) descriptors $pS$ and $pR$ are used throughout the manuscript to describe the planar chirality; see: Schögl, K. Top. Stereochem. 1967, 1, 39
21. (a) For related organomercury compounds negative optical rotation values are consistently observed for the $pS$-isomer. For example, $[\alpha]^{20}_D$ (c = 0.525, CHCl$_3$) = –395° for the silylpyridine derivative ($pS$)-1-chloromercurio-2-(2-trimethylsilylpyrid-6-yl)ferrocene; see also: Djukic, J.-P.; Hijazi, A.; Flack, H. D.; Bernardinelli, G., Chem. Soc. Rev. 2008, 37, 406-425.
23. We attribute this unusually large optical rotation to formation of an extended tricyclic ring system upon borane complexation.
24. The ee's for crude ($pR$)-3 and ($pS$)-3 were determined to be 90 and 58%, respectively.
27. When ($pS$)-2Sn was treated with one equivalent of PhBCl$_2$ in hexanes solution, a Me group on Sn was replaced with a chloro substituent and the resulting product, ($pS$)-4Cl, precipitated as an orange solid. Switching from hexanes to a 1:1 mixture of hexanes and toluene resulted in a mixture of ($pS$)-4Cl and ($pR$)-3. Clean conversion to the final product ($pR$)-3 was observed with 2 equivs of PhBCl$_2$, which resulted in Me$_2$SnCl$_2$ and Me$_3$SnCl as byproducts.
30. We also explored the reactivity toward BH$_3$, which is a much smaller borane. Indeed, when ($pS$)-2Sn was mixed with an excess of Me$_2$S•BH$_3$ in CDCl$_3$ at room temperature, ca. 20% of ($pS$)-2Sn was converted to the borane adduct ($pS$)-2Sn•BH$_3$ according to $^1$H and $^{11}$B NMR analysis; in a follow-up reaction with the CDCl$_3$ solvent, complete conversion to ($pS$)-4Cl occurred over a period of 48 h.
Chapter 4 Synthesis and Characterization of Planar Chiral Lewis Pairs

Derived from Pyridylferrocenes

4.1 Introduction
As already mentioned in Chapter 1, the combination of sterically demanding electron-deficient Lewis acids (organoboranes, organoaluminum species, silylum cations, etc.) and bulky Lewis bases (phosphines, amines, pyridines and carbenes, etc.) results in so-called “frustrated Lewis pairs” (FLPs). For example, Stephan et al. investigated a system consisting of tris(pentafluorophenyl)borane and 2,6-dimethylpyridine (A). The Lewis adduct exists in thermal equilibrium with the free Lewis acid and base and is therefore capable of activating small molecules such as dihydrogen or THF.

In recent work in our group, we have pursued planar chiral ferrocene-based Lewis acids and their applications in small molecule activation and catalysis. In chapter 3, we discussed the study of developing a stereoselective process for the synthesis of heterocycles. The goal of this chapter is to introduce a new class of planar chiral Lewis pairs based on the pyridylferrocenylborane framework. We postulated that if the B-N interaction in heterocycles (B) is sufficiently weakened, a thermally labile or “frustrated” planar chiral Lewis pair could be generated. We therefore prepared a series of new planar chiral Lewis pairs, in which we varied the steric demand of the pyridyl Lewis base and the steric and electron effect of the substituents attached to the borane Lewis acid moiety. We also investigated the effect of ferrocene oxidation on the Lewis pair properties.

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a This chapter is adapted from a journal publication
4.2 Synthesis and Characterization

We explored two different methods for introducing steric bulk in the heterocyclic system B. A methyl group in the 5-position of the pyridyl ring was expected to result in steric repulsion with the hydrogen in 5-position of the substituted Cp ring, forcing the pyridyl moiety to rotate out of the Cp plane and thereby generating steric strain (back strain). In a second approach, we introduced a SiMe$_3$ substituent in the 6-position of the pyridyl group, which should directly interfere with the B-N bond formation (front strain).

The corresponding stannylated or mercurated precursors, (pS)-2-(3,5-dimethylpyrid-2-yl)-1-(trimethylstannyl)ferrocene ($\text{2-Sn}^\circ$) and (pS)-2-(2-trimethylsilylpyrid-6-yl)-1-(chloromercurio)ferrocene ($\text{3-Hg}$), were prepared in enantiomerically pure form using the synthetic protocols outlined in Scheme 4-1.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure41.png}
\caption{Examples of FLPs and planar chiral ferrocenes}
\end{figure}
Scheme 4-1. Synthesis of planar chiral pyridylferrocenes (pS)-2-Sn and (pS)-3-Hg (Lu = lutidyl or 3,5-dimethylpyrid-2-yl; SiPy-Br = 2-bromo-6-trimethylsilylpyridine; TMP = tetramethylpiperidyl)

Following Kagan’s protocol (S₅)-1 was prepared from tri-n-butyllstannylferrocene and then stereoselectively lithiated with LiTMP. The chiral sulfinylferrocene species (pS, S₅)-2-(3,5-dimethylpyrid-2-yl)-1-(p-tolylsulfinyl)ferrocene (2-SOtol)⁵⁶ and (pS, S₅)-2-(2-trimethylsilylpyrid-6-yl)-1-(p-tolylsulfinyl)ferrocene (3-SOtol) were obtained by Negishi coupling⁸ of the corresponding zincated ferrocene species with 2-iodo-3,5-dimethylpyridine⁹ and 2-bromo-6-trimethylsilylpyridine (SiPy-Br)¹⁰, respectively. Compounds 2-SOtol and 3-SOtol were then reacted with tert-BuLi at −78 °C, followed by treatment with a slight excess of trimethyltin chloride. After purification by column chromatography, ¹H NMR analysis revealed the desired stannylated product in the major faction, but in each case it was accompanied by a small amount of protonated pyridylferrocene as a byproduct. While analytically pure 2-Sn was readily obtained by recrystallization from MeOH, the more soluble 3-Sn could not be isolated by crystallization. Hence, the crude product was treated with one equivalent of HgCl₂ in
acetone to give (pS)-1-(chloromercuro)-2-(2-trimethylsilylpyrid-6-yl)ferrocene (3-Hg), which was crystallized from hexanes and isolated in an overall yield of 71%.

Several strategies are available for the introduction of diarylborane moieties: The stannylated or mercurated ferrocene can either be reacted directly with a borane Ar₂BX (X = Br, Cl) or it can be converted first to the ferrocenyldihaloborane, followed by reaction with a suitable organometallic reagent ArM (Scheme 4-2). The second approach tends to be more effective for the introduction of bulky aryl groups. Treatment of compound 2-Sn with BCl₃ in hexanes at –37 °C led to almost quantitative conversion to the dichloroboryl species 4-Cl according to ¹H NMR analysis. After removing all volatile components under high vacuum the crude product was reacted with 2 equivs of C₆F₅Cu in toluene at 80 °C to afford (pR)-2-[bis(pentafluorophenyl)boryl]-1-(3,5-dimethylpyrid-2-yl)ferrocene (4-Pf), which was isolated as a purple solid in 66% yield after crystallization from hexanes. Using a similar procedure, 4-Mes was obtained as a red solid from reaction of 4-Cl with MesCu (Mes = 2,4,6-trimethylphenyl). 4-Mes was isolated in 51% yield by silica gel column chromatography using hexanes as the eluent.

Reaction of 3-Hg with 1.1 equiv of BCl₃ in hexanes resulted in formation of the corresponding (pR)-2-(dichloroboryl)-1-(2-trimethylsilylpyrid-6-yl)ferrocene (5-Cl) in a yield of 80% after recrystallization (see Supporting Information). However, subsequent treatment with two equivs of C₆F₅Cu did not yield the expected product, 5-Pf; according to an NMR analysis of the crude product only one of the chloride substituents could be replaced with a C₆F₅ group, even at elevated temperature, which might be due to steric hindrance. On the other hand, direct reaction of 3-Hg with (C₆F₅)₂BCl proceeded readily at room temperature. The product, 5-Pf, was obtained as a purple solid that proved to be
highly soluble in hexanes. Single crystals were grown from a minimum amount of hexanes over a period of a month at –37 °C (34 % yield). Compound 5-Mes was obtained using a different route, by lithiation of 3-SOtol with tert-BuLi at –78 °C, followed by treatment with a slight excess of Mes$_2$BF. Column chromatography on aluminum oxide with ether/hexanes (1/1) as the eluent, followed by recrystallization from hot methanol, provided the product as purple needle-shaped crystals in 39% yield.

Scheme 4-2. Synthesis of planar chiral 2-boryl-1-pyridylferrocenes (pR)-4-Pf, (pR)-4-Mes, (pS)-5-Pf, and (pS)-5-Mes.

The stereochemical assignments were confirmed by single crystal X-ray diffraction analysis (vide infra) and are consistent with our earlier studies on the borylation of pyridylferrocenes.$^5$e With the stannylferrocene (pS)-2-Sn as the precursor the planar chirality of the borane product is inverted and optical rotations of $[\alpha]^20_D$ (c = 0.115, CHCl$_3$) = +2078° and $[\alpha]^20_D$ (c = 0.10, CH$_2$Cl$_2$) = +1900° were measured for (pR)-4-Pf.
and (pR)-4-Mes, respectively. This result is attributed to attack of the borane at the Cp-H3 position of the substituted Cp ring, followed by a proton shift that results in the rearranged species (pR)-4-Cl as discussed previously. In contrast, reaction of the mercurioferrocene (pS)-3-Hg with (C₆F₅)₂BCl occurs through direct Hg-C bond cleavage and results in retention of stereochemistry to give (pS)-5-Pf. Consequently, an optical rotation of \([\alpha]^{20}_D (c = 0.10, \text{CH}_2\text{Cl}_2) = -1496^\circ\) of opposite sign was measured. Similarly, for (pS)-5-Mes, retention of stereochemistry results in an optical rotation of \([\alpha]^{20}_D (c = 0.10, \text{CH}_2\text{Cl}_2) = -410^\circ\). The lower absolute value of the optical rotation of (pS)-5-Mes is attributed to the open chain structure that is adopted (vide infra). To further confirm the enantiomeric purity of the pyridylferrocene derivatives, chiral HPLC measurements were carried out. 4-Pf was selected for optimizing the conditions for separation since both enantiomers were available. For a sample of (pR)-4-Pf with about 40% ee the HPLC trace showed full separation into the individual enantiomers. All of the other compounds were measured under similar conditions and just one signal was observed, which could be correlated to the actual compound based on the corresponding UV-Vis absorption spectrum (PDA detector).

\(^{11}\text{B} \) NMR resonances at 3.3 ppm (4-Pf), 2.5 (4-Mes), and –1.5 (5-Pf) suggest a tetracoordinate configuration for the boron center, even in the case of the bulky mesityl groups in 4-Mes or the trimethylsilyl moiety in 5-Pf. Only when we combined the bulky Mes group on boron with a 6-silyl substituent on the pyridyl group in 5-Mes did we obtain a frustrated Lewis pair as evident from an \(^{11}\text{B} \) NMR shift of 77.1 ppm. The \(^{19}\text{F} \) NMR spectrum of 4-Pf shows two sets of signals, which confirms that there is no exchange of the \(\text{endo-} \) and \(\text{exo-} \)C₆F₅ rings, but the rotation of each ring about the C₆F₅-B
bond is not hindered. In contrast, **5-Pf** shows four sets of signals for the ortho- and meta-fluorines of the C₆F₅ rings, indicating a higher degree of steric congestion, but still a closed B-N heterocyclic structure. The ¹H and ¹³C NMR spectra are generally unremarkable; they are consistent with the proposed structures and show the typical pattern of 1,2-disubstituted ferrocenes. Of note is that the signal for the free Cp ring is upfield shifted to 3.60-3.67 ppm for all the compounds with a closed structure, which is attributed to the shielding effect of the aryl group in endo-position.

To further explore the strength of the B-N interaction we carried out X-ray diffraction experiments on single crystal of **4-Pf**, **4-Mes**, **5-Pf** and **5-Mes** (Figure 4-2). The X-ray structure of **4-Pf** shows the pyridine ring to be almost coplanar with the substituted Cp ring (Py//Cp 3.7(1)°). The B-N interaction is strong as evidenced by a relatively short distance of 1.631(3) Å, which falls into the classic B-N donor-acceptor bond range. Apparently the B-N interaction overcomes any back strain due to the methyl group on the 3-position of the pyridine ring. The B-N distance in compound **5-Pf** appears to be slightly longer at 1.647(4) Å, but this difference is not significant when applying 3σ error limits. Remarkably, however, the trimethylsilyl group is strongly bent away from the boryl moiety at an angle N1-C15-Si1 of 128.9(2)° that deviates significantly from the ideal angle of an sp² ring carbon. Enhanced steric strain is also reflected in a larger tilt of the two Cp rings in **5-Pf** (7.3(1)°) relative to **4-Pf** (4.9(2)°). We conclude that despite the steric hindrance and strong distortion of the trimethylsilyl group, a B-N interaction to form the heterocycle remains favorable. The geometry for the mesityl derivative **4-Mes** is very similar to that of **4-Pf**, with a slightly greater B-N bond distance of 1.653(4) Å that is similar to that of **5-Pf**. These results are fully consistent with our solution NMR studies,
suggesting that the introduction of bulkier groups on boron has little impact on the B-N interaction. To our delight, for the most congested system 5-Mes, single crystal X-ray diffraction analysis revealed a fully open conformation without any B-N interaction, which is consistent with the $^{11}$B NMR shift of 77.1 ppm in solution. A detailed investigation of the X-ray crystal structure indicated that the pyridyl group rotates away from the borane moiety to release some of the steric strain, resulting in a very long distance B-N distance of 4.468(4) Å. In this particular conformation further stabilization is achieved by a $\pi$-interaction between the pyridyl ring and one of the mesityl rings. The arene rings are oriented almost coplanar (11.1(1)$^\circ$) and the shortest interactomic distance is C11···C21 = 3.054(3) Å. The N1-C15-Si1 angle (114.17(18)$^\circ$) is much smaller than that in 5-Pf since steric strain due to B-N adduct formation is absent. 5-Mes is characterized as a frustrated Lewis pair given that the Lewis base component is accessible and binds to boron in 5-Pf, while the borane Lewis acid component binds to the less hindered dimethylpyridine in 4-Mes. Thus, the Lewis acid and base sites are unquenched and cannot form a complex in 5-Mes only due to steric constraints.

Figure 4-2. Ortep plots of (pR)-4-Pf, (pR)-4-Mes, (pS)-5-Pf and (pS)-5-Mes (50% thermal displacement ellipsoids). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles ($^\circ$): 4-Pf: B1-N1 1.631(3), B1-C2 1.606(3), C1-C2-B1 109.31(17), C2-B1-N1 97.07(15), B1-N1-C11 112.61(16), N1-C11-C1 109.87(16), C11-C1-C2 111.04(17), Cp//Cp 4.9(2), Py//Cp 3.7(1). 4-Mes: B1-N1 1.653(4), B1-C2 1.641(4), C1-C2-B1 110.4(2), C2-B1-N1
Compounds 4-Ar (Ar = Mes, Pf) turned out to be quite robust and perfectly stable to air and moisture. Heating an NMR sample of 4-Pf in d8-toluene to 80 °C did not result in coalescence of the distinct sets of 19F NMR signals for each of the C6F5 rings. Moreover, a 19F/19F EXSY spectrum showed no exchange peaks even at elevated temperature (80 °C, d8-toluene, mixing time: 1 s). This indicates that the B-N interaction is so strong that the B-N cycle does not open up even at high temperature. We also examined the reactivity of 4-Pf with 4 bars of H2 at 100 °C in toluene, but no reaction was observed. Even the treatment with one equiv of Jutzi’s acid, [H(OEt)2]+[B(C6F5)4]−, did not result in protonation of the pyridyl nitrogen with liberation of the tricoordinate boron center. All of the above experiments support the notion that the B-N interaction in 4-Pf is exceptionally strong and prevents this system from behaving as an FLP.

We hypothesized that the additional steric strain that is present in compound 5-Pf according to its X-ray structure should lead to enhanced reactivity. Upon heating of an NMR sample in d8-toluene to 80 °C, the Pf ring that experiences less steric hindrance (tentatively assigned as exo-Pf) coalesces into one set of signals, while the other Pf ring (in the endo-position) retains two sets of signals. More importantly, a 19F/19F EXSY spectrum (80 °C, mixing time: 1 s; Figure 4-3) showed clearly the presence of exchange peaks between the fluorine atoms of one Pf group and those of the other one. This observation strongly supports the notion that the B-N bond is cleaved at high
temperature, and the ensuing rapid rotation about the B-CC₃ leads to exchange of the Pf groups in \textit{exo-} and \textit{endo-}position. The \textsuperscript{11}B NMR resonance at 80 °C is almost identical to that at room temperature, indicating that the thermodynamic equilibrium still favors the tetracobaltate boron species, although, the exchange was facilitated at elevated temperature.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Sections of the \textsuperscript{19}F-\textsuperscript{19}F EXSY NMR spectrum of 5-Pf and illustration of the equilibrium between ‘closed’ and ‘open’ forms of 5-Pf.}
\end{figure}

In the case of the more strained species 5-Pf, treatment with 4 bars of H₂ gas at 100 °C in toluene for 24 h did not result in any detectable hydrogenation products. Even in the presence of the ketamine N-(1-phenylethylidene)aniline as a hydrogen acceptor hydrogen activation and subsequent hydrogenation of the substrate could not be observed (4 bars of H₂ at 100 °C in toluene for 2 days). However, more potent reagents do lead to ring-opening. Unlike compounds 4-Pf and 4-Mes, when 5-Pf was passed through a short plug
of silica gel, a new ring-opened species formed readily (Scheme 4-3). The $^1$H NMR spectrum of the product (6) showed the presence of 2 additional resonances at 18.24 and 3.23 ppm, which integrate as one proton each and correspond to the pyridinium proton and the OH group on boron. Single crystals of 6 were obtained from a 1:1 mixture of hexanes/ether and the X-ray structure unambiguously confirmed the addition of a water molecule (Figure 4-4). Hydrogen bonding occurs from the pyridinium donor Py-H1$_N$ to O1 as the acceptor as evident from the distance O1···H1$_N$ of 1.68(2) Å. A comparison of the X-ray data of 5-Pf and 6 reveals significant release of ring strain upon addition of the water molecule. After ring-opening with H$_2$O, the N1-C15-Si1 angle decreases from 128.9(2)$^\circ$ to 119.6(2)$^\circ$, which is very close to the ideal value of 120$^\circ$ for a trigonal environment. When the frustrated Lewis pair 5-Mes was purified on a short plug of alumina gel, a later fraction was identified as compound 7, generated by B-C$_{Mes}$ bond cleavage of 5-Mes with one equivalent of H$_2$O. The resulting borinic acid moiety in 7 forms an intramolecular hydrogen bond with the pyridine moiety. In contrast to compound 6, the nitrogen in compound 7 serves as the hydrogen bond acceptor for the borinic acid proton (N1···H1 1.82(3) Å). The position of the acidic proton was unequivocally identified in the difference Fourier electron density contour map in Figure 4-5, which confirmed the connectivity between the highest electron residue (H1) and O1. The acidic proton in the crystal lattice could be refined without distance and displacement restraints and without significant geometry change compared to the riding mode. Interestingly, the $^1$H NMR resonance of the acidic proton in CDCl$_3$ was observed at 13.9 ppm, which is comparable to the protontation product of the pyridyl ferrocene derivative (pS)-2-(3,5-dimethylpyrid-2-yl)-1-(trimethylstannyl)ferrocene] ($\delta$ = 12.2 ppm), but
strongly downfield shifted relative to typical H NMR resonances of borinic acids (6.0 – 7.0 ppm).13

Scheme 4-3. Reactions of (pS)-5-Pf and (pS)-5-Mes with H₂O.

Figure 4-4. Ortep plot for the ring-opened products 6 and 7 (50% thermal displacement ellipsoids).
Hydrogen atoms are omitted for clarity except for those of the N-H and O-H groups. Selected interatomic distances (Å) and angles (°): For 6: B1-C2 1.608(3), N1-H1ν 0.92(2), O1···H1ν 1.68(2), N1···O1 2.592(2), B1···N1 3.178(3), C1-C2-B1 131.11(17), C2-B1-O1 111.93(18), N1-C15-Si1 119.6(2), C1//C1 4.0(2), P1//C1 8.7(1). For 7: B1-C2 1.560(3), O1-H1 0.81(2), N1···H1 1.82(3), N1···O1 2.626(2), B1···N1 3.208(3), C1-C2-B1 134.19(18), C2-B1-O1 122.03(19), N1-C15-Si1 116.16(15), C1//C1 5.8(1), P1//C1 5.3(1).
Figure 4-5. Difference Fourier electron density contour map of compound 7 before adding the acidic proton into the model. The highest electron residue (Q1) is located close to O1, clearly indicating that the acidic proton is bound to O1 rather than the pyridyl moiety in the solid state.

The presence of the redox-active ferrocenyl moieties provides another possible handle to tune the B-N interaction electronically. At the same time, the oxidation potential of the iron center provides an important indication of the Lewis acid strength of the boryl group. Compounds 4-Pf and 5-Pf show a similar reversible oxidation event at +120 and +134 mV, respectively, relative to the ferrocene/ferrocenium redox couple (Figure 4-6). These values are close to the potential measured for the Lewis acid-base complex of NpFcB(C₆F₅)₂ with pyridine (+90 mV).⁵c They are significantly lower than for related uncomplexed ferrocenylboranes [cf. NpFcB(C₆F₅)₂ ⁵c +460 mV, FcB(C₆F₅)₂ ¹⁴ +450 mV], in which an interaction between the electron-deficient borane and the iron center results in large anodic shifts of the Fe redox potential. As expected, compound 4-Mes undergoes a reversible redox event at a more cathodic value (~174 mV) in comparison to
4-Pf (+120 mV), indicating that the more electron rich Mes groups decrease the electron density at the boron and iron centers. For the respective open-chain system 5-Mes a significant interaction of the ferrocene unit and the tricoordinate boron is evident from the much larger redox potential of +145 mV (cf. +181 mV for FcBMes₂ in acetonitrile)¹⁵ in comparison to that for 4-Mes.

![Cyclic voltammograms of compounds](image)

**Figure 4-6.** Cyclic voltammograms of compounds 4-Pf, 4-Mes, 5-Pf and 5-Mes (CH₂Cl₂, 0.05 M Bu₄N[B[C₆H₃(CF₃)₂]₄]); reported versus Fe/Fe⁺, which is taken as +610 mV versus Cp*₂Fe/Cp*₂Fe⁺ (indicated with an asterisk, Cp* = pentamethylyclopentadienyl) as an internal reference.

