OPTOELECTRONIC PROPERTIES AND PHOTOCHEMICAL REACTIVITY OF ORGANOBORON COMPOUNDS

by

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Dedicated to my Grandma.
Abstract

This thesis focuses on the investigation of the optoelectronic, photo and thermal-responsive properties of organoboron compounds. In search of blue phosphors for phosphorescent organic light emitting diodes, new triarylboron functionalized phosphorescent Pt(II) complexes were synthesized and their device performances were evaluated. In Pt(II) complexes with the 2-phenylpyridyl N,C-chelate ligand and an acetylacetonato ancillary ligand, it was found that BMes₂ substitution at the 4’ position of the phenyl ring can increase the phosphorescent emission energy, compared to the 5’-BMes₂ substituted analogue. This occurred without substantial loss of luminescent quantum efficiency. At 100 cd/m² luminance, electroluminescence devices with the newly synthesized Pt(II) complexes as emitters have achieved external quantum efficiency of ~ 4.7-13.4%.

Tuning of the photo-responsive properties of biaryl N,C-chelate dimesitylboron compounds was achieved by functionalization with either a bisthienyl moiety or ferrocene unit. It was demonstrated that the bisthienyl unit has the ability to completely stabilize a N,C-chelate boryl chromophore toward photoisomerization. With the ferrocene unit being part of the chelation backbone of BMes₂ moiety, the B–N bond of molecule B(2-ferrocenyl-N-Me-benzimidazolyl)Mes₂ was found to undergo a dynamic dissociation/association process in solution, leading to its slow hydrolysis under ambient conditions. The oxidized ferrocenium species has a notable spin delocalization through space from the Fe(III) center to a flanking mesityl group.

To further expand the photochromic family based on pyridyl N,C-chelate dimesitylboron compounds, a systematic study was carried out with the pyridyl N donor replaced by N-heterocyclic carbene donor and azolyl, benzoazolyl N donors. These new classes of organoboranes all underwent transformation to their corresponding dark isomer in a similar fashion as the pyridyl N,C-chelate dimesitylboron. However, a second-step photoisomerization
was observed in the NHC,C-chelate dark isomer via a “borylene”-like intermediate. The thiazolyl, benzoazolyl N,C-chelate dark isomers demonstrate multi-structural transformations, which include hydrogen atom transfer, 1,3-boryl shift and diastereomer interconversion via a spiropyran type ring-opening/closure process. The imidazolyl N,C-chelate dark isomer exhibits a consecutive photochromism phenomenon, namely an interconversion between azaboratabisnorcaradiene and azabenzotropilidene derivatives. The calculated mechanism for this bares an interesting resemblance to that of the “walk” rearrangement in norcaradiene.
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Statement of Originality

I hereby certify that all of the work described within this thesis is the original work of the author under the supervision of Prof. Suning Wang, with the following exceptions:

**Chapter 2:** The synthesis of compounds 2.1 and 2.2 was carried out by Prof. Youngjin Kang from Kangwon National University, South Korea, during his visit at Queen’s University in 2011-2012. The synthesis of compound 2.4 was carried out with the assistance from Dylan Schoenmakers. Electroluminescent devices were fabricated and tested by Yi-Lu Chang at the University of Toronto in the laboratory of Prof. Zheng-Hong Lu.

**Chapter 4:** EPR data of compound 4.3 was obtained by Prof. Tetsuro Kusamoto in the Department of Chemistry at the University of Tokyo, Japan.

**Chapter 5:** The DFT calculations for compounds 5.1/5.2, 5.1a/5.2a and 5.1b/5.2b were performed by Leanne D. Chen under the supervision of Prof. Nicholas J. Mosey.

**Chapter 6:** The DFT calculations for compounds 6.1a, 6.1b and 6.1c were also performed by Leanne D. Chen.

Any published (or unpublished) ideas and/or techniques from the work of others are fully acknowledged in accordance with the standard referencing practices.

(Yingli Rao)

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<th>Definition</th>
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<tr>
<td>°</td>
<td>degrees</td>
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<tr>
<td>°C</td>
<td>degrees Celsius</td>
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<td>chemical shift</td>
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<tr>
<td>λ</td>
<td>wavelength</td>
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<tr>
<td>μs</td>
<td>microsecond</td>
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<tr>
<td>τ</td>
<td>decay lifetime</td>
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<tr>
<td>Φ</td>
<td>quantum efficiency</td>
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<td>Ω</td>
<td>ohms</td>
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<td>angstrom</td>
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<td>A</td>
<td>absorbance</td>
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<td>=</td>
<td>double bond; equal to</td>
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<tr>
<td>acac</td>
<td>acetylacetonate</td>
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<tr>
<td>Alq$_3$</td>
<td>tris(8-hydroxyquinolate)aluminum (III)</td>
</tr>
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<td>Anal. Calcd</td>
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<td>a.u.</td>
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<td>br</td>
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<tr>
<td>CBP</td>
<td>4,4'-N,N'-dicarbazolebiphenyl</td>
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<tr>
<td>cd</td>
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<td>CE</td>
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<td>CIE</td>
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<td>COSY</td>
<td>correlation spectroscopy</td>
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<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
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<tr>
<td>CT</td>
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<td>d</td>
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<tr>
<td>DCM</td>
<td>dichloromethane</td>
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<td>-------------</td>
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<tr>
<td>DFT</td>
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</tr>
<tr>
<td>DMF</td>
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<td>DTE</td>
<td>dithienylethene</td>
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<tr>
<td>$E_{1/2}^{\text{ox}}$</td>
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<td>EL</td>
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<td>EML</td>
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<td>EPR</td>
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<td>ethyl</td>
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<td>electron transport layer</td>
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<td>EXSY</td>
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<tr>
<td>HMBC</td>
<td>heteronuclear multiple-bond correlation spectroscopy</td>
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<td>heteronuclear multi-quantum correlation spectroscopy</td>
</tr>
<tr>
<td>HSQC</td>
<td>heteronuclear single-quantum correlation spectroscopy</td>
</tr>
<tr>
<td>I</td>
<td>intensity</td>
</tr>
<tr>
<td>IC</td>
<td>internal conversion</td>
</tr>
<tr>
<td>IMe</td>
<td>1,3-bis-methylimidazol-2-ylidene</td>
</tr>
<tr>
<td>ISC</td>
<td>intersystem crossing</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>hv</td>
<td>light</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>high-resolution mass spectrometry</td>
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<tr>
<td>HTL</td>
<td>hole transport layer</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>$J$</td>
<td>coupling constant</td>
</tr>
<tr>
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<td>Kelvin</td>
</tr>
<tr>
<td>kJ</td>
<td>kilojoules</td>
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<tr>
<td>$k_{nr}$</td>
<td>rate of nonradiative decay</