Preparative oxidation of compound 4-Pf to the corresponding ferrocenium species was accomplished by treatment with the silver derivative of Krossing’s salt,¹⁶ [Ag(CH₂Cl₂)]⁺[Al[OC(CF₃)]₃]⁻. The product was isolated in the form of green crystals that were examined by X-ray diffraction analysis. The structure of one of two independent molecules of 4-Pf⁺ in the unit cell is shown in Figure 4-7. The major difference relative to neutral 4-Pf is that the C₇₀CEN’T‥C₇₀CEN’T distance increases from 3.3132(12) to 3.439(5) Å as expected for formation of a ferrocenium species. However,
the B-N distance of 1.644(9) Å proved to be very similar to that of the neutral precursor (4-Pf 1.631(3) Å). Upon oxidation, the pyridyl moiety would be expected to display a decreased Lewis basicity. However, prior studies show that the Lewis acidity of ferrocenyloboranes is strongly enhanced upon oxidation of the iron center. Based on the crystal structure data it appears that cancellation of these two effects results in a B-N interaction that is similar in strength to that of the neutral species. In this respect, the open system 5-Mes was also oxidized with Krossing’s Ag salt. The color of the mixture turned immediately from red to green and a precipitate formed, which was removed by filtration. 

$^1$H NMR of the crude product showed the typical signals for an oxidized species in the region between 28 and 45 ppm, while the $^{11}$B NMR resonance at around 65 ppm (5-Mes $\delta = 77.1$ ppm) indicated that the boron remained tricoordinate. The combined evidence suggests that the oxidation of 5-Mes does not likely promote the coordination from pyridyl to the boryl unit. Attempts to isolate the oxidized product failed due to the high reactivity. The color of a MALDI sample turned from green to red immediately after exposure to air. The high resolution mass spectrum indicated the species with oxygen insertion between boron and $C_{Cp}$ as the major decomposed product.
Scheme 4-4. Preparative oxidation of (pR)-4-Pf and (pS)-5-Mes.

Figure 4-7. Ortep plot for compound 4-Pf⁺ (50% thermal displacement ellipsoids). Hydrogen atoms and the aluminate counterion are omitted for clarity. Selected interatomic distances (Å) and angles (°): B1-N1 1.644(9), B1-C2 1.626(11), Fe1-C_{Cp1} 1.718(4), Fe1-C_{Cp2} 1.721(4), C_{Cp1}-C_{Cp2} 3.439(5), C1-C2-B1 110.2(6), C2-B1-N1 95.6(5), B1-N1-C11 113.9(6), N1-C11-C1 108.5(6), C11-C1-C2 111.7(6), C_{Py}/C_{Cp} 3.7(6), C_{Py}/C_{Cp} 1.0 (5). C_{Cp1} = centroid of substituted Cp ring; C_{Cp2} = centroid of unsubstituted Cp ring.

4.3 Conclusions

Two different methods were examined to influence the B-N interaction in ferrocene-based pyridine-borane Lewis pairs. While back strain induced by methylation of the pyridyl group in meta-position is overcome in the formation of the very stable B-N
adducts 4-Pf and 4-Mes, front strain due to a trimethylsilyl group in ortho-position of the pyridyl group in 5-Pf and 5-Mes decreases the B-N bond strength significantly. Although even for 5-Pf the Lewis pair adopts a ‘closed form’ in solution and the solid state, EXSY NMR studies offer clear evidence for B-N cleavage at elevated temperature. A fully open conformation in 5-Mes was achieved by incorporation of bulkier mesityl groups on boron. 5-Mes is characterized as a frustrated Lewis pair given that the Lewis base component is accessible and binds to boron in 5-Pf, while the borane Lewis acid component binds to the less hindered dimethylpyridine in 4-Mes. Thus, the Lewis acid and base sites are unquenched and cannot form a complex in 5-Mes only due to steric constraints. In the presence of H$_2$O ring-opening of 5-Pf occurred with formation of the corresponding pyridinium borate species 6, which corresponds to the product of H$_2$O addition across the B-N bond. In contrast, reaction of the open-chain species 5-Mes with H$_2$O yielded the B-C$_{Mes}$ cleavage product.

The influence of the electronic structure of the borane substituents on the redox potential of the iron center was also examined. The most significant difference was found when comparing the tetracoordinate ‘closed’ compounds with the tricoordinate species 5-Mes; the latter experienced a strong anodic shift of the Fe oxidation potential, which is consistent with a pronounced interaction between the Lewis acidic borane moiety and the electron-rich Fe center. On the other hand, the preparative oxidation of the ferrocene had little impact on the Lewis acid/base properties as 4-Pf adopted a closed and 5-Mes an open structure prior to and after oxidation. We attribute this unexpected result to a dual effect of ferrocene oxidation: while the Lewis acidity of the borane is enhanced, the Lewis basicity of the pyridine is diminished. In this respect, introduction of a non-
conjugated linker between the ferrocene and Lewis base units could prove beneficial for the future development of more redox-responsive Lewis pair systems. Another promising strategy for the development of more powerful Lewis pairs could be to incorporate borane substituents that promote higher electron-deficiency while offering sufficient steric bulk to stabilize the B-C bonds. Specifically, we expect the introduction of fluorinated mesityl groups to weaken the B-N bond due to steric constraints, while promoting FLP-type reactivity, hence allowing for activation of other small molecules such as the more challenging dihydrogen.

4.4 Experimental Section

Reagents and general methods. Bis(dibenzylideneacetone)palladium(0), tri-tert-butylphosphine, Me₃SnCl, ZnCl₂, HgCl₂, and t-butyl lithium (1.7 M in hexanes) were purchased from Aldrich and used without further purification. (S₅)-p-Tolylsulfinylferrocene (1),⁷a 2,2,6,6-tetramethylpiperidyl lithium (TMPLi) was freshly prepared by addition of n-butyl lithium (1.6 M in hexanes) to a THF solution of 2,2,6,6-tetramethylpiperidine at 0 °C, 2-bromo-6-trimethylsilylpyridine,¹⁰ (pS)-2-trimethylstanny1-1-(3,5-dimethylpyrid-2-yl)ferrocene (2-Sn),⁵C (C₆F₅)₂BCl,¹⁹ C₆F₅Cu,²⁰ MesCu,²¹ and [Ag(CH₂Cl₂)][Al(OC(CF₃)₃)₄]¹⁶ were prepared according to literature procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (MBraun). 499.9 MHz ¹H NMR, 125.7 MHz ¹³C NMR, 160.4 MHz ¹¹B NMR, 470.4 ¹⁹F NMR, 99.3 MHz ²⁹Si, 186.4 MHz ¹¹⁹Sn NMR and spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a boron-free 5
mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution $^1$H and $^{13}$C NMR spectra were referenced internally to solvent signals. $^{11}$B NMR spectra were acquired with boron-free quartz NMR tubes and referenced externally to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ($\delta = 0$), $^{119}$Sn NMR data to SnMe$_4$ ($\delta = 0$), $^{29}$Si NMR data to SiMe$_4$ ($\delta = 0$), and $^{19}$F NMR data to solvent signal. High resolution MALDI-MS data were obtained in positive mode on an Apex Ultra 7.0 Hybrid FTMS (Bruker Daltonics) using benzo[a]pyrene as the matrix. UV/Vis absorption data were acquired on a Varian Cary 500 UV/Vis/NIR spectrophotometer. Cyclic voltammetry measurements were carried out on a BAS CV-50W analyzer. The three-electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode, and an Ag wire as the pseudo-reference electrode. The scans were referenced after the addition of a small amount of decamethylferrocene as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple ($-610$ mV for Cp*$_2$Fe/Cp*$_2$Fe$^+$ in CH$_2$Cl$_2$ / 0.05 M Bu$_4$N[B(C$_6$H$_3$(CF$_3$)$_2$)$_4$]). Optical rotation analyses were performed on an Autopol III polarimeter, Rudolph Research Analytical, using a tungsten-halogen light source operating at $\lambda = 589$ nm. Chiral HPLC analyses were performed on a Waters Empower system equipped with a photodiode array detector and using a CHIRALPAK® IA-3 column. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD Diffractometer using CuK$\alpha$ (1.54178 Å) radiation at 100 K. The structures were refined by full-matrix least squares based on $F^2$ with all reflections. Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens
Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was applied. Crystallographic data for the structures of $(pR)$-4-Pf, $(pR)$-4-Mes, $(pS)$-5-Pf, $(pS)$-5-Mes, $(pS)$-5-Cl, $(pS)$-6, $(pS)$-7 and $[(pS)$-4-Pf]$^+${Al(OC(CF3)3)4}$^-$ have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 976017-976024. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

**Synthesis of $(pR, S_S)$-2-(1-Trimethylsilylpyridyl)-1-(p-tolylsulfinyl)ferrocene (3-SOtol).** To a pre-cooled ($-78$ °C) solution of $(S_S)$-p-tolylsulfinylferrocene (I) (2.00 g, 6.17 mmol) in THF (30 mL) was added dropwise a solution of LiTMP (0.5 M in THF, 14.8 mL, 7.40 mmol, 1.20 equiv) and the resulting mixture was kept stirring at the same temperature for 1 hour. A solution of ZnCl$_2$ (0.925 g, 6.79 mmol, 1.10 equiv) in THF (15 mL) was added. After 1 h at $-78$ °C the mixture was allowed to warm up and stirred for 1 h at 25 °C. For the cross-coupling reaction, bis(dibenzylideneacetone)palladium(0) (0.847 g, 0.926 mmol, 0.10 equiv), tri-tert-butylphosphine (0.374 g, 1.85 mmol, 0.20 equiv) and 2-bromo-6-trimethylsilylpyridine (3.55 g, 15.4 mmol, 2.50 equiv) were stirred in THF (20 mL) for 5 min and then added to the ferrocenylzinc reagent by syringe. The mixture was stirred for 2 days at 50 °C. After addition of saturated NH$_4$Cl solution (50 mL), the mixture was extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic layers were washed with brine and water, dried over sodium sulfate and then concentrated on a rotary evaporator. The residue was chromatographed on alumina with ethyl acetate/hexanes (1:2) as the eluent. Yield: 2.4 g (61%). $^1$H NMR (499.9 MHz, CDCl$_3$, 25
°C): \( \delta = 7.84 \) (d, \( J = 8.0 \) Hz, 2H; tolyl), 7.54 (m, 2H; Py), 7.37 (m, 3H; py, tolyl), 5.04 (nr, 1H; Cp), 4.40 (nr, \( J = 2.0 \) Hz, 1H; Cp), 4.07 (s, 5H; free Cp), 3.92 (nr, 1H; Cp), 2.47 (s, 3H; tolyl-Me), 0.43 (s, 9H; SiMe\(_3\)). \(^{13}\)C NMR (125.69 MHz, CDCl\(_3\), 25 °C): \( \delta = 168.0, 156.4, 141.2, 141.0, 133.9, 129.2, 126.2, 126.1, 120.5 \) (py, tolyl), 93.1 (Cp), 86.9 (Cp), 71.2 (Cp), 71.2 (free Cp), 70.4 (Cp), 69.7 (Cp), 21.5 (Me), –1.7 (SiMe\(_3\)). \(^{29}\)Si NMR (99.3 MHz, CHCl\(_3\), 25 °C) \( \delta = –5.4 \). Elemental analysis for C\(_{25}\)H\(_{27}\)FeNOSSi, calcd C 63.42, H 5.75, N 2.96, found C 63.34, H 5.80, N 2.76 %.

**Synthesis of \((p^S)\)-2-(2-Trimethylsilylpyrid-6-yl)-1-(chloromercurio)ferrocene (3-Hg).** A solution of \(\text{tert}\)-butyl lithium (1.04 mL, 1.78 mmol, 1.20 equiv) was added dropwise to a solution of 3-\(\text{SOtol}\) (700 mg, 1.48 mmol) in THF (10 mL) at –78 °C. The reaction mixture was kept stirring for 10 min at the same temperature and then a solution of Me\(_3\)SnCl (0.383 g, 1.92 mmol, 1.3 equiv) in THF (2 mL) was added via syringe. The resulting solution was stirred for 1 h and the temperature was then allowed to slowly raise to 25 °C. After addition of water the mixture was extracted with diethyl ether (3 \times 5 mL). The combined organic layers were washed with brine solution followed by water, dried over sodium sulfate and concentrated on a rotary evaporator. The residue was subjected to silica gel column chromatography with hexanes/triethylamine (100:1) as the eluent. A mixture of (2-trimethylsilylpyrid-6-yl)ferrocene and \((p\overline{S})\)-2-(2-trimethylsilylpyrid-6-yl)-1-(trimethylstannyl)ferrocene (3-Sn) was obtained, which was further reacted without further purification. A solution of the crude product in acetone (20 mL) was added into a solution of HgCl\(_2\) in acetone (20 mL). The mixture was stirred for 1 hour and then added to distilled water (100 mL) with stirring. Upon addition, a red precipitate formed, which was collected on a filter and dried under airflow. The solid was then taken up in hexanes.
Recrystallization at –37 °C gave red crystals suitable for X-ray diffraction analysis. Yield: 600 mg (71%). \(^1\)H NMR (499.9 MHz, CDCl\(_3\), 25 °C): \(\delta = 7.53\) (p, \(J = 7.5\) Hz, 1H; Py), 7.38 (d, \(J = 7.5\) Hz, 1H; Py), 7.34 (d, \(J = 7.5\) Hz, 1H; Py), 4.98 (d, \(J = 1.5\) Hz, 1H; Cp), 4.61 (p, \(J = 2.0\) Hz, 1H; Cp), 4.39 (nr, 1H; Cp), 4.06 (s, 5H; free Cp), 0.44 (s, 9H; SiMe\(_3\)). \(^{13}\)C NMR (125.69 MHz, CDCl\(_3\), 25 °C): \(\delta = 168.2\) (ipso-Py), 158.2 (ipso-Py), 134.5 (Py), 126.8 (Py), 119.5 (Py), 87.3 (ipso-Cp-C), 75.3 (Cp), 72.6 (Cp), 69.9 (free Cp), 68.0 (Cp), -1.1 (SiMe\(_3\)), ipso-Cp-Hg not observed. \(^{29}\)Si NMR (99.3 MHz, CDCl\(_3\), 25 °C) \(\delta = -5.1\). Elemental analysis for C\(_{18}\)H\(_{20}\)ClFeNSi, calcd C 37.89, H 3.54, N 2.46, found C 37.83, H 3.49, N 2.36 %.

**Synthesis of (pR)-2-[Bis(pentafluorophenyl)boryl]-1-(3,5-dimethylpyrid-2-yl)ferrocene (4-Pf).** To a solution of 2-Sn (100 mg, 0.22 mmol) in hexanes (20 mL) that was cooled to –37 °C was added a solution of BCl\(_3\) (1 M in hexanes, 0.24 mL, 0.24 mmol, 1.10 equiv) dropwise under stirring. A red precipitate developed, which redissolved upon addition of 30 mL of toluene. After stirring for 2 hours solvents, excess BCl\(_3\) and the byproduct Me\(_3\)SnCl were removed under high vacuum. The crude product (pR)-2-dichloroboryl-1-(3,5-dimethylpyrid-2-yl)ferrocene (4-Cl) was further reacted without additional purification. To a pre-cooled solution of crude 4-Cl in toluene (10 mL, –37 °C) was added a solution of C\(_6\)F\(_5\)Cu (101 mg, 0.44 mmol, 2.0 equiv) in toluene (5 mL). The reaction mixture was stirred at room temperature overnight and then at 80 °C for 2 hours. A white precipitate that had formed was removed by filtration and the filtrate was concentrated under vacuum. The residue was recrystallized from hot hexanes to give the product as dark red, X-ray quality crystals. Yield: 92 mg (66 %) \([\alpha]^{20}_{D} (c = 0.115, \text{CHCl}_3) = 2078^\circ\); \(^1\)H NMR (499.9 MHz, CDCl\(_3\), 25 °C): \(\delta = 8.14\) (s, 1H; Lu), 7.53 (s, 1H;
Lu), 4.79 (d, $J = 2.0$ Hz, 1H; Cp), 4.72 (br, 1H; Cp), 4.60 (p, $J = 2.0$ Hz, 1H; Cp), 3.67 (s, 5H; free Cp), 2.53 (s, 3H; Lu-Me), 2.32 (s, 3H; Lu-Me). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta = 148.3$ (d, $J(C,F) = 237$ Hz, o-C$_6$F$_5$), 147.1 (d, $J(C,F) = 245$ Hz, o-C$_6$F$_5$), 139.9 (d, $J(C,F) = 256$ Hz, p-C$_6$F$_5$), 138.8 (nr, p-C$_6$F$_5$), 137.1 (d, $J(C,F) = 253$ Hz, m-C$_6$F$_5$), 120.1 (br d, ipso-C$_6$F$_5$), 159.4, 143.7, 143.4, 129.6, 129.4 (Lu), 97.0 (br, ipso-Cp-B), 83.7 (ipso-Cp-C), 74.0 (Cp), 71.3 (Cp), 69.4 (free Cp), 64.2 (Cp), 18.5 (Me), 18.1 (Me). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta = -3.3$ ($\omega_{1/2} = 120$ Hz). $^{19}$F NMR (470.4 MHz, CDCl$_3$, 25 °C): $\delta = -130.0$ (d, $J(F,F) = 17$ Hz, 2F; ortho-F), $-134.0$ (d, $J(F,F) = 20$ Hz, 2F; ortho-F), $-157.4$ (t, $J(F,F) = 20$ Hz, 1F; para-F), $-159.7$ (t, $J(F,F) = 20$ Hz, 1F; para-F), $-163.3$ (p, $J(F,F) = 17$ Hz, 2F; meta-F), $-163.6$ (p, $J(F,F) = 18$ Hz, 2F; meta-F). High-resolution MALDI-MS (+ mode, benzo[$\alpha$]pyrene): m/z 635.0557 ([M]$^+$, 100%, calcd for $^{12}$C$_{29}$H$_{16}$B$_{11}$N$_{19}$F$_{10}$Fe 635.0565). Elemental analysis for C$_{29}$H$_{16}$BF$_{10}$FeN, calcd C 54.81, H 2.54, N 2.21, found C 54.66, H 2.37, N 2.09 %

**Synthesis of (pR)-2-[bis(2,4,6-trimethylphenyl)boryl]-1-(3,5-dimethylpyrid-2-yl)ferrocene (4-Mes).** Compound 4-C1 was synthesized as described above from a solution of 2-Sn (50 mg, 0.22 mmol) in hexanes (10 mL) and BCl$_3$ (1 M in hexanes, 0.12 mL, 0.12 mmol, 1.10 equiv). To a pre-cooled (–37 °C) solution of crude 4-C1 in toluene (5 mL) was added a solution of mesityl copper (MesCu, C$_9$H$_{11}$Cu) (40 mg, 0.48 mmol, 2.2 equiv) in toluene (5 mL). The reaction mixture was stirred at 90 °C overnight. A white precipitate that had formed was removed by filtration and the filtrate as concentrated under vacuum. The residue was subjected to chromatography using hexanes as the eluent. A dark red, fluffy solid formed after removal of the solvent. Yield: (30 mg) 51 %). $[\alpha]_{D}^{20}$ (c = 0.10, CH$_2$Cl$_2$) = 1900°; $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta = \ldots$
8.10 (s, 1H; Lu), 7.41 (s, 1H; Lu), 6.80 (s, 1H; Mes), 6.72 (s, 1H; Mes), 6.57 (s, 1H; Mes), 6.53 (s, 1H; Mes), 4.71 (nr, 1H; Cp), 4.68 (nr, 1H; Cp), 4.47 (nr, 1H; Cp), 3.61 (s, 5H; free Cp), 2.54 (s, 3H; Lu-Me), 2.22 (s, 3H; Lu-Me), 2.20 (s, 3H; Mes-Me), 2.18 (s, 3H; Mes-Me), 2.10 (s, 3H; Mes-Me), 1.97 (s, 3H; Mes-Me), 1.73 (s, 3H; Mes-Me), 1.35 (s, 3H; Mes-Me). 13C NMR (125.69 MHz, CDCl3, 25 °C): $\delta = 159.2, 145.5, 142.7, 142.3, 142.0, 141.1, 136.1, 134.4, 132.5, 129.9, 129.2, 129.2, 129.1, 129.1, 128.6, (Lu + Mes), 151.3 (ipso-Mes-B), 111.5 (ipso-Cp-B), 85.7 (ipso-Cp-C), 72.0 (Cp), 71.7 (Cp), 68.9 (free Cp), 62.1 (Cp), 26.2, 25.2, 24.8, 24.2, 20.7, 20.7, 18.8, 18.3 (Me). 11B NMR (160.4 MHz, CDCl3, 25 °C) $\delta = 2.5 \ (w_{1/2} = 800 \text{ Hz})$. High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 539.2474 ([M]$^+$, 50%, calcd for $^{12}$C$_{35}$H$_{38}^{11}$B$^{14}$N$_6$Fe 539.2447), 420.1609 ([M-Mes]$^+$, 100%, calcd for $^{12}$C$_{26}$H$_{27}^{11}$B$^{14}$N$_6$Fe 420.1585). Elemental analysis for C$_{35}$H$_{38}$BFeN, calcd C 77.90, H 7.10, N 2.60, found C 77.30, H 7.06, N 2.43 %.

**Synthesis of (pS)-2-(bis(pentafluorophenyl)boryl)-1-(2-trimethylsilylpyrid-6-yl)ferrocene (5-Pf).** To a solution of 3-Hg (100 mg, 0.175 mmol) in toluene (10 mL) that was cooled down to –37 °C was added a solution of (C$_6$F$_5$)$_2$BCl (70 mg, 0.184 mmol, 1.1 equiv) in toluene (5 mL). Upon addition the color of the solution turned purple. After stirring over night at room temperature the solvent was removed under vacuum. The residue was re-dissolved in 5 mL of hexanes and a small amount of a black solid was filtered off. The filtrate was kept at –37 °C for one month to give X-ray quality crystals of the product. Yield: 40 mg (34%). $[\alpha]^{20}_D \ (c = 0.10, \text{CH}_2\text{Cl}_2) = -1496^\circ$. 1H NMR (499.9 MHz, CDCl3, 25 °C): $\delta = 7.81 \ (\text{pst, } J = 7.5 \text{ Hz, 1H; Py}), 7.56 \ (d, \ J = 7.5 \text{ Hz, 1H; Py}), 7.54 \ (d, \ J = 8.0 \text{ Hz, 1H; Py}), 4.71 \ (d, \ J = 1.5 \text{ Hz, 1H; Cp}), 4.56 \ (\text{nr, 1H; Cp}), 4.54 \ (\text{nr, 1H; Cp}), 3.60 \ (s, \ 5H; \text{free Cp}), 0.05 \ (s, \ 9H; \text{SiMe}_3)$. 13C NMR (125.69 MHz, CDCl3, 25 °C): $\delta$
122

= 150-135 (br unresolved; ortho-, meta-, para-C₆F₅), 168.3, 166.2, 138.9, 128.2, 119.0 (Py), 85.2 (ipso-Cp-B), 73.2 (Cp), 70.9 (Cp), 70.8 (Cp), 69.4 (free Cp), 60.1 (Cp), 0.5 (SiMe₃). ¹¹B NMR (160.4 MHz, CDCl₃, 25 °C) δ = −1.5 (½w = 150 Hz). ¹⁹F NMR (470.4 MHz, CDCl₃, 25 °C): δ = −127.1 (br, 1F; ortho-F), −130.1 (br, 1F; ortho-F), −133.2 (dd, J(F,F) = 24 Hz, 7 Hz, 1F; ortho-F), −134.2 (br, 1F; ortho-F), −157.1 (t, J(F,F) = 20 Hz, 1F; para-F), −159.2 (t, J(F,F) = 20 Hz, 1F; para-F), −163.1 (br, 1F; meta-F), −163.9 (br, 1F; meta-F), −164.5 (m, 1F; meta-F), −165.0 (m, 1F; meta-F). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 679.0670 ([M]⁺, 100%, calcd for C₃₀H₂₀BF₁₀FeNSi). Elemental analysis for C₃₀H₂₀BF₁₀FeNSi, calcd C 53.02, H 2.97, N 2.06, found C 52.90, H 2.87, N 1.95 %.

Synthesis of Ring-opened Species 6. Compound 3-Hg (100 mg, 0.175 mmol) was first converted to 5-Pf as described above. Instead of recrystallization, the crude product was passed through a short silica gel column using ether/hexanes (1:1) as the eluent. A purple colored solid was obtained, which can be recrystallized in hot ether/hexanes (1:1). Yield: 50 mg (41%). [α]₂⁰D (c = 0.10, CH₂Cl₂) = -462°. ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 18.24 (br, 1H; Py-H⁺), 7.86 (ps, J = 8.0 Hz, 1H; Py), 7.66 (d, J = 8.5 Hz, 1H; Py), 7.41 (d, J = 7.0 Hz, 1H; Py), 4.76 (nr, 1H; Cp), 4.61 (nr, 1H; Cp), 4.31 (nr, 1H; Cp), 4.08 (s, 5H; free Cp), 3.22 (s, 1H; B-OH), 0.39 (s, 9H; SiMe₃). ¹³C NMR (125.69 MHz, CDCl₃, 25 °C): δ = 150-135 (br unresolved; ortho-, meta-, para-C₆F₅), 158.4, 154.2, 136.0, 121.6, 118.8 (Py), 90.9 (ipso-Cp-B), 76.1 (Cp), 71.4 (Cp), 67.6 (Cp), 65.2 (free Cp), 63.0 (Cp), −7.1 (SiMe₃). ¹¹B NMR (160.4 MHz, CDCl₃, 25 °C) δ = −2.7 (½w = 90 Hz). ¹⁹F NMR (470.4 MHz, CDCl₃, 25 °C): δ = −133.0 (d, J(F,F) = 16 Hz, 2F; ortho-F), −135.4 (br, 2F; ortho-F), −160.0 (t, J(F,F) = 20 Hz, 1F; para-F), −160.6 (t, J(F,F) = 20 Hz, 1F;
para-F), –164.4 (m, 2F; meta-F), –165.1 (m, 2F; meta-F). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 679.0669 ([M-H2O]+, 100%, calcd for $^{12}$C$_{30}$H$_{20}^{11}$B$_{14}$N$_{19}$F$_{10}^{29}$Si$_{56}$Fe 679.0648). Elemental analysis for C$_{30}$H$_{22}$BF$_{10}$FeNOSi, calcd C 51.65, H 3.18, N 2.01, found C 51.46, H 3.15, N 2.13 %.

Synthesis of (pS)-2-bis(2,4,6-trimethylphenyl)boryl-1-(2-trimethylsilylpyrid-6-yl)ferrocene (5-Mes) and Compound 7. A solution of tert-butyllithium (0.42 mL, 0.72 mmol, 1.1 equiv) was added dropwise to a solution of 3-SOtol (310 mg, 0.66 mmol) in THF (10 mL) at –78 °C. The reaction mixture was kept stirring for 10 min at the same temperature and then a solution of Mes$_2$BF (211 mg, 0.79 mmol, 1.2 equiv) in THF (5 mL) was added via syringe. The resulting solution was stirred for 1 h and the temperature was then allowed to slowly raise to 25 °C. After concentration under high vacuum the residue was redissolved in minimum amount of hexanes. The mixture was subjected to aluminum oxide column chromatography with hexanes/ether (1:1) as the eluent. The first band that was collected was purple colored. Recrystallization in methanol at –37 °C gave purple crystals suitable for X-ray diffraction analysis. Yield: 150 mg (39%). $[\alpha]_{20}^D$ (c = 0.10, CH$_2$Cl$_2$) = –410°. $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.00 (d, $J$ = 6.5 Hz, 1H; Py), 6.87 (d + pst, 2H; Py), 6.55 (s, 4H, Mes), 5.30 (nr, 1H; Cp), 4.73 (nr, 1H; Cp), 4.56 (nr, 1H; Cp), 4.11 (s, 5H; free Cp), 2.19(s, 12H, Mes-Me), 2.16 (s, 6H, Mes-Me), 0.32 (s, 9H; SiMe$_3$). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta$ = 165.3, 158.3, 139.2, 137.0, 130.8, 127.7, 124.6, 124.5 (Py + Mes), 142.8 (ipso-Mes-B), 92.7 (ipso-Cp-B), 83.9 (Cp), 82.3 (ipso-Cp-C), 74.6 (Cp), 72.0 (Cp), 71.2 (free Cp), 23.8, 20.9 (Mes-Me)-1.7 (Si-Me). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 77.1 ($\nu_{1/2}$ = 1600 Hz). $^{29}$Si NMR (99.3 MHz, CDCl$_3$, 25 °C) $\delta$ = –6.4. High-resolution MALDI-MS (+ mode,
benzo[α]pyrene): \( m/z \ 583.2527 \) ([M]⁺, 100%, calcd for \(^{12}\text{C}_{36}\text{H}_{42}\text{B}^{14}\text{N}^{29}\text{Si}^{56}\text{Fe} \ 583.2531\)). Elemental analysis for C\(_{36}\)H\(_{42}\)BFeNSi, calcd C 74.08, H 7.26, N 2.40, found C 73.60, H 7.28, N 2.12 %. When the crude product of 5-Mes (see above) was subjected to aluminum oxide column chromatography with hexanes/ether (1:1) as the eluent, a second orange band was isolated at a longer retention time. Recrystallization in hexanes at –37 °C gave red crystals suitable for X-ray diffraction analysis. Yield: 100 mg (32%). Compound 7 also formed upon treatment of pour 5-Mes with silica gel similar to the procedure used to prepare compound 6 from 5-Pf. \([\alpha]^{20}_D\) (c = 0.10, CH\(_2\)Cl\(_2\)) = –316°. \(^1\)H NMR (499.9 MHz, CDCl\(_3\), 25 °C): \( \delta = 13.89 \) (s, 1H, OH) 7.62 (p extremely, 1H; Py), 7.51 (d, \( J = 8.0 \) Hz, 1H; Py), 7.41 (d, \( J = 7.0 \) Hz, 1H; Py), 6.26 (br, 2H, Mes), 5.04 (nr, 1H; Cp), 4.54 (nr, 1H; Cp), 4.26 (nr, 1H; Cp), 4.03 (s, 5H; free Cp), 2.67 (br, 3H, Mes-Me), 2.30 (s, 3H, Mes-Me), 2.15 (br, 3H, Mes-Me), 0.45 (s, 9H; SiMe\(_3\)). \(^{13}\)C NMR (125.69 MHz, CDCl\(_3\), 25 °C): \( \delta = 166.3, 161.0, 136.7, 135.4, 127.2, 126.1, 120.6 \) (Py + Mes), 139.3 (ipso-Mes-B), ipso-Cp-B not observed, 87.5 (ipso-Cp-C), 81.0 (Cp), 72.7 (Cp), 71.7 (Cp), 70.2 (free Cp), 22.6, 21.2 (Mes-Me), -1.8 (Si-Me). \(^{11}\)B NMR (160.4 MHz, CDCl\(_3\), 25 °C) \( \delta = 48.4 \) (\( w_{1/2} = 1400 \) Hz). \(^{29}\)Si NMR (99.3 MHz, CDCl\(_3\), 25 °C) \( \delta = -4.3 \). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): \( m/z \ 481.1696 \) ([M]⁺, 100%, calcd for \(^{12}\text{C}_{27}\text{H}_{32}\text{B}^{14}\text{Fe}^{14}\text{N}^{29}\text{Si}^{56}\) 481.1696). Elemental analysis for C\(_{27}\)H\(_{32}\)BFeNOSi, calcd C 67.35, H 6.70, N 2.91, found C 67.46, H 6.88, N 2.75 %.

**Synthesis of [4-Pf][Al(O(CF\(_3\)))\(_4\)]\(^-\).** To a solution of 4-Pf (10.9 mg, 0.017 mmol) in CHCl\(_3\) (1 mL) that was cooled down to –37 °C was added a solution of [Ag(CH\(_2\)Cl\(_2\))]Al(O(CF\(_3\)))\(_4\) (20 mg, 0.017 mmol, 1.0 equiv) in CHCl\(_3\) (0.5 mL) under stirring. The color of the mixture turned from purple to green. After removal of a white
precipitate by filtration, the solvent was removed under vacuum. The residue was redissolved in 1 mL of CH$_2$Cl$_2$ and the product crystallized at −37 °C. Yield: 20 mg (73 %). $^1$H NMR (499.9 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = 39.5 (br, 1H; Cp), 35.9 (br, 1H; Cp), 31.1 (br, 5H; free Cp), 29.9 (br, 1H; Cp), 0.63 (s, 1H; Lu), 0.24 (s, 1H; Lu), −5.75 (s, 3H; Lu-Me), −16.5 (br, 3H; Lu-Me). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 1.1 ($\sigma_{1/2}$ = 180 Hz). $^{19}$F NMR (470.4 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ = −76.2 (s, 36F; CF$_3$), −148.7 (br, 2F; ortho-F), −150.1 (br, 2F; ortho-F), −151.4 (t, $J$(F,F) = 20 Hz, 1F; para-F), −153.7 (t, $J$(F,F) = 19 Hz, 1F; para-F), −156.7 (pst, 2F; meta-F), −170.0 (br, 2F, meta-F). Elemental analysis for C$_{45}$H$_{16}$AlBF$_{46}$FeNO$_4$, calcd C 33.73, H 1.01, N 0.87, found C 33.62, H 0.76, N 1.65%.

NMR scale reaction for [5-Mes]$_2$[Al[OC(CF$_3$)$_3$]$_4$]$^–$. To a solution of 5-Mes (9.9 mg, 0.017 mmol) in CDCl$_3$ (0.5 mL) that was cooled down to −37 °C was added a solution of [Ag(CH$_2$Cl$_2$)]Al[OC(CF$_3$)$_3$]$_4$ (20 mg, 0.017 mmol, 1.0 equiv) in CDCl$_3$ (0.5 mL) under stirring. The color of the mixture turned from red to green. After removal of a white precipitate by filtration, the filtrate was transferred to a J Young’s NMR tube for acquisition of the $^1$H and $^{11}$B NMR. Attempts to isolate the oxidized species failed due to high reactivity of the product. $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta$ = 43.8 (br, 1H; Cp), 32.0 (br, 2H; Cp), 29.4 (br, 5H; free Cp), 19.0 (br, 1H), 15.1 (br, 1H), 5.40 (br), 2.52 (br), 0.15 (br), −1.34 (br), −2.52 (br), −3.71 (br), −21.0 (br). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 64.5 ($\sigma_{1/2}$ = 600 Hz).
4.5 Supporting Information

Table 4-1. Crystal data and structure refinement details for 4-Pf, 5-Pf, 4-Mes, 5-Mes, 4-Pf$^+$, 5-Cl, 6 and 7.

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<td>0.61 / –0.56</td>
<td>0.21 / –0.16</td>
</tr>
<tr>
<td>absolute structure parameter</td>
<td>0.006(3)</td>
<td>0.004(4)</td>
<td>0.023(6)</td>
<td>0.019(4)</td>
</tr>
</tbody>
</table>
Synthesis of (pS)-5-Cl. To a solution of 3-Hg (68 mg, 0.12 mmol) in hexanes (10 mL) that was cooled down to –37 °C was added a solution of BCl₃ (1.0 M in hexanes, 0.13 mL, 0.13 mmol, 1.10 equiv) dropwise under stirring. A red precipitate developed, which redissolved upon addition of 10 mL of toluene. The reaction mixture was stirred overnight at room temperature and then for 2 hours at 80 °C. The solvents were removed under vacuum and the residue was re-dissolved in hot toluene/hexanes (1:1). An insoluble black solid was filtered off and the filtrate was kept at –37 °C for recrystallization. Yield: 40 mg (80%). ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.76 (t, \(J = 8.0 \text{ Hz}, 1\text{H; Py}) \), 7.62 (d, \(J = 8.0 \text{ Hz}, 1\text{H; Py}) \), 7.38 (d, \(J = 8.0 \text{ Hz}, 1\text{H; Py}) \), 4.79 (d, \(J = 2.0 \text{ Hz}, 1\text{H; Cp}) \), 4.74 (d, \(J = 2.0 \text{ Hz}, 1\text{H; Cp}) \), 4.63 (p, \(J = 2.0 \text{ Hz}, 1\text{H; Cp}) \), 4.06 (s, 5H; free Cp), 0.66 (s, 9H; SiMe₃). ¹¹B NMR (160.4 MHz, CDCl₃, 25 °C) δ = 7.53 (\(w_{1/2} = 110 \text{ Hz}) \).

Figure 4-8. Ortep plot for compound 5-Cl (50% thermal displacement ellipsoids). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): B1-N1 1.614(3), B1-C2 1.571(4), B1-C11 1.878(3), B1-Cl2 1.857(3), C1-C2-B1 107.6(2), C2-B1-N1 100.66(19), B1-N1-C11 109.63(19), N1-C11-C1 110.3(2), C11-C1-C2 111.4(3), N1-C15-Si1 128.98(16), Cp//Cp 1.97, Py//Cp 4.88.
Figure 4-9. MALDI-MS data of compound 4-Mes.
Figure 4-10. Comparison of UV-Vis absorption spectra in CHCl₃.
Figure 4-11. Chiral HPLC trace and the corresponding UV-Vis spectrum of 4-Pf (40% ee).

Figure 4-12. Chiral HPLC trace and the corresponding UV-Vis spectrum of (pR)-4-Pf.
Figure 4-13. Chiral HPLC trace and the corresponding UV-Vis spectrum of (pR)-4-Mes.

Figure 4-14. Chiral HPLC trace and the corresponding UV-Vis spectrum of (pS)-5-Pf.

Figure 4-15. Chiral HPLC trace and the corresponding UV-Vis spectrum of (pS)-5-Mes.
Figure 4-16. Chiral HPLC trace and the corresponding UV-Vis spectrum of (pS)-6.

Figure 4-17. Chiral HPLC trace and the corresponding UV-Vis spectrum of (pS)-7.
Figure 4-18. $^{19}$F-$^{19}$F EXSY spectrum of 4-Pf at 80 °C in d$_8$-toluene.
Figure 4-19. $^{19}$F-$^{19}$F EXSY spectrum of 5-Pf at 80 °C in d$_8$-toluene. Trace impurity is due to hydrolysis and subsequent boroxine formation with C$_6$F$_5$H(*) as impurity signals.
4.6 Notes and References


11. A very similar observation is made for the chloro-substituted species 5-Cl. The B-N distance of 1.615(3) Å suggests a strong Lewis acid-base interaction, which forces the trimethylsilyl group to bend away from the boryl moiety (N1-C15-Si1 = 129.0(2)°). See Supporting Information for details of the X-ray structure of 5-Cl.
12. A direct comparison of the N1-C15-Si1 angles in compounds 5-Pf [128.9(2)°], 6 [119.6(2)°] and 5-Mes [114.2(2)°] reveals that the steric congestion at the Lewis base decreases from pyridine-borane pair to pyridinium, then to free pyridine. The angle for 5-Mes is less than 120° due to the lower steric demand at N versus the C-H in ortho-position.
Chapter 5  Catalytic Application of Planar Chiral Ferrocenyl Lewis Acids: Studies of Lewis Acidity, Substrate Binding and Asymmetric Process

5.1 Introduction

In this chapter we describe the first planar chiral ferrocenylborenium species (pR)-3⁺, which is obtained in enantiopure form by halide abstraction from the corresponding chloroborane adduct (pR)-2 using Krossing’s salt. Competition experiments suggest that the Lewis acidity of (pR)-3⁺ is higher than that of B(C₆F₅)₃ towards anions and slightly lower towards neutral Lewis bases. The ferrocenylborenium species (pR)-3⁺ is examined as a catalyst for the stereoselective hydrosilylation of ketones.

Highly Lewis acidic organoboranes continue to attract tremendous interest and current applications range from Lewis acid catalysis of organic transformations¹ and polymerization reactions² to small molecule activation,³ sensors for anions,⁴ and the development of new and unusual electronic materials.⁵ Many of the earlier studies have focused on installing electron withdrawing fluorine substituents onto organoboranes as a means of increasing the electron-deficient character of boron, and B(C₆F₅)₃ is nowadays broadly applied not only in academia but has also found its way into a wide range of industrial processes.⁶ An alternative approach involves the incorporation of tricoordinate boron into antiaromatic cyclics as in borole and diborabenzene derivatives. In this case, Lewis acid-base adduct formation is energetically favored by conversion to non-aromatic species.⁷ Most recently, highly reactive borenium species⁸ have been introduced, in

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¹ This chapter is adapted from a journal publication
which the cationic charge further enhances the potency of tricoordinate borane Lewis acids.9

![Figure 5-1. Examples of highly Lewis acidic organoboranes](image)

Borenium species have proven highly advantageous especially in the promotion of electrophilic aromatic substitution chemistries.8b,10 Very recently the first studies of their use in hydrogenation and hydroboration catalysis have also been reported.11 For broad application in organic synthesis it is desirable to develop and utilize chiral borenium Lewis acids. Chiral alkyl- and arylboranes, including fluorinated derivatives, are widely applied as reagents and catalysts in stereoselective synthesis.14-16 We have over the past several years pursued planar chiral ferrocene-based Lewis acids.15, 17-19 We have demonstrated, for example, the utility of a bifunctional ferrocene-based Lewis acid as a stereoselective reagent for the allylation of ketones with ee’s of up to 80%.12 We have also introduced fluorinated arylboranes attached to a chiral naphthylferrocenyl framework.13 Related planar-chiral $\eta^5$-1,2-azaborolyl iron complexes have been utilized by Fu and coworkers in Mukayama aldol reactions and in stereoselective additions to imines.14 Interestingly, planar chiral borenium cations were proposed as intermediates in these processes. We describe in here the first synthesis of an isolable planar-chiral ferrocenylborenium cation, discuss the Lewis acid properties and present a proof-of-principle investigation of its utility in the hydrosilylation of ketones.
5.2 Synthesis and Characterization

Scheme 5-1. Synthesis of (pR)-3⁺

(i) 2 PhBCl₂, toluene/hexanes, –37 °C to rt. (ii) Method A: [Ag(CH₂Cl₂)]{Al[OC(CF₃)₃]₄}, CHCl₃, –37 °C to rt; Method B: Li{Al[OC(CF₃)₃]₄}, CDCl₃, rt.

The chloroborane adduct (pR)-3 was prepared by treatment of the organotin compound (pS)-1 with an excess of PhBCl₂ in hexanes/toluene mixture (Scheme 5-1). Based on ¹H NMR studies (Figure 5-2a) two different species (ratio 2.5:1) are present in solution, which are attributed to the exo-Ph and endo-Ph isomers of (pR)-2. According to a 2D NOESY experiment, the major isomer features the Ph group in exo-position and the minor isomer in endo-position. Coalescence was not observed in the 1D ¹H NMR spectra even at temperatures up to 70 °C. This indicates that isomerization is slow on the NMR time scale.

We initially attempted to prepare the corresponding borenium cation by Cl⁻ abstraction with B(C₆F₅)₃. Indeed, when compound (pR)-3 was mixed with one equivalent of B(C₆F₅)₃, coalescence into a single set of broad ¹H NMR resonances was observed (Figure 5-2b). However, the Lewis acid strength of B(C₆F₅)₃ proved to be far too low to
bring about complete abstraction of Cl\textsuperscript{−}. In contrast, treatment of (pR)-2 with 1 equiv of Krossing’s salt\textsuperscript{18}

![Figure 5-2](image)

**Figure 5-2.** Expansion of the Cp region of the \textsuperscript{1}H NMR spectra for a) (pR)-2 (exo- and endo-isomers), b) (pR)-2 + B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and c) (pR)-3\textsuperscript{+} (CDCl\textsubscript{3}) and photographs illustrating the associated color change.

[Ag(CH\textsubscript{2}Cl\textsubscript{2})]{Al[OC(CF\textsubscript{3})\textsubscript{3}]\textsubscript{4}} or Li{Al[OC(CF\textsubscript{3})\textsubscript{3}]\textsubscript{4}} in CHCl\textsubscript{3} led to quantitative chloride abstraction with formation of the tricoordinate borenium cation (pR)-3\textsuperscript{+} (Scheme 5-1). The \textsuperscript{1}H NMR spectrum showed strongly downfield shifted signals at 5.75, 5.58 and 5.48 ppm for the substituted Cp ring, consistent with attachment of a highly electron-deficient borenium cation (Figure 5-2c). In the \textsuperscript{11}B NMR spectrum a broad signal was observed at 45.4 ppm for the cation and in the \textsuperscript{19}F NMR spectrum a sharp signal at −75.4 ppm for the anion. Another characteristic feature of the borenium cation (pR)-3\textsuperscript{+} is its deep purple color (Figure 5-2, \textlambda\textsubscript{max} = 566 nm, ε = 2200 M\textsuperscript{−1}cm\textsuperscript{−1}). This unusual color is likely due to enhanced charge transfer from iron to the more extended and highly electron-deficient \textpi-system of the pyridylborenium heterocycle in (pR)-3\textsuperscript{+}\textsuperscript{19}

A single crystal X-ray diffraction analysis confirmed retention of the planar chirality upon halide abstraction from (pR)-2 to give (pR)-3\textsuperscript{+} (Figure 5-3a). As expected, the
highly electron-deficient nature of the borenium moiety results in a strong interaction between B and the electron-rich Fe, which is reflected in pronounced bending of the boryl group out of the Cp plane, towards the iron center. The tilt angles for the boryl groups in two independent cations are 14.1° (Fe···B 2.925 Å) and 14.5° (Fe···B 2.907 Å), respectively, which is similar to Piers’ perfluorophenyl-substituted FcB(C₆F₅)₂²⁰ (16°, Fe···B 2.924 Å) and FcBB₂²¹ (17.7, 18.9°; Fe···B 2.856/2.840 Å).²² Noteworthy is that the CpCENT···CpCENT distance of 3.316 Å is consistent with a neutral ferrocene,²³ supporting the assignment of (pR)-3⁺ as a borenium-substituted ferrocene rather than a borane-substituted ferrocenium species.²⁴ Another interesting aspect is that the planar π-conjugated structure of (pR)-3⁺ favors formation of inter-molecular π-π dimers that consist of two independent cations.†

![Figure 5-3](image)

**Figure 5-3.** a) Ortep plot of (pR)-3⁺ (50% thermal ellipsoids); counteranions and H atoms are omitted. Selected distances (Å) and angles (°) [2nd independent molecule]: B1-N1 1.544(7) [1.550(9)], B1-C2 1.519(9) [1.539(9)], B1-C18 1.524(9) [1.504(10)], C2-B1-N1 102.2(5) [100.6(5)], C2-B1-C18 131.4(5) [132.2(6)], C18-B1-N1 126.3(5) [127.1(6)]. (b) A π dimer consisting of two independent molecules of (pR)-3⁺ (only substituted Cp rings shown).

### 5.3 Lewis Acidity Determination and Substrate Binding

A first indication of the high Lewis acidity of (pR)-3⁺ came from the fact that the reaction of (pR)-2 with an equimolar amount of B(C₆F₅)₃ led to only a very modest
downfield shift of the Cp resonances (see Figure 5-2b). This implies that only partial abstraction (<50%) of chloride from (pR)-2 occurs and suggests that (pR)-3+ as a cation has a higher affinity than B(C₆F₅)₃ towards anionic Lewis bases such as Cl⁻.

According to Gutman-Beckett’s method, the $^{31}$P NMR shift difference of Et₃PO before and after complexation to a Lewis acid could serve as a measurement of Lewis acidity. The larger downfield chemical shift is an indication of higher Lewis acid strength. This method was utilized to examine the relative Lewis acidity of (pR)-3+. The chemical shift difference $\Delta \delta$ is larger for (pR)-3+ (32.6 ppm) than for B(C₆F₅)₃ (26.5 ppm), which would indicate higher Lewis acidity of (pR)-3+ toward Et₃PO (Figure 5-4).

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ ($^{31}$P) [/ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et₃PO</td>
<td>50.4</td>
</tr>
<tr>
<td>Et₃PO·B(C₆F₅)₃</td>
<td>76.9</td>
</tr>
<tr>
<td>$\Delta \delta$ for B(C₆F₅)₃</td>
<td>26.5</td>
</tr>
<tr>
<td>Et₃PO·(pR)-3+</td>
<td>83.0</td>
</tr>
<tr>
<td>$\Delta \delta$ for (pR)-3+</td>
<td>32.6</td>
</tr>
</tbody>
</table>

**Figure 5-4.** Competitive binding of (pR)-3+ and B(C₆F₅)₃ to Et₃PO examined by $^{31}$P NMR spectroscopy in CD₂Cl₂ at room temperature (0.02 M solutions). a) Et₃PO; b) Et₃PO + B(C₆F₅)₃. c) Et₃PO + (pR)-3+. d) Et₃PO + 1.0 (pR)-3+ + 1.0 B(C₆F₅)₃.

However, to gain more insight into the Lewis acid properties of (pR)-3+ we performed a competitive binding study, in which a mixture of the borenium species (pR)-3+ and B(C₆F₅)₃ was treated with an equimolar amount of the neutral Lewis base Et₃PO (Figure 5-5). The complexes Et₃PO·(pR)-3+ and Et₃PO·B(C₆F₅)₃ are present in a ratio of 1:3.6 at
room temperature, which shows that slightly more Et$_3$PO binds to B(C$_6$F$_5$)$_3$ than to (pR)-3$^+$, indicating that B(C$_6$F$_5$)$_3$ is a stronger Lewis acid toward Et$_3$PO. The fact that the $^{31}$P chemical shift difference is larger for the binding of Et$_3$PO to (pR)-3$^+$ could be related to delocalization of the positive charge on the phosphorous. Clearly, the Gutmann-Beckett method cannot be used to directly compare the Lewis acidity of ionic and neutral borane species, instead a competition experiment has to be performed. We conclude that (pR)-3$^+$ has a higher affinity than B(C$_6$F$_5$)$_3$ towards anionic Lewis bases such as Cl$^-$ and is only slightly less Lewis acidic than B(C$_6$F$_5$)$_3$ towards neutral Lewis bases such as Et$_3$PO. In short, (pR)-3$^+$ proved to be a remarkably strong Lewis acid.

![Figure 5-5](image.png)

**Figure 5-5.** Competitive binding of (pR)-3$^+$ and B(C$_6$F$_5$)$_3$ to Et$_3$PO examined by $^{11}$B NMR spectroscopy in CD$_2$Cl$_2$ at room temperature (0.02 M solutions). a) (pR)-3$^+$; b) (pR)-3$^+$ + Et$_3$PO; c) 1.0 (pR)-3$^+$ + 1.0 B(C$_6$F$_5$)$_3$ + 1.0 Et$_3$PO. The ratios in plot c) are consistent with those obtained by $^{31}$P NMR (see Figure 5-4).

An application of Lewis acids in organic synthesis that has attracted considerable interest is the metal-free hydrosilylation of ketones. This process was first studied for B(C$_6$F$_5$)$_3$ by Piers and coworkers.$^{26}$ Piers demonstrated that activation of the Si-H functionality in silanes with B(C$_6$F$_5$)$_3$ plays a key role$^{3c}$ and more recent studies by Oestreich further support this notion.$^{27}$ However, the development of enantioselective versions of this process continues to be a challenge.$^{28}$
We first examined the reactivity of (pR)-3+ toward ketones and silanes, respectively. When (pR)-3+ was mixed with 1 equiv of HSiEt3 in CDCl3 at RT, the 1H NMR spectra of both components were unchanged. However, at elevated temperature a loss of H-Si-CH2 coupling was clearly observed (Figure 5-6), which is consistent with an R’Si-H…BR3 interaction according to studies by Bergman and coworkers29 on related Al-based systems. Treatment of compound (pR)-3+ with acetophenone resulted in a distinct color change from deep purple to orange-red due to adduct formation. The Lewis acid strength of (pR)-3+ toward acetophenone proved to be about one order of magnitude lower than that of B(C6F5)3 according to the competition study (see Figure 5-14). The complex (pR)-3+(acetophenone) can be readily isolated as a crystalline solid and its single crystal X-ray structure shows binding of the acetophenone from the endo-side of the ferrocene (B-O = 1.560(8) [1.577(8)] Å, Figure 5-7).

Figure 5-6. VT 1H NMR spectra for a mixture of (pR)-3+ and Et3SiH in CDCl3.
Figure 5-7. Ortep plots of Substrate binding of \((pR)-3^+\) with acetone, acetophenone and hydride (50% thermal ellipsoids), counteranions and H atoms are omitted. Selected distances (Å) and angles (°) for \((pR)-3^+\) (acetophenone) [2nd independent molecule]: B1-N1 1.603(9) [1.592(9)], B1-O1 1.560(8) [1.577(8)], B1-C2 1.580(11) [1.593(10)], B1-C18 1.603(11) [1.594(10)], O1-C24 1.257(8) [1.255(8)].

5.4 Asymmetric Catalytic Process

When a sample of this complex was treated with an excess of HSiEt₃, the acetophenone was reduced and fully converted to the hydrosilylation product. The color of the solution changed back from orange-red to dark purple, and the ¹H NMR data were consistent with re-formation of the free borenium ion \((pR)-3^+\). The fact that the lower basicity of the product resulted in release from the Lewis acid suggested that a catalytic process is feasible (Scheme 5-2). Indeed, with a 5% loading of the borenium species \((pR)-3^+\) as the catalyst 60% conversion of acetophenone was achieved over 12 h at RT. Hydrolysis to the corresponding alcohol and subsequent chiral GC-FID analysis revealed a 20% ee for the \(R(+)\) product in both the stoichiometric and catalytic process. Ketones and silanes with different steric properties are also examined for the catalytic scope (Table 5-1). Increased the size of the ketones (entry 4) or decreased size of the silanes (entry 2) resulted in higher conversion with shorter reaction times. In fact, for the bulkiest
silane Ph₃SiH (entry 3), only trace amount of product was detected. This observation is consistent with the silane activation mechanism, in which the ketones with higher degree of steric hindrance and silanes with lower degree of steric hindrance are favored since the Si-H activation becomes more accessible.

Scheme 5-2. Hydrosilylation of ketones catalyzed by (pR)-3⁺.

Table 5-1. Hydrosilylation of different ketones with silanes in the presence of (pR)-3⁺ as catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ketone</th>
<th>Silane</th>
<th>Cat. (%)</th>
<th>Conv. (%)ab</th>
<th>ee (%)ab</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R¹=Ph, R²=Me</td>
<td>Et₃SiH</td>
<td>5</td>
<td>65</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R-(+)</td>
</tr>
<tr>
<td>2</td>
<td>R¹=Ph, R²=Me</td>
<td>PhMe₂SiH</td>
<td>5</td>
<td>92</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R-(+)</td>
</tr>
<tr>
<td>3</td>
<td>R¹=Ph, R²=Me</td>
<td>Ph₃SiH</td>
<td>5</td>
<td>trace</td>
<td>ND</td>
</tr>
<tr>
<td>4</td>
<td>R¹=tBu, R²=Me</td>
<td>Et₃SiH</td>
<td>2</td>
<td>&gt;95</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S-(+)</td>
</tr>
<tr>
<td>5</td>
<td>R¹=tBu, R²=Me</td>
<td>PhMe₂SiH</td>
<td>2</td>
<td>&gt;95</td>
<td>5</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>S-(+)</td>
</tr>
<tr>
<td>6</td>
<td>R¹=1-Np, R²=Me</td>
<td>Et₃SiH</td>
<td>3</td>
<td>29</td>
<td>ND</td>
</tr>
<tr>
<td>7</td>
<td>R¹=1-Np, R²=Me</td>
<td>PhMe₂SiH</td>
<td>3</td>
<td>44</td>
<td>ND</td>
</tr>
</tbody>
</table>

*Conversion determined by ¹H NMR (reaction time: ca. 12 h except for entries 4,5 which went to completion within 10 min).

b The silylated product was first converted to the corresponded alcohol, then the ee was determined by chiral GC-FID (Entry 1) or HPLC (Entry 2).

c The silylated product was converted to the corresponded alcohol, isolated by distillation, and then reacted with the chemical shift reagent (S)-(+)α-methoxy-α-trifluoromethylphenylacetyl chloride as described by Mosher.³⁰

In conclusion, halide abstraction from the Lewis acid-base pair (pR)-2 was accomplished using the Ag or Li derivative of Krossing’s salt, resulting in a novel planar-
chiral borenium-type Lewis acid. The Lewis acid strength of chiral (pR)-3$^+$ proved to be comparable to that of B(C$_6$F$_5$)$_3$. While modest enantiomeric excess was achieved in the hydrosilylation of ketones with (pR)-3$^+$ as a catalyst, this study represents the first application of a planar-chiral borenium Lewis acid in the stereoselective reduction of ketones. Further modification of the steric demand of the pyridyl ligand and the exocyclic boron substituent is expected to allow for significantly enhanced selectivities, while the activity can likely be optimized through tuning of the electronic effect of the exocyclic B-aryl group.

5.5 Experimental Section

Reagents and General Methods. PhBCl$_2$ and Et$_3$PO were purchased from Aldrich and used without further purification. (pS)-1, Mosher’s acid, and the Krossing salts were prepared according to literature procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (MBraun). 499.9 MHz $^1$H NMR, 125.7 MHz $^{13}$C NMR, 160.4 MHz $^{11}$B NMR, and 470.4 MHz $^{19}$F spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution $^1$H and $^{13}$C NMR spectra were referenced internally to solvent signals. $^{11}$B NMR spectra were acquired with boron-free quartz NMR tubes and referenced to BF$_3$ · Et$_2$O ($\delta = 0$). The following abbreviations are used for signal assignments: Lu = 3,5-dimethylpyrid-2yl, Fc = ferrocenyl, Cp = cyclopentadienyl. High resolution MALDI-MS data (benzo[α]pyrene as matrix) were obtained in positive mode on an Apex Ultra 7.0 Hybrid FTMS (Bruker
Daltonics). UV/Vis absorption data were acquired on a Varian Cary 500 UV/Vis/NIR spectrophotometer. Optical rotation analyses were performed on an Autopol III polarimeter, Rudolph Research Analytical, using a tungsten-halogen light source operating at $\lambda = 589$ nm. GC-FID analyses were performed on a Varian CP3800 GC instrument using an Rt-BetaDex-sm chiral column. Chiral HPLC analyses were performed on a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, and a 2998 photodiode array detector; a CHIRALPAK® IA-3 column was used for separation. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD Diffractometer using CuKα ($1.54178$ Å) radiation at 100 K. The structures were refined by full-matrix least squares based on $F^2$ with all reflections (SHELXTL V5.10; G. Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was applied. Crystallographic data for the structures of \((pR)3^+\) and \((pR)-3^+(acetophenone)\) have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 907178-907179. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).
Synthesis of [(pS)-LuFcB(C₆H₅)Cl · 0.5 C₇H₈] ((pR)-2). A solution of (pS)-1 (100 mg, 0.22 mmol) in a mixture of hexanes/toluene (10/10 mL) was cooled down to −37 °C and then a solution of PhBCl₂ (70 mg, 0.44 mmol, 2.0 equiv) in toluene (2 mL) was added dropwise under stirring. The mixture was stirred over night at room temperature before applying high vacuum to remove the solvents. The residue was taken back up in a mixture of hot hexanes/toluene (1/1). When stored at −37 °C crystals were obtained that contain half an equivalent of toluene. Yield: 55 mg (55%). [α]²⁰_D (c = 0.10, CH₂Cl₂) = 2110°. ¹H NMR (499.9 MHz, CDCl₃, 25 °C): Major : Minor = 2.5 : 1; δ = 8.23 (s, 1H, Lu; Minor), 8.13 (s, 1H; Lu, Major), 7.58 (s, 1H; Lu, Minor), 7.53 (d, J = 7 Hz, 2H; o-Ph, Minor), 7.48 (s, 1H; Lu, Major), 7.37 (pst, J = 7 Hz, 2H; m-Ph, Minor), 7.32 (d, J = 7 Hz, 2H; o-Ph, Major), 7.26 (nr, 1H, p-Ph, Minor), 7.16 (pst, J = 7 Hz, 2H; m-Ph, Major), 7.13 (m, 1H, p-Ph, Major), 4.77 (dd, J = 2.5 Hz, 1.0 Hz, 1H; Cp, Major), 4.71 (overlapped, 2H; Cp, Minor), 4.62 (dd, J = 2.5 Hz, 1.0 Hz, 1 H; Cp, Major), 4.58 (m, 2H; Cp, Major + Minor), 4.22 (s, 5H; free Cp, Major), 3.65 (s, 5H; free Cp, Minor), 2.52 (s, 3H; Lu- Me, Major), 2.51 (s, 3H; Lu-Me, Minor), 2.38 (s, 3H; Lu-Me, Minor), 2.30 (s, 3H; Lu-Me, Major). ¹¹B NMR (160.4 MHz, CDCl₃, 25° C) δ = 6.0 (w₁/₂ = 210 Hz). ¹³C NMR (125.69 MHz, CDCl₃, 25 °C) δ = 158.3, 157.3, 143.3, 142.8, 142.4, 141.5, 131.5, 131.5, 130.4, 130.3, 129.5, 128.9, 127.3, 127.3, 126.4, 126.2 (Lu + Ph), ipso-Ph-B not observed, 84.0 (ipso-Cp-C, Major), 82.5 (ipso-Cp-C, Minor), 74.7 (Cp, Minor), 74.4 (Cp, Major), 70.3 (ipso-Cp-B, Major), 70.2 (ipso-Cp-B, Minor), 70.1 (free Cp, Major), 69.8 (free Cp, Minor), 64.6 (Cp, Minor), 64.5 (Cp, Major), 18.3 (Lu-Me, Major), 18.3 (Lu-Me, Minor), 18.2 (Lu-Me, Minor), 18.1 (Lu-Me, Major). UV-Vis (CH₂Cl₂): λ_max = 413 (ε = 1900 M⁻¹ cm⁻¹), 503 (ε = 2700 M⁻¹ cm⁻¹). High-resolution MALDI-MS (+ mode, benzo[α]pyrene):
m/z 413.0828 ([M]$^+$, 40%, calcd for $^{12}$C$_{23}$H$_{21}^{11}$B$^{14}$N$^{35}$Cl$^{56}$Fe 413.0804); m/z 378.1137 ([M-Cl]$^+$, 100%, calcd for $^{12}$C$_{23}$H$_{21}^{11}$B$^{14}$N$^{35}$Cl$^{56}$Fe 378.1115).

**Synthesis of [(pR)-LuFcB(C$_6$H$_5$)]$^+${Al[OC(CF$_3$)$_3$]$_4$}$^-$ ((pR)-3$^+$).** **Method A:** To a solution of LuFcB(C$_6$H$_5$)Cl · 0.5 C$_7$H$_8$ ((pR)-2; 4.9 mg, 0.0106 mmol) in CHCl$_3$ (0.5 mL) that was cooled down to –37 °C was added a solution of [Ag(CH$_2$Cl$_2$)]{Al[OC(CF$_3$)$_3$]$_4$} (14.0 mg, 0.012 mmol, 1.1 equiv) in CHCl$_3$ (0.5 mL) under stirring. The color of the solution turned from red to purple. After filtering off a small amount of a white precipitate, the filtrate was carefully layered with 1 mL of hexanes and kept at –37 °C for recrystallization. Yield: 6.0 mg (42 %). **Method B:** To a sample of Li{Al[OC(CF$_3$)$_3$]$_4$} (13.4 mg, 0.0138 mmol) in a 10 mL Schlenk flask was added a solution of LuFcB(C$_6$H$_5$)Cl · 0.5 C$_7$H$_8$ ((pR)-2; 6.3 mg, 0.0138 mmol) in CDCl$_3$ (1 mL) under vigorous stirring. Upon addition the color of the solution turned from red to purple. The mixture was stirred for 2 hours and then filtered. $^1$H NMR analysis showed complete conversion to the product. $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta$ = 8.31 (s, 1H; Lu), 7.95 (d, $J$ = 7 Hz, 2H; o-Ph), 7.83 (s, 1H; Lu), 7.81 (nr, 1H; p-Ph), 7.67 (pst, $J$ = 7 Hz, 2H; m-Ph), 5.75 (nr, 1H; Cp), 5.58 (nr, 1H; Cp), 5.48 (nr, 1H; Cp), 4.32 (s, 5H; free Cp), 2.40 (s, 3H; Lu-Me), 2.39 (s, 3H; Lu-Me). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta$ = 156.4, 148.0, 140.1, 134.6, 134.5, 134.1, 131.6, 129.9, (Lu + Ph), 121.2 (q, $J$(C,F) = 293 Hz, CF$_3$), 85.7 (Cp), 82.9 (ipso-Cp-C), ipso-Cp-B not observed, 79.2 (Cp), 76.6 (Cp), 76.5 (free Cp), 17.7 (Lu-Me), 17.2 (Lu-Me). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 45.4 ($\omega _{1/2}$ = 750 Hz). $^{19}$F NMR (470.4 MHz, CDCl$_3$, 25 °C): $\delta$ = −75.4. UV-Vis (CH$_2$Cl$_2$): $\lambda _{max}$ = 407 ($\varepsilon$ = 2000 M$^{-1}$ cm$^{-1}$), 566 ($\varepsilon$ = 2200 M$^{-1}$ cm$^{-1}$). Elemental analysis
Synthesis of [(pR)-LuFcB(C6H5)-PhC(O)CH3]+{Al[OC(CF3)3]4}− ((pR)-3+(acetophenone)). In a glove box, a solution of LuFcB(C6H5)Cl · 0.5 C7H8 ((pR)-2; 11.0 mg, 0.0242 mmol) in CH2Cl2 (5 mL) was added to a sample of Li{Al[OC(CF3)3]4} (23.5 mg, 0.0242 mmol) in a vial under vigorous stirring. Upon addition the color of the solution turned from red to purple. The mixture was stirred for 2 hours and then a solution of PhC(O)CH3 in CH2Cl2 (1.0 M, 0.0242 mmol, 0.0242 mL) was added. The color of the solution turned from purple to red. The solution was filtered and concentrated under high vacuum. The residue was re-dissolved in CH2Cl2 (5 mL), carefully layered with hexanes (5 mL) and then placed in a freezer at −37 °C to obtain purple red crystals. Yield: 20 mg (57 %). 1H NMR (499.9 MHz, CD2Cl2, 25 °C): δ = 8.31, 8.03, 7.76, 7.37 (br, 10H; Ph), 8.22 (s, 1H; Lu), 7.76 (s, 1H; Lu), 5.16 (br, 1H; Cp), 5.02 (br, 1H; Cp), 4.72 (br, 1H; Cp), 4.02 (s, 5H; free Cp), 3.15 (br, 3H; Me), 2.54 (s, 3H; Lu-Me), 2.42 (s, 3H; Lu-Me). 1H NMR (499.9 MHz, CD2Cl2, −20 °C): δ = 8.43 (d, J = 8 Hz, 2H; o-Ph), 8.17 (s, 1H; Lu), 8.11 (t, J = 8 Hz, 1H; p-Ph), 7.82 (t, J = 8 Hz, 2H; m-Ph), 7.72 (s, 1H; Lu), 7.32-7.26 (m, 3H; m-Ph + p-Ph), 7.22 (d, J = 7 Hz, 2H; o-Ph), 5.09 (nr, 1H; Cp), 4.90 (nr, 1H; Cp), 4.60 (nr, 1H; Cp), 3.94 (s, 5H; free Cp), 3.26 (s, 3H; Me), 2.53 (s, 3H; Lu-Me), 2.39 (s, 3H; Lu-Me). 11B NMR (160.4 MHz, CDCl3, 25 °C) δ = 10.7 (w1/2 = 960 Hz). Elemental analysis for C47H29AlBF36FeNO5, calcd C 38.52, H 1.99, N 0.96, found C 38.36, H 2.04, N 0.95%.

Hydrosilylation Catalysis. Stock solutions (1.0 M) of the ketones and silanes were prepared in CH2Cl2. A predetermined quantity of (pR)-3+ was dissolved in a minimum
amount of CH₂Cl₂ and the corresponding amount of the silane solution was added. The mixture was cooled down to –37 °C, an equimolar amount of the ketone solution was added and the progress of the reaction was monitored by taking an aliquot and measuring the ¹H NMR in CD₂Cl₂. After completion of the reaction, the mixture was treated with dilute HCl (aq.) solution and stirred vigorously overnight. To determine the enantioselectivity, the resulting (desilylated) alcohol was either directly examined by chiral GC-FID or HPLC, or isolated by distillation and then reacted with the chemical shift reagent (S)-(+)/-α-methoxy-α-trifluoromethylphenylacetyl chloride as described by Mosher⁴⁰. In a typical procedure, to a solution of the alcohol (5 mg) in 0.7 mL of CDCl₃ in a NMR tube is added 1 equivalent of Mosher’s chemical shift reagent and an excess amount of pyridine-d₅. The mixture is heated to 50 °C for 2 days and then filtered. The filtrate is transferred to another NMR tube and measured directly.

5.6 Supporting Information
(a) Data corresponding to Entry 1 in Table 5-1 – Chiral GC-FID analysis of 1-phenylethanol:
(b) Data corresponding to Entry 2 in Table 5-1 – Chiral HPLC analysis of 1-phenylethanol:

![Chiral HPLC Analysis](image1)

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<th>Height (μV)</th>
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(c) Data corresponding to Entry 4 in Table 5-1 – ^1^H NMR spectrum of the product from reaction of 3,3-dimethyl-2-butanol with Mosher’s chemical shift reagent:

![^1^H NMR Spectrum](image2)

(d) Data corresponding to Entry 5 in Table 5-1 – ^1^H NMR spectrum of the product from reaction of 3,3-dimethyl-2-butanol with Mosher’s chemical shift reagent:
Figure 5-8. Data corresponding to determination of enantiomeric excess of catalysis products.

Figure 5-9. Chiral HPLC analysis for compound (pR)-2 (99% ee) in 93:7 hexanes:THF.
Figure 5-10. Complete $^1$H NMR spectra of (pR)-2 (top), (pR)-2 + B(C₆F₅)₃ (middle), and (pR)-3⁺ (bottom) in CDCl₃.
Figure 5-11. 2D-NOESY spectra of compound (pR)-2 in C₆D₆.
Figure 5-12. a) Photographs of CH$_2$Cl$_2$ solutions of compounds (pR)-2 and (pR)-3$^+$. b) Photographs of a mixture of (pR)-2 + B(C$_6$F$_5$)$_3$ in CH$_2$Cl$_2$ solution and in the solid state after solvent removal. c) Comparison of UV-Vis spectra of compounds (pS)-1 (CHCl$_3$), (pR)-2 and (pR)-3$^+$ (CH$_2$Cl$_2$).

Note that the color change upon removal of solvent from the mixture of (pR)-2 + B(C$_6$F$_5$)$_3$ in CH$_2$Cl$_2$ suggests that halide abstraction by B(C$_6$F$_5$)$_3$ with formation of (pR)-3$^+$ becomes more favorable in the absence of the solvent CH$_2$Cl$_2$. 
Figure 5-13. High-resolution MALDI-MS spectra of compound (pR)-2 acquired at different laser power levels and comparison to simulated spectra of (pR)-2 and (pR)-3+. With increasing laser power, the ion (pR)-3+ becomes more dominant, suggesting facile Cl− abstraction under these conditions.
Figure 5-14. (top) Competitive binding of (pR)-3\(^+\) and B(C\(_6\)F\(_5\))\(_3\) to acetophenone (ratio of 1.0 (pR)-3\(^+\) : 1.0 B(C\(_6\)F\(_5\))\(_3\) : 1.0 PhC(O)Me) examined by \(^{11}\)B NMR spectroscopy in CD\(_2\)Cl\(_2\) at –20 °C. (bottom) Corresponding \(^{19}\)F NMR data. The ratio of complexation products was estimated to be ca. 10:1 in favor of complex formation with B(C\(_6\)F\(_5\))\(_3\), which is significantly larger than in the case of Et\(_3\)PO.
**Figure 5-15.** a) Ortep plot of the second independent molecule of (pR)-3⁺ (50% thermal displacement ellipsoids). Hydrogen atoms and the counterion are omitted for clarity. Selected interatomic distances (Å) and angles (°): B2-N2 1.550(9), B2-C25 1.539(9), B2-C41 1.504(10), C25-B2-N2 100.6(5), C25-B2-C41 132.2(6), C41-B2-N2 127.1(6). b) Asymmetric unit of compound (pR)-3⁺ (hydrogen atoms are omitted for clarity except in CHCl₃). Although the data set was acquired at 100 K, the anions were slightly disordered due to free rotation of the perfluorinated t-butyl groups. c) A π dimer consisting of two independent molecules of (pR)-3⁺ (only substituted Cp rings shown).
Figure 5-16. a) Ortep plots of two independent molecules of (pR)-3⁺(acetophenone) (50% thermal displacement ellipsoids). Hydrogen atoms and the counterions are omitted for clarity. Selected distances (Å) [second independent molecule]: B1-N1 1.603(9) [1.592(9)], B1-O1 1.560(8) [1.577(8)], B1-C2 1.580(11) [1.593(10)], B1-C18 1.603(11) [1.594(10)], O1-C24 1.257(8) [1.255(8)]. b) Asymmetric unit of compound (pR)-3⁺(acetophenone) (hydrogen atoms are omitted for clarity except in CH₂Cl₂). The positional disorder of the solvent CH₂Cl₂ could be modeled and refined as two parts
without any problems. Both sites of the disordered CH$_2$Cl$_2$ are shown in the asymmetric cell; the site occupancy factors are 0.54 (solid) and 0.46 (dash).

**Table 5-2.** Details of X-ray analyses of (pR)-3 and (pR)-3$^+$ (acetophenone).

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<td>907179</td>
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<td>[C$<em>{16}$AlF$</em>{36}$O$_4$]$^-$ • CH$_2$Cl$_2$</td>
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16806 [R(int) = 0.038]
Absorption correction  
Numerical  
Numerical
data/restraints/para’s  
15330 / 15 / 1535  
16808 / 50 / 1718
goodness-of-fit on $F^2$  
1.02  
1.03
final R indices  
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$R_1 = 0.075$
[ I > 2\sigma(I) ] $^a$  
w$R_2 = 0.180$  
w$R_2 = 0.189$
R indices (all data) $^a$  
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w$R_2 = 0.201$
Peakmax/holemin (e \text{Å}^{-3})  
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1.56 / -0.66
Absolute structure parameter  
0.019(5)  
0.022(6)

$^a$ $R_1 = \Sigma||F_o||-|F_c||/\Sigma|F_o|$; w$R_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

5.7 Notes and References


15. The IUPAC-recommended Cahn–Ingold–Prelog (CIP) descriptors pS and pR are used throughout the manuscript to describe the planar chirality; see: Schlögl, K. *Top. Stereochem.* 1967, 1, 39.

16. The selective formation of (pR)-2 is surprising, because the isomer (pS)-2 of opposite planar chirality would be expected in an ipso-borodestannylation reaction. Mechanistic details of this unusual rearrangement is discussed in Chapter 3.

17. A single crystal X-ray structure of (pR)-2 confirmed the stereochemical assignment and revealed the exo-Ph isomer as the only stereoisomer in the solid state.


22. To date, the largest dip angle of any borylferrocene derivative was found in the antiaromatic ferrocenylborole FcBC₄Ph₄ (29.4°; Fe...B 2.664 Å). Braunschweig, H.; Breher, F.; Chiu, C.-W.; Gamon, D.; Nied, D.; Radacki, K., *Angew. Chem. Int. Ed.* 2010, 49, 8975-8978.


6.1 Introduction

In this chapter we describe our efforts towards a novel class of chiral Lewis acids and Lewis pairs based on two ferrocenes that are doubly linked by heteroatoms. A survey of the recent literature reveals that only the 1,2-di-silylated (A) and 1,2-di-borylated species (B) have been reported. For the doubly silyl-bridged ferrocene derivatives, the synthesis involved addition of FeCl₂ to a mixture of disila-s-indacene dianion and CpNa (excess amount). The desired product was isolated from the crude mixture, which consisted of anti-isomer (A), syn-isomer, and other multi-nuclear species that contain more than two ferrocene units.¹ In a different way, system B was obtained by the boron-tin exchange of a 1,2-distannylated ferrocene and BCl₃. After the first boron-tin exchange, the intermediate, a 1-stannyl-2-boryl-ferrocene, could further undergo a second transmetalation to give the doubly boryl-bridged ferrocenes. Replacement of the chlorine atoms on the boron with aromatic substituents allows for tuning of the electronic properties of these systems. Due to the presence of a weak interaction between the iron and boron centers, the boryl units are bent away from the plane of the substituted Cp rings. Remarkably, this type of interaction could be interrupted by the oxidation of the ferrocene unit, reduction of the boryl moiety, or Lewis base complexation to the boron center, resulting in a geometry change to a more co-planar conformation.² Related 1,1’-disubstituted ferrocene derivatives have attracted considerable efforts during the past two decades. This family of compounds can be readily obtained from the 1,1’-dilithiated ferrocene precursor. Elements ranging from group 13 and 14 such as B,³ Si,⁴ Sn,⁵ Pb,⁶ Al⁷
and Ga\textsuperscript{8} were incorporated as bridges. One of the examples showing very intriguing properties in supramolecular chemistry is the complex C reported by Wagner and coworkers. This diferrocene system served as a lithium ion scavenger to form complex C, where a Li\textsuperscript{+} is positioned in the middle of a diferrocenyl diborate framework and stabilized by the electron rich borate and Fe(II) moieties. Interestingly, the system was able to expel the Li\textsuperscript{+} ion after oxidation of the diferrocene unit.\textsuperscript{3}

\[ \text{Fe} \quad \begin{array}{c} \text{X} \\ \text{Fe} \end{array} \quad \text{Fe} \]

\[ \text{Fe} \quad \begin{array}{c} \text{X} \\ \text{Fe} \end{array} \quad \text{Fe} \]

\[ \text{X} = \text{B, Si} \]

\[ \text{A: R=Me, Et, Bu} \]

\[ \text{B} \]

\[ \text{X} = \text{BR, SiR}_2, \text{SnR}_2, \text{PbR}_2, \text{AlR, GaR} \]

\[ \text{C} \]

\[ \begin{array}{c} \text{Me}_2 \\ \text{BMe}_2 \end{array} \quad \text{Fe} \]

\[ \text{Fe} \quad \begin{array}{c} \text{Li}^+ \\ \text{BMe}_2 \end{array} \]

\[ \text{Fe} \quad \begin{array}{c} \text{Me} \\ \text{Me} \end{array} \quad \text{Fe} \]

\[ \begin{array}{c} \text{B} \\ \text{Si} \end{array} \quad \text{Me} \]

\[ \text{T1} \]

**Figure 6-1.** Representative examples of element-bridged diferrocenes.

We envisioned that replacement of one of the boron atoms with silicon or phosphorus will break the symmetry in compound B resulting in chiral Lewis acids. With phosphorus an ambiphilic system would be generated that features both a Lewis acidic boron and a Lewis basic phosphorus center. Related benzene-based ambiphilic phosphaborin systems (D) have been reported by Kawashima and coworkers.\textsuperscript{9} Studies on
electronic and optical properties indicated an intramolecular charge transfer from phosphorus to boron upon photo excitation. Moreover, the alkylation of phosphorus resulted in the formation of a cationic phosphonium species, which became more soluble in polar solvents and had a high affinity towards anions such as fluoride and bromide.\textsuperscript{10} A lot of effort has also been directed to applications where boron and phosphorus could work in a cooperative manner. For instance, borane-phosphine systems can serve as FLPS and be utilized to activate small molecules as discussed in Chapter 1. In addition, these types of amphoteric molecules could coordinate to transition metals in different and unique ways. Ligands for transition metal coordination can be classified as the following three types: 2e-donor ligands (L), 1e-donor ligands (X) and 0e-donors/2e-acceptors (Z).\textsuperscript{11} Ambiphilic ligands can be described as molecules bearing donor moieties (L and/or X) and at least one Lewis acid unit (Z). Last but not least, in order to retain the ambiphilic features, it is imperative to prevent the strong interaction between the Lewis basic and Lewis acidic units by tuning both electronic and steric properties of the appendant substituents. There are also several coordination modes that could be involved: (1) the metal binds solely to the Lewis base moiety (L) and the Lewis acid (Z) interacts with an incoming substrate (S) (Figure 6-2a); (2) the Lewis acid (Z) can interact with the ligand (X) within the coordination sphere of the metal (Figure 6-2b); (3) the Lewis acid could bind cooperatively to a nucleophilic metal center, forming a dative interaction from the metal to the Lewis acid (Figure 6-2c). The first type of coordination mode mimics the working behavior of enzymes in nature. The second and third types have also been studied extensively in the past decade. For example, by tuning the Lewis acidity of the boron center, the ambiphilic ligands $E$ bind to the metal via $P\rightarrow M\rightarrow B$ or $P\rightarrow M\rightarrow Cl\rightarrow B$. 
interactions (M: rhodium or gold). This rare interacting mode (M→Z σ-donation) provides an opportunity to investigate the coordination of various Lewis acids (B, Al, Ga, In, Si, Sn) to different transition metals (Rh, Ni, Pd, Pt, Cu, Ag, Au etc.). The increasing interest and successful examples in this emerging area raised a fundamental question on the nature of such interactions. For example, Bourissou and coworkers carried out comparative studies on the structural geometry and the electronic configuration of an ambiphilic complex \([\{\kappa^3-(o-(iPr_2P)C_6H_4)BPh\}AuCl]\). The solid state structure indicated a square planar geometry, which is usually adopted by Au\(^{III}\) \(d^8\) complexes. However, the computational data suggested that the dative Au→B interaction did not lead to the formal two-electron oxidation of Au\(^I\) to Au\(^{III}\), which was also supported by the Mössbauer spectroscopic analysis. As a result, the Au metal retained a \(d^{10}\) configuration with an unexpected square planar geometry.

Herein we describe the synthesis of the first examples of planar chiral diferrocenylsilaborin Lewis acid (T1) and an ambiphilic diferrocenylphosphaborin derivative (T2). We also discuss the redox properties, binding behavior in the presence of external Lewis acids or transition metals to (T2), as well as an investigation of the electron donating property in the corresponding Vaska-type complex.
6.2 Results and Discussions

Initially, we explored methods to link two ferrocene units with different hetero atoms. Li-Fc-SOTol, prepared by diastereoselective lithiation of FcSOTol with LDA according to Kagan’s method, was chosen as the precursor because of its facile preparation and excellent stereoselectivity in the synthesis of planar chiral 1,2-disubstituted ferrocenes. The lithiated species was then treated with Me₂SiCl₂, PhPCl₂ or Me₂SnCl₂. In the case of Me₂SiCl₂, a yellow solid was isolated after chromatography. However, NMR studies indicated a mono-substituted ferrocene derivative (1-Si). We propose that the Li-Fc-Tol was not able to attack Me₂SiCl₂ due to steric effects. As the temperature increased, isomerization occurred to give a benzyl anion with less steric hindrance, which could undergo the nucleophilic substitution at the silicon atom and give the corresponding unexpected ferrocene dimer. In the reaction with PhPCl₂, several fractions of unidentified
species formed, which could not be separated well by chromatography. Fortunately, switching to a better electrophile Me₂SnCl₂ provided the expected bridged product. Column chromatography followed by crystallization gave the desired product (1-Sn) in a yield of 80% (Scheme 6-1).

Scheme 6-1. Synthesis of planar chiral tin-bridged diferrocene 1-Sn.

The dilithiation of compound 1-Sn proceeded readily upon treatment with 2 equivalents of t-BuLi at -78 °C. Cyclic systems 2-SnSn and 2-SnSi were obtained after the metathesis of the dilithiated species with the corresponding element dichloride (Me₂SnCl₂ and Me₂SiCl₂, respectively). Compounds 2-SnSn and 2-SnSi (Scheme 6-2) were purified by silica gel column chromatography using hexanes as eluent, followed by crystallization in methanol (yield of 65% for 2-SnSn and 62% for 2-SnSi). Only one set of 1,2-disubstituted Cp signals is observed in the ¹H NMR, which is consistent with the C2 symmetry of the molecules.
We next investigated the replacement of the dimethylstannyl unit in 2-SnSi by a boryl unit. Reaction of 2-SnSi with 2 equivalents of HgCl₂ in acetone (1 h) resulted in the complete conversion into the corresponding dimercurated species. ¹H NMR showed the typical patterns for the 1,2-disubstituted ferrocene derivative and the absence of the Sn-Me signal suggested the replacement of tin with mercury. The product reacted readily with PhBCl₂ in toluene at 90 °C overnight to give a new cycle 2-BSi in a yield of 47% (Scheme 6-3). The incorporation of boron is evident from multinuclear NMR data. ¹H NMR indicates a set of aromatic B-Ph signals as well as a downfield shift for the substituted Cp ring due to the electron deficiency of the boron. An ¹¹B NMR resonance at δ = 53.9 denotes a typical tricoordinate boron (Figure 6-3).
Figure 6-3. Comparison of NMR data for cycles 2-SnSn, 2-SnSi, 2-BSi.

The solid state characterization of the achiral system, 2-SnSn, is hampered by the unsolved disorder of the ferrocenyl units. The chiral derivative 2-SnSi suffered minor disorder as well. Nonetheless, its structure could be solved in the chiral C₂ space group. In both of the independent molecules of 2-SnSi, the tin and silicon atoms are almost coplanar with the substituted Cp rings. The ferrocene units are positioned in an anti-fashion and adopt a pR configuration according to the CIP protocol. The introduction of boron resulted in a dramatic change of the solid state structure. The B-Si compound crystallized in the P2₁ space group with an unchanged pR configuration for the diferoocene unit (Figure 6-4). Selective distances and angles are summarized in Table 6-1. The bridge angles (γ, see Chapter 1) in 2-SnSi are 101.7(5)° [102.4(6)°] at the Sn center and 108.7(8)° [111.2(7)°] at the Si center. The bridge angles in compound 2-BSi are 102.60(11)° at the Si and 118.4(2)° at the B. The large difference between γ for 2-
SnSi and 2-BSi can be attributed to the planarization upon changing the tetrahedral geometry of Sn to a trigonal geometry of B. A considerable interaction between the tricoordinate electron deficient boryl unit and the iron center is deduced from the dip angles of the boron out of the Cp planes (13.9° and 13.7°) (α, see Chapter 1), towards the metal centers (Figure 6-4). As a result, the substituted Cp rings in 2-BSi are positioned in a distorted orientation with the dihedral angle (Cp//Cp) of 14.12°, which is very different from cycle 2-SnSi. The substituted Cp rings in 2-SnSi are coplanar due to the C₂ symmetry.

Figure 6-4. a) Ortep plot of 2-SnSi and 2-BSi (50% thermal ellipsoids); H atoms are omitted.

Table 6-1. Selected distances (Å), angles (°) and parameters of 2-SnSi and 2-BSi.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>2-SnSi [2nd molecule]</th>
<th>2-BSi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn1-C1</td>
<td>2.115(9) [2.137(9)]</td>
<td>Si1-C1: 1.861(3);</td>
</tr>
<tr>
<td>Sn1-C11</td>
<td>2.149(9) [2.147(9)]</td>
<td>Si1-C11: 1.851(3);</td>
</tr>
<tr>
<td>Si1-C2</td>
<td>1.882(12) [1.878(11)]</td>
<td>Si1-C21: 1.878(3);</td>
</tr>
<tr>
<td>Si1-C12</td>
<td>1.856(12) [1.881(12)]</td>
<td>Si1-C22: 1.879(3);</td>
</tr>
<tr>
<td>B1-C2</td>
<td>1.543(4)</td>
<td>B1-C2: 1.543(4);</td>
</tr>
<tr>
<td>B1-C12</td>
<td>1.555(4)</td>
<td>B1-C12: 1.555(4);</td>
</tr>
<tr>
<td>B1-C23</td>
<td>1.570(4)</td>
<td>B1-C23: 1.570(4);</td>
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<table>
<thead>
<tr>
<th>Dip angleα (°)</th>
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<th>2-BSi</th>
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<tr>
<td></td>
<td>--</td>
<td>13.9 &amp; 13.7</td>
</tr>
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<table>
<thead>
<tr>
<th>Bridge angle (°)</th>
<th>2-SnSi</th>
<th>2-BSi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1-Sn1-C1’ 101.7(5) [102.4(6)];</td>
<td>C2-B1-C12 118.4(2);</td>
</tr>
<tr>
<td></td>
<td>C2-Si1-C2’ 108.7(8) [111.2(7)];</td>
<td>C1-Si1-C11 102.60(11);</td>
</tr>
<tr>
<td>Tilt angle(^b) (°)</td>
<td>3.99 [1.96]</td>
<td>0.72 &amp; 0.97</td>
</tr>
<tr>
<td>---------------------</td>
<td>------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Cp//Cp(^c) (°)</td>
<td>0 [0]</td>
<td>14.12</td>
</tr>
<tr>
<td>ΣEc//Ec(^d) (°)</td>
<td>--</td>
<td>B1: 360</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.114(17)</td>
<td>0.007(3)</td>
</tr>
</tbody>
</table>

[a] Applied to cycles with boron bridges;
[b] Data correspond to lower Fc and upper Fc;
[c] Dihedral angles of two substituted Cp planes;
[d] Sum of bond angles around the bridging element B or P.

The electrochemistry of **2-SnSn**, **2-SnSi** and **2-BSi** was examined by cyclic voltammetry and square wave voltammetry (Figure 6-5). CV data show that all compounds undergo quasi-reversible mono- and di- oxidation for the diferrocene moieties. The peak separations for **2-SnSn**, **2-SnSi** and **2-BSi** are 374, 394 and 574 mV, respectively. The redox behavior of compounds **2-SnSn** and **2-SnSi** is almost identical, suggesting that the switching between tin and silicon bridges has just a minor influence on the geometry and electronic coupling between the ferrocene units. In contrast, incorporation of boron resulted in dramatic anodic shifts of both the 1\(^{st}\) and 2\(^{nd}\) oxidation potentials, as well as an enlargement of the peak separation (Table 6-2). Interestingly, **2-SnSn** and **2-SnSi** exhibited two redox waves with equal intensities, while compound **2-BSi** showed a considerably smaller current for the 2\(^{nd}\) oxidation. Notably, Compton and coworkers studied the double reduction behavior of anthraquinone in low electrolyte support and observed the same phenomenon.\(^{15}\) They attribute this phenomenon to a fast comproportionation rate that leads to accumulation of the mono- anion, hence the transport of it becomes rate-limiting. The fast comproportionation is thermodynamically more favorable if the peak separation for two redox processes is larger. In the case of low electrolyte support, the diffusion of the mono- anion is reduced by repulsion from the negatively charged reaction layer. As a result, the magnitude for the 2\(^{nd}\) reduction is
decreased. Although we already used a relatively well-supported system (ca. 50 fold amount of the electrolyte compared to the substrates), we still observe this similar phenomenon due to ineffective screening of the electric field in compound 2-BSi as well as other compounds with large peak separation (*vide infra*). The cycle 2-BSi was also chemically oxidized by treatment with 2 equivalents of the Ag derivative of Krossing’s salt. The $^1$H NMR resonances shifted to 44.4 ppm for the free Cp and 29.0, 22.4, 18.1 ppm for the substituted Cp ring. Unfortunately, attempts to characterize the product by crystallography failed. Under ambient conditions a hydrolyzed species precipitated from a CH$_2$Cl$_2$ solution of the oxidized compound and was analyzed by single-crystal X-ray diffraction (Figure 6-6). The oxidation of both ferrocene units was evident from the distances of the centroids of two Cp rings (3.420 Å), which falls into the typical range for oxidized ferrocene.

*Figure 6-5.* Left: cycle voltammetry data for 2-SnSn, 2-SnSi, 2-BSi (CH$_2$Cl$_2$, 25 mV/s, 0.05 M Bu$_4$N[B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] as electrolyte, reported versus Fe/Fe$^+$, which is taken as +610 mV versus Fe*/Fe$^{**}$ as an internal reference); Right: square wave voltammetry data for 2-SnSn, 2-SnSi, 2-BSi.
Table 6-2. Redox potentials derived from cyclic voltammetry or square-wave voltammetry data; CH$_2$Cl$_2$, 0.05 M Bu$_4$N[B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] as electrolyte, reported vs Fc/Fc$^+$

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<th>$E_{1/2}$ (1) (mV)</th>
<th>$E_{1/2}$ (2) (mV)</th>
<th>$\Delta E_{1/2}$ (mV)</th>
</tr>
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<tr>
<td>2-SnSn$^a$</td>
<td>-101</td>
<td>273</td>
<td>374</td>
</tr>
<tr>
<td>2-SnSi$^a$</td>
<td>-88</td>
<td>306</td>
<td>394</td>
</tr>
<tr>
<td>2-BSi$^a$</td>
<td>10</td>
<td>557</td>
<td>547</td>
</tr>
<tr>
<td>BPh-BPh$^b$</td>
<td>60</td>
<td>570</td>
<td>510</td>
</tr>
</tbody>
</table>

[a] Calculated from square-wave voltammetry data  
[b] Cyclic voltammetry Data from ref. [2a]

Figure 6-6. Solid state structure of a doubly oxidized species derived from 2-BSi (Hydrogen atoms omitted except for B-OH).

Following a similar strategy as described for the chiral Lewis acid 2-BSi, 1-Sn was dilithiated and treated with dichlorophosphines for the synthesis of ambiphilic phosphorus-containing cycles (Scheme 6-4). An initial attempt with the alkyl phosphine $t$-BuPCl$_2$ followed by reaction with BH$_3$ in THF led to a trace amount of the product 3a-SnP, which is complexed with BH$_3$ to avoid oxidation of the phosphorus. The steric bulk as well as the electron rich character of the $t$-butyl group possibly hampered the efficient nucleophilic replacement of the chlorine atoms with the ferrocene units. Switching to the
aryl phosphine PhPCl₂, a better electrophile with less steric hindrance, led to an increase in the yield to 40% for the product 3b-SnP. Both compounds formed red crystals suitable for structure determination. They crystallize in the P2₁2₁2₁ space group with one independent molecule for the t-butyl derivative and two for the phenyl derivative in the unit cell. The structural parameters are generally very similar as they adopt very similar geometries (Figure 6-7 and Table 6-3). But the individual ferrocene moieties experience different spatial environments. While one is closer to the BH₃ group, the other is adjacent to the t-butyl or phenyl group on phosphorus. Due to the bulky pendent groups on the phosphorus, the substituted Cp rings adopt a butterfly orientation, rather than a coplanar conformation. The dihedral angles (Cp//Cp) of the substituted Cp rings are measured to be 43.76° and 53.78° [45.49°] for 3a-SnP and 3b-SnP, respectively. The bridge angles in 3a-SnP are 96.16(10)° at the Sn center and 107.18(11)° at the P center. The bridge angles in 3b-SnP are 95.87(10)° [95.99(10)°] at the Sn center and 105.00(12)° [106.07(12)°] at the P center. The steric hindrance is also reflected in the tilt angles (γ) of the ferrocene moiety that is closest to the P substituent, which are 11.86° for the t-butyl derivative and 4.96° [6.17°] for the phenyl derivative. The difference in the tilt angle is consistent with the lower yield for the ring formation in the case of t-BuPCl₂.

**Scheme 6-4.** Synthesis of planar chiral cycles 3a-SnP and 3b-SnP.
Figure 6-7. a) Ortep plots of 3a-SnP and 3b-SnP (50% thermal ellipsoids); H atoms are omitted.

Table 6-3. Selected distances (Å), angles (°) and parameters of 3a-SnP and 3b-SnP.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>3a-SnP</th>
<th>3b-SnP [2nd molecule]</th>
</tr>
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<tr>
<td>Sn1-C1: 2.128(2); Sn1-C11: 2.135(3); Sn1-C21: 2.139(3); Sn1-C22: 2.146(3); P1-C2: 1.815(2); P1-C12: 1.805(3); P1-C23: 1.866(3); P1-B1: 1.932(3);</td>
<td>Sn1-C1: 2.126(3) [2.133(3)]; Sn1-C11: 2.142(3) [2.138(3)]; Sn1-C21: 2.134(3) [2.132(3)]; Sn1-C22: 2.132(3) [2.143(3)]; P1-C2: 1.799(3) [1.810(3)]; P1-C12: 1.797(3) [1.799(3)]; P1-C23: 1.825(3) [1.817(3)]; P1-B1: 1.924(3) [1.925(3)];</td>
<td></td>
</tr>
<tr>
<td>Bridge angle (°)</td>
<td>C1-Sn1-C11: 96.16(10); C1-Sn1-C12: 107.18(11);</td>
<td>C1-Sn1-C11: 95.87(10) [95.99 (10)]; C1-Sn1-C12: 105.00(12) [106.07(12)];</td>
</tr>
<tr>
<td>Tilt angle (°)</td>
<td>11.86 &amp; 3.79</td>
<td>4.93 [6.17] &amp; 1.68 [1.78]</td>
</tr>
<tr>
<td>Cp/Cp (°)</td>
<td>43.76</td>
<td>53.78 [45.49]</td>
</tr>
<tr>
<td>ΣC-E-C (°)</td>
<td>P1: 320.47</td>
<td>P1: 320.14 [318.40]</td>
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<tr>
<td>Flack parameter</td>
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<td>0.013(3)</td>
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[a] Data correspond to upper Fc and lower Fc;
[b] Dihedral angles of two substituted Cp planes;
[c] Sum of bond angles around the bridging element B or P.
The phenyl derivative 3b-SnP was used as precursor for the synthesis of a 4-BP because of its higher yield. Similar to the previous synthetic protocol, 3b-SnP was initially treated with 2 equiv of HgCl₂ for the synthesis of the dimercurated species. However, ¹H NMR indicated that only 1 equivalent of HgCl₂ had reacted. Cleavage of only one of the Sn-C₅₇ bonds results in the formation of a species bearing a chlorodimethylstannyl and a chloromercurio group. The retention of the chlorodimethylstannyl group was evident from the ¹H NMR resonances at 1.05 and 1.32 ppm that each integrated as 3 protons. Attempts to use longer reaction times led to no further conversion and higher reaction temperature resulted in the loss of the chloromercurio group. Fortunately, the intermediate reacted smoothly with PhBCl₂ to give the desired product. After heating in toluene to 90 °C for 12 h and subsequent column chromatography, the analytically pure cycle 4-BP was obtained in a yield of 49%. The broad signals at 1.16 ppm in the ¹H NMR and a signal at -35.2 ppm in the ¹¹B NMR indicate the attachment of the BH₃ group. On the other hand, MALDI-MS data show a major signal corresponding to the loss of BH₃. In the solid state, 4-BP crystallizes in the P2₁ space group. The Σ∠C-B-C around boron is 360.0°, indicating that B adopts an almost perfect trigonal planar geometry. Σ∠C-P-C around phosphorus is 314.33°, which is consisting with pyramidalization at phosphorus. The bridge angles were measured to be 117.0(3)° at the B and 101.97(13)° at the P. The dip angles of the boron towards the iron centers are 13.5° and 14.5°, respectively (Figure 6-8 and Table 6-4).
Scheme 6-5. Synthesis of the ambiphilic ligand 5-BP.

Figure 6-8. a) Ortep plots of 4-BP and 5-BP (50% thermal ellipsoids); H atoms (except BH$_3$) are omitted

Table 6-4. Selected distances (Å) and angles (°) of 4-BP and 5-BP.

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<thead>
<tr>
<th></th>
<th>4-BP</th>
<th>5-BP</th>
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<td>B1-C2</td>
<td>1.547(5)</td>
<td>B1-C2: 1.533(4);</td>
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<tr>
<td>B1-C12</td>
<td>1.531(5)</td>
<td>B1-C12: 1.544(4);</td>
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<td>B1-C27</td>
<td>1.570(5)</td>
<td>B1-C27: 1.568(4);</td>
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<td>P1-C1</td>
<td>1.800(3)</td>
<td>P1-C1: 1.823(2);</td>
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<td>P1-C11</td>
<td>1.789(3)</td>
<td>P1-C11: 1.809(2);</td>
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<td>P1-C21</td>
<td>1.818(3)</td>
<td>P1-C21: 1.846(2);</td>
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<td>P1-B2</td>
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<td>Dip angle°</td>
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<td>Bridge angle°</td>
<td>C2-B1-C12: 117.0(3)</td>
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<td>C1-P1-C11: 99.48(11)</td>
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<td>Tilt angle°</td>
<td>3.69 &amp; 0.97</td>
<td>2.53 &amp; 2.23</td>
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The cleavage of BH$_3$ under MALDI-MS spectrometry conditions encouraged us to explore synthetic methods to prepare the free cycle $5$-$\text{BP}$. Reaction of $4$-$\text{BP}$ with a slight excess of DABCO at $50 \ ^\circ\text{C}$ for 2 days led to formation of the deprotected species, which was purified by aluminum oxide column chromatography with THF/hexanes (1:1) as the eluent in a glovebox. $^1$H, $^{11}$B and $^{31}$P NMR spectroscopy confirmed the successful removal of the BH$_3$ group in the product. The compound $5$-$\text{BP}$ crystallized in the P3$_2$ space group after slow evaporation of a hexanes solution (Figure 6-8). The bending of the boron (dip angle, $\alpha$) towards the iron centers is $14.6^\circ$ and $15.6^\circ$, respectively. The $\Sigma_{\angle\text{C-P-C}}$ around the phosphorus is $305.7^\circ$ ($314.33^\circ$ for $4$-$\text{BP}$). The lone pair of electrons of the tricoordinate phosphorus typically makes only a very small contribution to the conjugation of $\pi$ systems, hence the phosphorus usually adopts a pyramidal structure.$^{9a}$ Removal of the BH$_3$ group has very little impact on the P-C bonds distances. The geometry around boron ($\Sigma_{\angle\text{C-B-C}}$ of $360.0^\circ$) remained similar when compared to $4$-$\text{BP}$ (Table 6-4). After exposure to the air, $5$-$\text{BP}$ was converted to a new species (see Supporting Information). The $^{31}$P NMR signal shifted from $-24.9$ to $29.0$ ppm and the MALDI-MS spectrum indicated the addition of an oxygen atom to the molecule, suggesting that the phosphine unit had been oxidized to the phosphine oxide, likely due to the electron-rich environment provided by the biferrocene framework.
For the chiral cyclic compounds, it is crucial to investigate the stereo-selectivity for each step. One method is the absolute configuration as determined by the Flack parameter. We determined the Flack parameters for compounds $2$-$\text{SnSi}$ [0.114(17)], $2$-$\text{BSi}$ [0.007(3)], $3\text{a}$-$\text{SnP}$ [0.008(4)], $3\text{b}$-$\text{SnP}$ [0.013(3)] and $4$-$\text{BP}$ [0.012 (4)] and $5$-$\text{BP}$ [0.004(3)]. All of the values fell into the satisfactory range except that for cycle $2$-$\text{SnSi}$. We attribute it to the minor disorder (see Supporting Information) in the crystal lattice of $2$-$\text{SnSi}$. The Flack parameter could also be affected by any unsolved disorder problem. To further confirm the enantiopurity of these compounds, the same batches of crystals were used for chiral HPLC and optical rotation measurements for $2$-$\text{SnSi}$, $2$-$\text{BSi}$, $3\text{b}$-$\text{SnP}$ and $4$-$\text{BP}$. All of them showed one major signal from the chiral HPLC trace, which was identified as the individual cycle with the PDA detector by comparison with UV-Vis spectra of pure cycles. The chiral HPLC and optical rotation measurements for the free ligand $5$-$\text{BP}$ were not carried out due to its susceptibility to oxidation under ambient condition. However, it is reasonable to believe that the deprotection of BH$_3$ to form $5$-$\text{BP}$ occurs with chiral retention.
Figure 6-9. Square-wave voltammetry data for 3b-SnP, 4-BP, 5-BP (CH₂Cl₂, 0.05 M Bu₄N[B(C₆H₅(CF₃)₂)₄] as electrolyte, reported versus Fc/Fc⁺, which is taken as +610 mV versus Fc*/Fc*⁺ as an internal reference)

Table 6-5. Redox potentials derived from square wave voltammetry data; CH₂Cl₂, 0.05 M Bu₄N[B(C₆H₅(CF₃)₂)₄] as electrolyte, reported vs Fc/Fc⁺.

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<th>E₁/₂ (1) (mV)</th>
<th>E₁/₂ (2) (mV)</th>
<th>ΔE₁/₂ (mV)</th>
</tr>
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<tbody>
<tr>
<td>3b-SnP</td>
<td>138</td>
<td>557</td>
<td>419</td>
</tr>
<tr>
<td>4-BP</td>
<td>255</td>
<td>940</td>
<td>685</td>
</tr>
<tr>
<td>5-BP</td>
<td>-2</td>
<td>591 / 787</td>
<td>-</td>
</tr>
</tbody>
</table>

The redox properties of 3b-SnP, 4-BP and 5-BP were studied by cyclic and square wave voltammetry (Figure 6-9 and Table 6-5). For the BH₃-protected species, a reversible 1ˢᵗ oxidation and quasi-reversible 2ⁿᵈ oxidation were observed. Incorporation of B resulted in an anodic shift for both potentials as well as an enlarged peak separation. For the free cycle 5-BP, the removal of the BH₃ renders an increase of electron density of
the system, leading to a cathodic shift for the 1\textsuperscript{st} redox process ($E_{1/2} (1) = -2 \text{ mV}$). Another two signals at higher potential were recorded (591 and 787 mV). Although we were not able to assign them unequivocally, we postulate that one of them corresponds to the 2\textsuperscript{nd} oxidation of the diferrocene backbone, while the other might be derived from the electron transfer between the ferrocene and the phosphine moieties, followed by reaction with trace amount of water.\textsuperscript{16}

The 5-BP system could be potentially used as a tunable tertiary phosphine ligand. The compound reacted readily with 0.25 equiv of [Rh(CO)\textsubscript{2}Cl]\textsubscript{2} to give the corresponding Vaska-type rhodium complex (Scheme 6-6). For such a complex, the monodentate phosphine ligands usually occupy the trans positions, which is consistent with the observation that only one set of $^1$H NMR signals is present for the ligand. The $^{31}$P NMR resonance at 7.6 ppm (doublet) is downfield shifted when compared to that of the free ligand (-24.9 ppm), due to reduced electron density after binding to the rhodium. Moreover, the direct bonding between the Rh and P is evident from the $^2J^{(103)}$Rh,P coupling constant of 124 Hz (Figure 6-10). The MADLI-MS data further confirmed the incorporation of two ligands into the complex. The signal with highest intensity at m/z 1110.0461 was assigned to be [M-CO-Cl-FeCp]$^+$, corresponding to loss of the CO and Cl$^-$ ligands as well as a CpFe fragment.

The coordination of the phosphine to the rhodium stabilizes the lone pair of electrons and removes the electron density from the ferrocene. As a consequence, the diferrocenyl moieties exhibited more reversible and anodic oxidation processes compared to the free ligand (Figure 6-11). In fact, the redox behavior of the Rh complex is quite similar to that of the BH\textsubscript{3} complex. More interestingly, due to the presence of two redox-active ligands
(namely L₁ and L₂), the oxidations are split into two-step single-electron processes. The potentials and peak separations measured by square-wave voltammetry are summarized in Table 6-6. The signals at 130 and 862 mV were assigned as the 1ˢᵗ and 2ⁿᵈ oxidations of the diferrocenylphosphino ligand L₁. Similarly, the signals at 254 and 1000 mV were attributed to the second ligand L₂. The peak separations (732 and 746 mV) are the largest in this series of diferrocene derivatives.

\[
\text{Scheme 6-6. Synthesis of a Vaska-type rhodium compound.}
\]

\[
\text{Figure 6-10. } ^1\text{H and } ^{31}\text{P NMR spectra for complex (5-BP)}_2\text{Rh(CO)}\text{Cl in CD}_2\text{Cl}_2.
\]
Figure 6-11. Cyclic voltammetry (CH$_2$Cl$_2$, 50 mV/s, 0.05 M Bu$_4$N[B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] as electrolyte, reported versus Fc/Fc$^+$, which is taken as +610 mV versus Fc*/Fc$^{*+}$ as an internal reference) and square-wave voltammetry data for (5-BP)$_2$Rh(CO)Cl complex.

Table 6-6. Redox potentials derived from square-wave voltammetry data of (5-BP)$_2$Rh(CO)Cl; CH$_2$Cl$_2$, 0.05 M Bu$_4$N[B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] as electrolyte, reported vs Fc/Fc$^+$.

<table>
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<th></th>
<th>$E_{1/2}$ (1) (mV)</th>
<th>$E_{1/2}$ (2) (mV)</th>
<th>$\Delta E_{1/2}$ (mV)</th>
</tr>
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<tbody>
<tr>
<td>$L_1$</td>
<td>130</td>
<td>862</td>
<td>732</td>
</tr>
<tr>
<td>$L_2$</td>
<td>254</td>
<td>1000</td>
<td>746</td>
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The synthesis of a Vaska-type Rh(I) complex allows us to monitor the CO stretching frequency in the presence of different cis- phosphine ligands.$^{17}$ This IR band can serve as a probe for the steric and electronic properties of the phosphine ligand. The $\nu$(CO) of
1965 cm$^{-1}$ for (5-BP)$_2$Rh(CO)Cl (Figure 6-12, blackline) lies in between that of the acyclic mono-ferrocenyl ligand (PPh$_2$Fc, 1970 cm$^{-1}$) and diferrocenyl (PPhFc$_2$, 1957 cm$^{-1}$) complexes. Apparently, the incorporation of boron results in some degree of electron density reduction when compared to the unfunctionalized derivative. More interestingly, after addition of an excess amount of tetrabutylammonium fluoride to the rhodium complex, the $\nu$(CO) shifted dramatically to 1937 cm$^{-1}$, suggesting a pronounced enhancement of the “electron releasing” characteristic of the ligand after the fluoride binding (Figure 6-12). A possible explanation is that an increase of the electron density at the metal center and the resulting enhanced $d-\pi^*$ back bonding leads to a weakening of the C≡O bond. In a control experiment, the addition of tetra-n-butylammonium fluoride to (PPh$_3$)$_2$Rh(CO)Cl did not affect the $\nu$(CO), which excludes other possibilities such as ligand exchange. In comparison, substitution of the para-position of triphenylphosphine as the ligand with electron-donating groups such as –OMe or electron-withdrawing groups such as –F and –Cl results in only a slight change in the CO stretching frequency (within $\Delta$ 5 cm$^{-1}$ even all of the substituents in the phosphorus are replaced). On the other hand, Peters et al. pointed out that the formal charge of the entire metal complex should be considered, since cationic late transition metal ions can have a strong polarization effect on the CO, which leads to a higher CO stretching frequency. They synthesized two families of metal complexes: one consists of zwitterionic complexes with bis(phosphino)borate ligands and the other of cationic complexes with the corresponding bis(phosphino)silane ligands. For the cationic platinum species, the $\pi$-back-bonding is weak due to the net positive charge, which results in a high energy CO stretching frequency (2094 cm$^{-1}$). For the borate platinum complex they mentioned, this
polarization effect is reduced because of the negative charge on the boron (regardless of whether the complex is in zwitterion form or not, as long as the overall charge is 0). As a consequence, the ν(CO) shifts to lower energy (2070 cm⁻¹). Therefore, the absolute shift of ν(CO) is a result of a polarization effect and the electronic contributions. In our case, it is reasonable to believe the fluoborate ligand is more electron-donating,¹⁸ but the polarization effect of the overall negative charge of the complex likely also contributes to the increased backbonding and lower ν(CO).

Figure 6-12. IR spectra for complex (5-BP)₂Rh(CO)Cl (black line, transmission mode) before and after addition of increasing amounts of F⁻. (The CO stretching band is indicated by an asterisk)
6.3 Conclusions

We have established a practical protocol for the synthesis of a number of hetero-atom linked differrocenes, ranging from group 13 to group 15 elements such as boron, silicon, tin and phosphorus. While the compounds with tricoordinate boron feature a trigonal fragment, the others adopt tetrahedral configurations. The successful introduction of planar chirality was supported by single-crystal X-ray crystallography, chiral HPLC and optical rotation measurements. Electrochemical studies reveal that the cycles 2-SnSn, 2-SnSi and 2-BSi undergo 2-step reversible oxidations for the Fc units. The introduction of boron results in anodic shifts for both of the potentials. For the most interesting system, 5-BP, the 1st quasi-reversible process suggests the possibility to serve as a redox responsive ligand. In the solid state structure of 5-BP, the tricoordinate phosphorus adopts a pyramidal conformation, indicating very little contribution of its lone pair of electrons to the extended $\pi$ system. The 5-BP cycle is a relatively strongly basic ligand as is evident from the $\nu$(CO) stretching frequency (1965 cm$^{-1}$) of the corresponding Vaska-type rhodium complex. More interestingly, the binding of F$^-$ to the boron shifts the $\nu$(CO) to 1937 cm$^{-1}$, which is similar to the respective complex with the highly electron-rich alkyl phosphine PCy$_3$ complex at $\nu$(CO) of 1943 cm$^{-1}$.

6.4 Experimental Section

Reagents and General Methods. Me$_2$SnCl$_2$, PhBCl$_2$, $t$-BuPCl$_2$, BH$_3$ (1.0 M in THF), $t$-butyl lithium (1.7 M in hexanes), 1,4-diazabicyclo[2.2.2]octane (DABCO), di-$\mu$-chlorotetracarbonyldirhodium ([Rh(CO)$_2$Cl]$_2$) and tetra-$n$-butylammonium fluoride were purchased from Aldrich and used without further purification. PhPCl$_2$ was purchased
from Aldrich and distilled prior to use. Me$_2$SiCl$_2$ was purchased from Aldrich and distilled over CaH$_2$ prior to use. Lithium diisopropylamide (LDA) was freshly prepared by addition of $n$-butyl lithium (1.6 M in hexanes) to a THF solution of diisopropylamine at 0 °C. (pS)-1, and the Krossing salts$^{20}$ were prepared according to literature procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (MBraun). 499.9 MHz $^1$H NMR, 125.7 MHz $^{13}$C NMR, 160.4 MHz $^{11}$B NMR, 470.4 MHz $^{19}$F NMR, 99.3 MHz $^{29}$Si NMR, 202.4 MHz $^{31}$P NMR and 186.4 MHz $^{119}$Sn NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). $^1$H, $^{13}$C, $^{19}$F, $^{29}$Si, $^{31}$P and $^{119}$Sn NMR spectra were referenced internally to solvent signals. $^{11}$B NMR spectra were acquired with boron-free quartz NMR tubes and referenced to BF$_3$ · Et$_2$O ($\delta = 0$). The following abbreviations are used for signal assignments: Ph = phenyl, Fc = ferrocenyl, Cp = cyclopentadienyl. High resolution MALDI-MS data (benzo[$\alpha$]pyrene as matrix) were obtained in positive mode on an Apex Ultra 7.0 Hybrid FTMS (Bruker Daltonics). UV/Vis absorption data were acquired on a Varian Cary 500 UV/Vis/NIR spectrophotometer. Optical rotation analyses were performed on an Autopol III polarimeter, Rudolph Research Analytical, using a tungsten-halogen light source operating at $\lambda = 589$ nm. Chiral HPLC analyses were performed on a Waters Empower system equipped with a 717plus autosampler, a 1525 binary HPLC pump, and a 2998 photodiode array detector; a CHIRALPAK® IA-3 column was used for separation. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. IR Measurements were carried out on a Thermo
Nicolet 6700 spectrometer (Thermo Electron Corporation, Madison, WI, USA) of a 
\( \text{CH}_2\text{Cl}_2 \) solution by either transmission or ATR mode.

X-ray diffraction intensities were collected on a Bruker SMART APEX CCD 
Diffractometer using CuK\( \alpha \) (1.54178 Å) radiation at 100 K. The structures were refined 
by full-matrix least squares based on \( F^2 \) with all reflections (SHELXTL V5.10; G. 
Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with 
anisotropic displacement coefficients, and hydrogen atoms were treated as idealized 
contribution. SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens Area 
Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption 
correction was applied. Crystallographic data for the structures of 1-Sn, 2-SnSn, 2-SnSi, 
2-BSi, 3a-SnP, 3b-SnP, 4-BP and 5-BP will be deposited with the Cambridge 
Crystallographic Data Center as supplementary publications. Copies of the data can be 
obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, 
UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Synthesis of Fc(SOTol)(\( \mu \)-SnMe\( _2 \))Fc(SOTol). To a pre-cooled (-78 °C) solution of 
FcSOTol (4.00 g, 12.3 mmol) in THF (60 mL) was added a pre-made LDA solution (0.50 
M, 27.2 mL, 13.6 mmol, 1.10 equiv) dropwise and the mixture was kept stirring for 1 
hour. Me\( _2 \)SnCl\( _2 \) (1.63 g, 7.38 mmol, 0.60 equiv) in THF (10 mL) was added slowly. The 
reaction mixture was kept stirring at the same temperature for 1 hour and then allowed to
warm up overnight before quenching with water. The mixture was extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic layers were washed with brine and water, dried over sodium sulfate and concentrated. The residue was chromatographed on a silica column with THF/hexanes/triethyl amine (25: 75: 1) as the eluent. X-ray quality crystals were obtained by recrystallization in hot THF. Yield: 3.9 g (80 %). $[\alpha]_{20}^{20} \text{D} (c = 0.10, \text{CH}_2\text{Cl}_2) = -34^\circ$; $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.44 (d, $J = 8.0$ Hz, 4H; toyl), 7.10 (d, $J = 8.0$ Hz, 4H; toyl), 4.48 (nr, 2H; Cp), 4.39 (nr, 2H; Cp), 4.37 (nr, 2H; Cp), 4.29 (s, 10H; free Cp), 2.33 (s, 6H; Me), 0.80 (s/d, $^2J(^{117/119}\text{Sn},\text{H}) = 60$ Hz, 6H; SnMe$_2$). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta = 142.5$, 140.8, 129.3, 125.2 (tolyl), 97.6 (s/d, $^2J(^{117/119}\text{Sn},\text{C}) = 39$ Hz; ipso-Cp-S), 77.6 (s/d, $^2J(^{117/119}\text{Sn},\text{C}) = 41$ Hz, Cp), 73.2 (s/d, $^3J(^{117/119}\text{Sn},\text{C}) = 38$ Hz, Cp), 70.6 (ipso-Cp-Sn), 69.9 (free Cp), 69.0 (s/d, $^3J(^{117/119}\text{Sn},\text{C}) = 27$ Hz; Cp), 21.4 (Me), -3.8 (s/d, $^1J(^{117/119}\text{Sn},\text{C}) = 422/442$ Hz; SnMe$_2$). $^{119}$Sn NMR (186.4 MHz, C$_6$D$_6$, 25 °C) $\delta = -25.5$. Elemental analysis for C$_{36}$H$_{36}$Fe$_2$O$_2$S$_2$Sn, calcd C 54.38, H 4.56, found C 54.56, H 4.21

**Synthesis of Fc$_2$Sn$_2$Me$_4$.** A solution of Fc(SOTol)(µ-SnMe$_2$)Fc(SOTol) (100 mg, 0.126 mmol) in THF (10 mL) was cooled to -78 °C and a solution of $t$-butyl lithium in hexanes (0.155 mL, 0.264 mmol, 2.10 equiv) was added dropwise under stirring. The reaction mixture was kept stirring for 10 min at the same temperature and a solution of
Me₂SnCl₂ (0.029 g, 0.132 mmol, 1.05 equiv) in THF (1.5 mL) was added via syringe. The resulting solution was stirred for 1 h and the temperature was slowly raised to 25 °C. After addition of water the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with brine solution followed by water, dried over sodium sulfate and concentrated. The residue was subjected to silica gel column chromatography with hexanes/triethylamine (100:1) as the eluent to give the product as a red solid. Yield: 54 mg (65%). ¹H NMR (499.9 MHz, C₆D₆, 25 °C): δ = 4.51 (t, 2H, J = 2.5 Hz; Cp), 4.30 (d, 4H, J = 2.5 Hz; Cp), 3.99 (s, 10H; free Cp), 0.48 (s/d, J(¹¹⁷/¹¹⁹Sn,H) = 54/56 Hz, 12H; SnMe₂). ¹³C NMR (125.69 MHz, C₆D₆, 25 °C): δ = 77.1 (s/d, J(¹¹⁷/¹¹⁹Sn,C) = 513/535 Hz; ipso-Cp-Sn), 77.1 (s/d, 2/3 J(¹¹⁷/¹¹⁹Sn,C) = 46/63 Hz; Cp), 73.2 (s/d, 3 J(¹¹⁷/¹¹⁹Sn,C) = 40 Hz; Cp), 69.1 (free Cp), -6.5 (s/d, 1 J(¹¹⁷Sn,¹¹⁹Sn) = 350/366 Hz; SnMe₂). ¹¹⁹Sn NMR (186.4 MHz, C₆D₆, 25 °C) δ = -22.1 (s/d, 3 J(¹¹⁷Sn,¹¹⁹Sn) = 122 Hz). UV-Vis (CH₂Cl₂): λₘₐₓ = 460 (ε = 310 M⁻¹ cm⁻¹). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 650.8678 ([M-Me]⁺, 40%, calcd for ¹²C₂₃¹H₂₅⁵⁶Fe₂¹¹⁹Sn₂ 650.8702), 665.8913 ([M]⁺, 100%, calcd for ¹²C₂₄¹H₂₈⁵₆Fe₂¹¹⁹Sn₂ 665.8937).

**Synthesis of Fe₂SnMe₂SiMe₂.** A solution of Fe(SOTol)(μ-SnMe₂)Fc(SOTol) (400 mg, 0.504 mmol) in THF (40 mL) was cooled to -78 °C and a solution of t-butyllithium in hexanes (0.62 mL, 1.06 mmol, 2.10 equiv) was added dropwise under stirring. The
reaction mixture was kept stirring for 10 min at the same temperature and a solution of Me₂SiCl₂ (0.091 g, 0.706 mmol, 1.4 equiv) in THF (1.5 mL) was added via syringe. The resulting solution was stirred for 1 h and the temperature was slowly raised to 25 °C. After addition of water the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine solution followed by water, dried over sodium sulfate and concentrated. The residue was subjected to silica gel column chromatography with hexanes/triethylamine (100:1) as the eluent to give the product as a red solid. Recrystallization in hot methanol at -37 °C gave X-ray quality crystals. Yield: 179 mg (62%). [α]²₀° (c = 0.10, CH₂Cl₂) = -88° ; ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 4.55 (nr, 2H; Cp), 4.42 (nr, 2H; Cp), 4.36 (nr, 2H; Cp), 3.96 (s, 10H; free Cp), 0.52 (s/d, ²J¹¹⁷/¹¹⁹Sn,C) = 56 Hz, 6H; SnMe₂), 0.48 (s, 6H; SiMe₂). ¹³C NMR (125.69 MHz, C₆D₆, 25 °C): δ = 78.5 (ipso-Cp), 77.4 (s/d, ²J¹¹⁷/¹¹⁹Sn,C) = 59 Hz; Cp), 76.5 (ipso-Cp), 76.1 (s/d, ²J¹¹⁷/¹¹⁹Sn,C) = 43 Hz; Cp), 73.2 (s/d, ²J¹¹⁷/¹¹⁹Sn,C) = 41 Hz; Cp), 69.2 (free Cp), 2.3 (SiMe₂), -6.7 (s/d, ²J¹¹⁷/¹¹⁹Sn,C) = 349, 370 Hz; SnMe₂). ²⁰Si NMR (99.3 MHz, C₆D₆, 25 °C) δ = -6.4. ¹¹⁹Sn NMR (186.4 MHz, C₆D₆, 25 °C) δ = -24.3. UV-Vis (CH₂Cl₂) : λ_max = 461 (ε = 280 M⁻¹ cm⁻¹). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 575.9671 ([M]⁺, 100%, calcd for C₂₄H₂₈Si⁵⁶Fe²¹¹⁹Sn 575.9680).
**Synthesis of Fc₂SiMe₂Hg₂Cl₂.** A solution of Fc₂SiMe₂SnMe₂ (0.129 g, 0.224 mmol) in acetone (10 mL) was added into a solution of HgCl₂ (0.112 g, 0.448 mmol, 2.0 equiv) in acetone (10 ml). The mixture was stirred for 1 hour before adding it to water (50 mL). Upon addition, a yellow precipitate was formed, which was collected on a filter paper, washed with hexanes (10 mL) and dried under air flow. Yield: 185 mg (71%). ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 4.75 (nr, 2H; Cp), 4.54 (nr, 2H; Cp), 4.37 (nr, 2H; Cp), 4.23 (s, 10H; free Cp), 0.64 (s, 6H; SiMe₂). ¹³C NMR (125.69 MHz, C₆D₆, 25 °C): δ = 90.1 (ipso-Cp-Hg), 77.3 (Cp), 75.6 (ipso-Cp-Si), 75.5 (Cp), 73.6 (Cp), 68.8 (free Cp), 0.1 (SiMe₂). ²⁹Si NMR (99.3 MHz, C₆D₆, 25 °C) δ = -6.8.

**Synthesis of Fc₂SiMe₂BPh.** To a solution of Fc₂SiMe₂Hg₂Cl₂ (0.225 g, 0.250 mmol) in toluene (20 mL) was added a solution of PhBCl₂ (0.047 g, 0.300 mmol, 1.2 equiv) in toluene (2 mL) at -37 °C inside a glove box. The mixture was then heated to 90 °C overnight in a sealed flask. A grey solid formed, which was removed by filtration. The filtrate was concentrated, taken back up in hot hexanes and kept at -37 °C for recrystallization. Yield: 60 mg (47%). [α]²⁰D (c = 0.10, CH₂Cl₂) = -2122° ; ¹H NMR (499.9 MHz, CDCl₃, 25 °C): δ = 7.90 (m, 2H; o-Ph), 7.48 (m, 3H; m-Ph, p-Ph), 4.85 (pst, J = 2.0 Hz, 2H; Cp), 4.74 (nr, 2H; Cp), 4.61 (nr, 2H; Cp), 3.97 (s, 10H; free Cp), 0.46 (s, 6H; SiMe₂). ¹³C NMR (125.69 MHz, CDCl₃, 25 °C): δ = 132.6 (Ph), 128.2 (Ph), 127.3 (Ph), ipso-Ph-B not observed, 80.3 (ipso-Cp-B), 78.8 (Cp), 78.7 (Cp), 77.5 (ipso-Cp-Si), 77.1 (Cp), 69.5 (free Cp), 2.2 (SiMe₂). ¹¹B NMR (160.4 MHz, CDCl₃, 25 °C) δ = 53.9 (w₁/₂ = 750 Hz). ²⁹Si NMR (99.3 MHz, CDCl₃, 25 °C) δ = -9.4. UV-Vis (CH₂Cl₂): λₘₐₓ = 367 (ε = 5460 M⁻¹ cm⁻¹), 471 (ε = 7060 M⁻¹ cm⁻¹). High-resolution MALDI-MS (+
mode, benzo[α]pyrene): m/z 514.0683 ([M]+, 100%, calcd for $^{12}$C$_{28}^{1}$H$_{27}^{11}$BSi$_{56}$Fe$_{2}$ 514.0669).

**Synthesis of Fc$_2$SnMe$_2$P(BH$_3$)$_t$Bu.** A solution of Fc(SOTol)(µ-SnMe$_2$)Fc(SOTol) (0.500 g, 0.628 mmol) in THF (40 mL) was cooled to -78 °C and a solution of $t$-butyl lithium in hexanes (0.760 mL, 1.29 mmol, 2.05 equiv) was added dropwise under stirring. The reaction mixture was kept stirring for 10 min at the same temperature and a solution of $t$BuPCl$_2$ (0.105 g, 0.66 mmol, 1.05 equiv) in THF (5 mL) was added via syringe. After subsequent addition of a BH$_3$·THF solution (1.0 M, 0.75 ml, 1.2 equiv), the resulting solution was stirred for 1 h and the temperature was slowly raised to 25 °C. An aqueous NaHCO$_3$ solution was added and the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine solution followed by water, dried over sodium sulfate and concentrated. The residue was subjected to silica gel column chromatography with hexanes/triethylamine (100:1) as the eluent to give the product as a red solid. Recrystallization in hexanes at -37 °C gave X-ray quality crystals. Yield: 40 mg (10%). $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta$ = 5.11 (nr, 1H; Cp), 4.83 (nr, 1H; Cp), 4.79 (d, $J$ = 2.0 Hz, 1H; Cp), 4.58 (d, $J$ = 2.0 Hz, 1H; Cp), 4.54 (nr, 1H; Cp), 4.34 (nr, 1H; Cp), 4.26 (s, 5H; free Cp), 3.83 (s, 5H; free Cp), 1.35 (d, $J$ = 2.5 Hz, 9H, $t$-Bu), 1.0 (very br, 3H; BH$_3$), 0.60 (s/d, $^2J^{(117/119)Sn,H} = 58$ Hz, 3H; SnMe), 0.60 (s/d, $^2J^{(117/119)Sn,H} = 56$ Hz, 3H; SnMe). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta$ = 79.2 (d, $J$ = 20 Hz; Cp), 77.8 (d, $J$ = 18 Hz; Cp), 76.6 (d, $J$ = 5 Hz; ipso-Cp-Sn), 76.4 (overlapped d; ipso-Cp-P), 76.3 (d, $J$ = 7 Hz; Cp), 73.9 (d, 63 Hz; ipso-Cp-P), 73.5 (d, $J$ = 9 Hz; Cp), 72.3 (d, $J$ = 9 Hz; Cp) 71.8 (d, $J$ = 4 Hz; ipso-Cp-Sn), 70.2 (free Cp), 70.0
(free Cp), 30.8 (d, $^1J = 34$ Hz; tBu), 26.4 (d, $^2J = 3$ Hz; Cp), -3.5 (s/d, $^1J^{117/119}$Sn,C) = 377,390 Hz; SnMe), -6.8 (SnMe s/d, $^1J^{117/119}$Sn,C) = 377,395 Hz;), one Cp resonance not observed due to solvent signal overlap. $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta$ = -39.0 (m, $w_{1/2} = 400$ Hz). $^{31}$P{$^1$H} NMR (202.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 28.9. $^{119}$Sn{$^1$H} NMR (186.4 MHz, CDCl$_3$, 25 °C) $\delta$ = -28.0 (d, $^3J^{31}$P,$^{119}$Sn) = 5 Hz). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 548.9182 ([M-BH$_3$-tBu]$^+$, 100%, calcd for $^{12}$C$_{22}$$^{1}$H$_{22}$$^{31}$P$^{56}$Fe$^{120}$Sn 548.9179); m/z 605.9888 ([M-BH$_3$]$^+$, 1%, calcd for $^{12}$C$_{26}$$^{1}$$H$_{31}$$^{31}$P$^{56}$Fe$^{120}$Sn 605.9884).

Synthesis of Fe$_2$SnMe$_2$P(BH$_3$)Ph. A solution of Fc(SOTol)(µ-SnMe$_2$)Fc(SOTol) (1.60 g, 2.01 mmol) in THF (150 mL) was cooled to -78 °C and a solution of t-butyl lithium in hexanes (2.49 mL, 4.23 mmol, 2.10 equiv) was added dropwise under stirring. The reaction mixture was kept stirring for 10 min at the same temperature and a solution of PhPCl$_2$ (0.396 g, 2.21 mmol, 1.1 equiv) in THF (5 mL) was added via syringe. After subsequent addition of a BH$_3$-THF solution (1.0 M, 3.02 mL, 1.50 equiv), the resulting solution was stirred for 1 h and the temperature was slowly raised to 25 °C. All volatile components were removed under high vacuum. The residue was redisolved in CH$_2$Cl$_2$, an aqueous NaHCO$_3$ solution added and the aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine solution followed by water, dried over sodium sulfate and concentrated. The residue was subjected to aluminum oxide column chromatography with THF/hexanes/triethylamine (20:80:1) as the eluent to give the product as a red solid. Recrystallization in hexanes at -37 °C gave X-ray quality crystals. Yield: 510 mg (40%). $[\alpha]^{20}_D$ (c = 0.10, CH$_2$Cl$_2$) =
+206° ; $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta = 7.82$ (m, 2H; m-Ph), 7.41 (br, 3H; o-Ph, p-Ph), 5.20 (nr, 1H; Cp), 4.88 (nr, 1H; Cp), 4.66 (nr, 1H; Cp), 4.63 (d, $J = 2.0$ Hz, 1H; Cp), 4.52 (nr, 1H; Cp), 4.40 (nr, 1H; Cp), 3.92 (s, 5H; free Cp), 3.67 (s, 5H; free Cp), 1.2 (br, 3H, BH$_3$), 0.64 (s/d, $^2J^{(117/119}$Sn,H) = 58 Hz, 3H; SnMe), 0.60 (s/d, $^2J^{(117/119}$Sn,H) = 58 Hz, 3H; SnMe). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta = 136.4$ (d, $^1J = 56$ Hz; ipso-Ph-P), 132.0 (d, $J = 11$ Hz; o-Ph), 130.4 (br; p-Ph), 127.9 (d, $J = 9$ Hz; m-Ph), 79.9 (d, $^1J = 67$ Hz; ipso-Cp-P), 77.8 (d, $J = 7$ Hz; Cp), 76.4 (d, $J = 8$ Hz; Cp), 76.0 (d, $J = 8$ Hz; Cp), 73.8 (d, $J = 10$ Hz; Cp), 73.7 (d, $^1J = 75$ Hz; ipso-Cp-P), 73.7 (d, $J = 5$ Hz; ipso-Cp-Sn), 72.4 (d, $J = 5$ Hz; ipso-Cp-Sn), 71.7 (d, $J = 11$ Hz; Cp), 70.3 (free Cp), 69.2 (free Cp), −4.6 (s/d, $^1J^{(117/119}$Sn,C) = 370, 386 Hz; SnMe), −8.2 (s/d, $^1J^{(117/119}$Sn,C) = 377, 393 Hz; SnMe). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta = −38.6$ (w$_{1/2}$ = 350 Hz). $^{31}$P${}^1$H NMR (202.4 MHz, CDCl$_3$, 25 °C) $\delta = 10.3$ (m). $^{119}$Sn${}^1$H NMR (186.4 MHz, CDCl$_3$, 25 °C) $\delta = −26.9$ (d, $^3J^{(31}$P, $^{119}$Sn) = 10 Hz). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 625.9557 ([M-BH$_3$]$^+$, 1%, calcd for $^{12}$C$_{28}$H$_{27}$P$_{3}$Fe$_{2}^{120}$Sn 625.9572).

**Synthesis of Fe$_2$SnMe$_2$ClHgClP(BH$_3$)Ph.** A solution of Fe$_2$SnMe$_2$P(BH$_3$)Ph (0.120 g, 0.188 mmol) in acetone (3 mL) was added into a solution of HgCl$_2$ (0.051 g, 0.188 mmol, 1.0 equiv) in acetone (2 mL). The mixture was stirred for 1 hour before adding it to water (50 mL). Upon addition, a yellow precipitate formed, which was collected on a filter paper, washed with hexanes (10 mL), dried under high vacuum at 60 °C overnight and used in the next step without further purification. Fe$_2$SnMe$_2$ClHgClP(BH$_3$)Ph: Yield: 145 mg (85%). Purity: ca. 90% by $^1$H NMR. $^1$H NMR (499.9 MHz, CDCl$_3$, 25
°C): δ = 7.84 (pst, J = 9 Hz, 2H; m-Ph), 7.51 (m, 3H; o-Ph + p-Ph), 5.13 (nr, 1H; Cp), 4.85 (nr, 1H; Cp), 4.80 (nr, 1H; Cp), 4.79 (nr, 1H; Cp), 4.70 (nr, 1H; Cp), 4.32 (nr, 1H; Cp), 4.10 (s, 5H; free Cp), 3.84 (s, 5H; free Cp), 1.6 (br, 3H; BH3), 1.31 (s/d, \( ^2J(^{117/119}\text{Sn},\text{H}) = 67 \text{ Hz, 3H; SnMe} \)), 1.05 (s/d, \( ^2J(^{117/119}\text{Sn},\text{H}) = 62 \text{ Hz, 3H; SnMe} \)). \(^{11}\text{B} \) NMR (160.4 MHz, CDCl3, 25 °C) δ = -37.4 (m, \( w_{1/2} = 320 \text{ Hz} \)). \(^{31}\text{P} \{^1\text{H} \} \) NMR (202.4 MHz, CDCl3, 25 °C) \( \delta = 8.7 \) (m). \(^{119}\text{Sn} \{^1\text{H} \} \) NMR (186.4 MHz, CDCl3, 25 °C) δ = 65.6 (d, \( J = 30 \text{ Hz} \)).

**Synthesis of Fc\(_2\)BPhP(BH\(_3\))Ph.** To a solution of Fc\(_2\)SnMe\(_2\)ClHgClP(BH\(_3\))Ph (0.145 g, 0.159 mmol) in toluene (10 mL) was added a solution of PhBCl\(_2\) (0.028 mg, 0.175 mmol, 1.2 equiv) in toluene (2 mL) at -37 °C inside a glove box. The mixture was stirred at room temperature for 2 days before heated to 90 °C overnight in a sealed flask. A grey solid formed, which was removed by filtration. The filtrate was concentrated and then subjected to silica gel column chromatography using THF/hexanes/triethylamine (20:80:1) as eluent. The product was obtained as an analytically pure red solid by recrystallization in hot hexanes. Fc\(_2\)BPhP(BH\(_3\))Ph: Yield: 45 mg (49%). \([\alpha]^{20}_D \) (c = 0.10, CH\(_2\)Cl\(_2\)) = -1484°). \(^1\text{H} \) NMR (499.9 MHz, CDCl\(_3\), 25 °C): δ = 8.00 (br, 2H; Ph), 7.62 (br, 2H; Ph), 7.52 (br, 3H; Ph), 7.44 (br, 3H; Ph), 5.21 (nr, 1H; Cp), 5.09 (nr, 1H; Cp), 5.0 (nr, 1H; Cp), 4.90 (nr, 1H; Cp), 4.80 (nr, 2H; Cp), 4.22 (s, 5H; free Cp), 3.38 (s, 5H; free Cp), 1.2 (br, 3H; BH3). \(^{13}\text{C} \) NMR (125.69 MHz, CDCl\(_3\), 25 °C): δ = 142.2 (ipso-Ph-B), 137.1 (d, \( J = 54 \text{ Hz; ipso-Ph-P} \)), 132.7 (BPh), 131.2 (d, \( J = 10 \text{ Hz; PPh} \)), 130.4 (br; PPh), 129.1 (BPh), 128.1 (d, \( J = 10 \text{ Hz; PPh} \)), 127.9 (BPh), 79.7 (d, \( ^2J = 16 \text{ Hz; Cp} \)), 79.1 (d, \( ^3J = 5 \text{ Hz; Cp} \)) 78.3 (d, \( ^1J = 62 \text{ Hz; ipso-Cp-P} \)), 78.2 (d, \( ^3J = 10 \text{ Hz; Cp} \)), 76.5 (d, \( ^3J = 8 \text{ Hz; Cp} \)), 76.2 (d, \( ^2J = 18 \text{ Hz; Cp} \)), 73.3 (d, \( J = 74 \text{ Hz; ipso-Cp-P} \)), 71.8 (free Cp), 70.2 (free
Cp), ipso-Cp-B and one of the Cp resonance not observed due to solvent signal overlap.

$^{11}$B NMR (160.4 MHz, CDCl$_3$, 25°C) $\delta$ = 52.1 ($w_{1/2} = 800$ Hz), -35.2 ($w_{1/2} = 400$ Hz).

$^{31}$P$_{1}{^1}$H} NMR (202.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 11.2. High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 564.0575 ([M-BH$_3$]$^+$, 100%, calcd for $^{12}$C$_{32}$$^1$H$_{26}$$^{11}$B$^{31}$P$^{56}$Fe$_2$ 564.0565).

**Synthesis of Fe$_2$BPhPPh** To a CDCl$_3$ (0.7 mL) solution of Fe$_2$BPhP(BH$_3$)Ph (35.0 mg, 0.061 mmol) was added an equimolar amount of DABCO (7.47 mg, 0.067 mmol) at room temperature. The solution was transferred into a J. Young’s NMR tube and heated to 50 °C. $^1$H NMR data confirmed the full conversion to product after 2 days. The reaction mixture was subjected to a short aluminium oxide column with THF/hexanes (1:4) as eluent. Yield: 30 mg (88%). $^1$H NMR (499.9 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.95 (m, 2H; Ph), 7.51 (m, 3H; Ph), 7.44 (t, $J = 7$ Hz, 2H; Ph), 7.38 (t, $J = 7$ Hz, 2H, Ph), 7.34 (t, $J = 7$ Hz, 1H; Ph), 5.07 (nr, 1H; Cp), 4.92 (nr, 1H; Cp), 4.74 (nr, 1H; Cp), 4.71 (nr, 1H; Cp), 4.70 (nr, 2H; Cp), 4.62 (nr, 1H; Cp), 4.02 (s, 5H; free Cp), 3.42 (s, 5H; free Cp). $^{13}$C NMR (125.69 MHz, CDCl$_3$, 25 °C): $\delta$ = 144.2 (d, $J = 23$ Hz; ipso-Ph-P), 143.1 (ipso-Ph-B), 132.8 (Ph), 131.1 (d, $J = 18$ Hz; Ph), 128.7 (Ph), 127.9 (br, 2 signals overlapping; Ph), 127.6 (Ph), 88.0 (ipso-Cp-B), 80.1 (d, $J = 26$ Hz; Cp), 79.0 (Cp), 75.5(Cp), 75.4 (d, $J = 23$ Hz; Cp), 70.9 (free Cp), 70.0 (free Cp). $^{11}$B NMR (160.4 MHz, CDCl$_3$, 25 °C) $\delta$ = 53.0 ($w_{1/2} = 1000$ Hz). $^{31}$P$_{1}{^1}$H} NMR (202.4 MHz, CDCl$_3$, 25 °C) $\delta$ = -24.9. High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 564.0575 ([M]$^+$, 100%, calcd for $^{12}$C$_{32}$$^1$H$_{26}$$^{11}$B$^{31}$P$^{56}$Fe$_2$ 564.0565).

**Synthesis of (Fe$_2$BPhPPh)$_2$Rh(CO)Cl.** To a solution of Fe$_2$BPhPPh (10 mg, 0.018 mmol) in CD$_2$Cl$_2$ (0.7 mL) was added di-μ-chloro-tetracarbonyldirhodium (1.72 mg,
0.0044 mmol, 0.25 equiv). \(^1\)H NMR measurement indicated full conversion. All volatile components were removed under high vacuum. Analytically pure compound was obtained by slow diffusion of hexanes vapor into an acetone solution of the crude product. Yield: 11 mg (92%). \(^1\)H NMR (499.9 MHz, CDCl\(_3\), 25 °C): \(\delta = 8.00\) (d, \(J = 7\) Hz, 4H; Ph), 7.69 (nr, 4H; Ph), 7.54 (m, 6H; Ph), 7.41 (m, 6H; Ph), 5.94 (nr, 4H; Cp), 5.05 (nr, 4H; Cp), 5.04 (nr, 4H; Cp), 4.82 (nr, 4H; Cp), 4.81 (nr, 4H; Cp), 4.72 (s, 4H; free Cp), 4.43 (s, 10H; free Cp), 3.37 (s, 10H; free Cp). \(^1^3\)C NMR (125.69 MHz, CD\(_2\)Cl\(_2\), 25 °C): \(\delta = 144.5\) (br, ipso-Ph-B), 142.3 (t, \(J = 21\) Hz; ipso-Ph-P), 134.7 (BPh), 133.7 (t, \(J = 6\) Hz; PPh), 131.0 (BPh), 130.7 (PPh), 129.6 (BPh), 129.5 (t, \(J = 5\) Hz; PPh), 86.8 (t, \(J = 26\) Hz; ipso-Cp-P), 84.7 (t, \(J = 8\) Hz; Cp), 80.4 (Cp), 80.2 (t, \(J = 5\) Hz; Cp), 80.0 (t, \(J = 10\) Hz; Cp), 78.5 (br; ipso-Cp-B), 78.1 (t, \(J = 5\) Hz; Cp), 78.0 (t, \(J = 3\) Hz; Cp), 77.5 (t, \(J = 28\) Hz; ipso-Cp-P), 73.9 (free Cp), 72.3 (free Cp), one of the ipso-Cp-B is not observed. \(^{11}\)B NMR (160.4 MHz, CD\(_2\)Cl\(_2\), 25 °C) \(\delta = 52.2\) (w\(_{1/2} = 2800\) Hz). \(^{31}\)P{\(^1\)H} NMR (202.4 MHz, CD\(_2\)Cl\(_2\), 25 °C) \(\delta = 7.61\) (d, \(2J(\text{Rh},\text{P}) = 121\) Hz). High-resolution MALDI-MS (+ mode, benzo[\(\alpha\])pyrene): m/z 1231.0218 ([M-CO-Cl]\(^+\), 20%, caled for \(^{12}\)C\(_{64}\)\(^{1}\)H\(_{52}\)\(^{11}\)B\(_2\)\(^{31}\)P\(_2\)\(^{56}\)Fe\(_4\)\(^{103}\)Rh 1231.0203) 1110.0461 ([M-CO-Cl-FeCp]\(^+\), 100%, caled for \(^{12}\)C\(_{59}\)\(^{1}\)H\(_{47}\)\(^{11}\)B\(_2\)\(^{31}\)P\(_2\)\(^{56}\)Fe\(_3\)\(^{103}\)Rh 1110.0459).

**NMR Scale Reactions:**

**Synthesis of Fc\(_2\)BPhP(O)Ph.** A solution of Fc\(_2\)BPhPPh in CDCl\(_3\) was exposed to air and stirred for one hour. \(^1\)H NMR showed full conversion to the oxidized product. \(^1\)H NMR (499.9 MHz, CDCl\(_3\), 25 °C): \(\delta = 7.94\) (br, 2H; BPh), 7.83 (br m, 2H; PPh), 7.53 (br, 3H; Ph), 7.49 (br, 3H; Ph), 5.24 (nr, 1H; Cp), 5.16 (nr, 1H; Cp), 5.07 (nr, 1H; Cp),
4.93 (nr, 1H; Cp), 4.81 (nr, 1H; Cp), 4.72 (nr, 1H; Cp), 4.28 (s, 5H; free Cp), 3.48 (s, 5H; free Cp). \(^{11}\)B NMR (160.4 MHz, CDCl₃, 25 °C) \(\delta = 51.7 \) (\(w_{1/2} = 1000 \) Hz). \(^{31}\)P NMR (202.4 MHz, CDCl₃, 25 °C) \(\delta = 29.0\). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 580.0526 ([M]⁺, 100%, calcd for \(^{12}\)C\(_{32}\)^{1}H\(_{26}\)^{11}\(^{11}\)B\(^{31}\)P\(^{32}\)O\(^{56}\)Fe\(^{2}\) 580.0514)

**Synthesis of Fe₂BPhPPhAuCl.** To a solution of Fe₂BPhPPh (5 mg) in CDCl₃ (0.7 mL) was added an equimolar amount of (tht)AuCl. The mixture was stirred for 0.5 h inside the glovebox. All volatile components were removed under high vacuum. The residue was redissolved in 0.7 mL of CDCl₃ for NMR measurements. \(^{1}\)H NMR (499.9 MHz, CDCl₃, 25 °C): \(\delta = 7.94 \) (br, 2H; BPh), 7.54 (br, 3H; Ph), 7.49 (br, 3H; Ph), 5.26 (nr, 1H; Cp), 5.13 (nr, 1H; Cp), 4.94 (nr, 1H; Cp), 4.92 (nr, 1H; Cp), 4.84 (nr, 2H; Cp), 4.24 (s, 5H; free Cp), 3.44 (s, 5H; free Cp). \(^{11}\)B NMR (160.4 MHz, CDCl₃, 25 °C) \(\delta = 50.8 \) (\(w_{1/2} = 1000 \) Hz), -6.6 (\(w_{1/2} = 160 \) Hz). \(^{31}\)P NMR (202.4 MHz, CDCl₃, 25 °C) \(\delta = 12.9\). High-resolution MALDI-MS (+ mode, benzo[α]pyrene): m/z 795.9951 ([M]⁺, 100%, calcd for \(^{12}\)C\(_{32}\)^{1}H\(_{26}\)^{11}\(^{11}\)B\(^{31}\)P\(^{35}\)Cl\(^{56}\)Fe\(^{2}\)Au 795.9920)
6.5 Supporting Information

Figure 6-13a. $^1$H NMR spectrum of 3b-SnP in CDCl$_3$.

Figure 6-13b. $^1$H NMR spectrum of 4-BP in CDCl$_3$.

Figure 6-13c. $^1$H NMR spectrum of 5-BP in CDCl$_3$. 
Figure 6-13d. $^1$H NMR spectrum of (5-BP)$_2$Rh(CO)Cl in CD$_2$Cl$_2$

Figure 6-13e. $^1$H NMR spectrum of oxidized 4-BP in CDCl$_3$

Figure 6-13f. $^1$H NMR spectrum of 4-BP + Au(tht)Cl in CDCl$_3$
Figure 6-13g. $^1$H NMR spectrum of doubly oxidized 2-BSi cycle in CD$_2$Cl$_2$
Figure 6-14. UV/Vis absorption spectra of cycles 2-SnSn (red), 2-SnSi (blue) and 2-BSi (black) in CH$_2$Cl$_2$. 
Figure 6-15. Maldi-MS data of compounds 2-SnSn and 2-SnSi.
Figure 6-16. Maldi-MS data of compound 3b-SnP.

Figure 6-17. Maldi-MS data of compound 3a-SnP.
Figure 6-18. Maldi-MS data of compound 4-BP.
Figure 6-19. Ortep plot of 1-Sn (50% thermal ellipsoids); H atoms are omitted. Selected distances (Å) and angles (°): Sn1-C22 2.133(4), Sn-C1 2.136(4), Sn1-C21 2.144(4), Sn1-C11 2.169(4), S1-O1 1.499(3), S1-C2 1.769(4), S2-O2 1.501(3), S2-C12 1.758(3), C1-Sn1-C11 104.47(14)
Figure 6-20a. During the refinement of the structure for 2-SnSi, another set of Q peaks, representing the possible orientation of the disordered diferrocene unit, could be found (dashed line, all hydrogens and methyl carbons are omitted for clarity). However, the disorder was not modeled. Constraints such as ISOR and DELU were used to compensate this issue.

Figure 6-20b. Supramolecular structure of 2-SnSi.
Figure 6-20c. Supramolecular structure of 2-BSi.

Figure 6-21a. Chiral HPLC trace and the corresponding UV-Vis spectrum of 2-SnSi using hexanes/THF (98:2) as eluent.
Figure 6-21b. Chiral HPLC trace and the corresponding UV-Vis spectrum of 2-BSi using hexanes/THF (98:2) as eluent

Figure 6-21c. Chiral HPLC trace and the corresponding UV-Vis spectrum of 3a-SnP using hexanes/THF (90:10) as eluent

Figure 6-21d. Chiral HPLC trace and the corresponding UV-Vis spectrum of 3b-SnP using hexanes/THF (90:10) as eluent
6.6 Notes and References


Overall Conclusions

We developed a general synthetic method which led to a variety of fluorinated acidic boranes such as 1-Pf and 2-Pf via a series of organometallic substitution reactions in Chapter 2. The structures were confirmed by single-crystal X-ray diffraction and the steric effect around the boron center was examined by variable temperature $^{19}$F NMR spectroscopy, suggesting that the naphthylferrocene framework provides a rigid chiral environment for the borane moiety. In related work we pursued the corresponding boronic acid derivative.

In Chapter 3 and 4, we prepared enantiomerically pure lutidylferrocene derivatives by Negishi coupling and subsequent transmetallation reactions. A new stereoselective borylation procedure was introduced by using different transmetallation methods (Sn-B and Hg-B metathesis, respectively) to generate both planar chiral enantiomers from just one enantiomer of the precursor. The ipso-substitution of the mercuriated precursor proceeds as expected. However, the observed directed borylation with chiral inversion in the tin-boron exchange process is unusual and a detailed mechanistic study indicated the formation of a Lewis acid-base complex in the first step and then possibly a reactive borenium cation as an intermediate. The enantiomeric excess for the chiral inversion process is more than 90% by chiral HPLC analysis. The mechanistic studies support the involvement of a borenium cation intermediate as strong electrophile that attacks the ortho position of the substituted Cp ring. With the aim to construct the planar chiral FLPs as asymmetric catalysts, electron-deficient pentafluorophenyl (Pf) and bulky mesityl (Mes) groups were introduced to tune the Lewis acidity and steric hindrance at the boron
(4-Mes and 5-Pf). Despite the steric effect a strong B-N bond formed, which is intact even under strongly acidic conditions. A bulky TMS group was then incorporated in the ortho position of the pyridine ring to further increase the steric congestion and thus to weaken the B-N interaction (5-Pf and 5-Mes). 5-Pf formed a labile B-N bond which opened at elevated temperature and activated a water molecule to generate a ring-opened pyridinium borate. In contrast, 5-Mes adopted an open conformation in which the entire pyridyl group was flipped to release steric repulsion.

In Chapter 5, we described the synthesis and catalytic application of a novel planar chiral borenium cation (pR)-3+. A competition study showed that its Lewis acidity is almost as strong as that of the widely used tris(pentafluorophenyl)borane and its affinity towards anions such as Cl⁻ is even stronger. The borenium species can not only bind to Lewis basic substrates such as ketones and THF, but also activate the Si-H bond of silanes such as Et₃SiH. Finally, this unique Lewis acid was tested as a catalyst for the hydrosilylation of ketones with excellent conversion but moderate enantiomeric excess. Further work on optimizing the electronic and steric properties of this novel family of borenium cations is expected to improve the stereo-selectivity.

Last but not least, we established a practical protocol for the synthesis of a number of hetero-atom linked diferrocenes, ranging from group 13 to group 15 elements such as boron, silicon, tin and phosphorus. While the compounds with tricoordinate boron feature a trigonal fragment in the bridge, the others adopt tetrahedral configurations. The successful introduction of planar chirality was supported by single-crystal X-ray crystallography, chiral HPLC and optical rotation measurements. Electrochemical studies reveal that the cycles 2-SnSn, 2-SnSi and 2-BSi undergo 2-step reversible oxidations for
the Fc units. The introduction of boron results in anodic shifts for both of the potentials. For the most interesting system, 5-BP, the 1st quasi-reversible process suggests the possibility to serve as a redox responsive ligand. In the solid state structure of 5-BP, the tricoordinate phosphorus adopts a pyramidal conformation, indicating very little contribution of its lone pair of electrons to the extended π system. The 5-BP cycle is a relatively strongly basic ligand as is evident from the ν(CO) stretching frequency (1965 cm⁻¹) of the corresponding Vaska-type rhodium complex. More interestingly, the binding of F⁻ to the boron shifts the ν(CO) to 1937 cm⁻¹, which is similar to the respective complex with the highly electron-rich alkyl phosphine PCy₃ complex at ν(CO) of 1943 cm⁻¹.

In conclusion, we have established a practical protocol towards the synthesis of multifunctional planar chiral systems, including Lewis acids, Lewis pairs and ambiphilic ligands. We have already shown our preliminarily studies on the hydrosilylation of ketones using the highly Lewis acidic borenium cation derivative. The future efforts on these projects will focus on fine-tuning the steric and electronic effects of this class of catalysts for higher stability and better stereoselectivity. It would be interesting to introduce our chiral Lewis acids and Lewis pairs to the area of FLP chemistry. Moreover, for the ambiphilic species 5-BP, we expect to trigger the change of the electron donating property by oxidation of the biferrocene backbone and anion binding to the boryl moiety. One interesting aspect would be applying 5-BP as a responsive ligand to stereoselective transition metal-catalyzed reactions (e.g., rhodium-catalyzed asymmetric hydrogenation).
List of Publications

1. "Planar Chiral Organoborane Lewis Acids Derived from Naphthylferrocene"
2. "Reversible Formation of a Planar Chiral Ferrocenylboroxine and its Supramolecular Structure"
3. "Synthesis and Supramolecular Assembly of the Bifunctional Borinic Acid [1,2-fcB(OH)]_2"
4. "Synthesis and Lewis acid properties of a ferrocene-based planar-chiral borenium cation"
5. "Stereoselective Ortho Borylation of Pyridylferrocenes"
6. “Organoborane Lewis Pairs Derived from Pyridylferrocene”
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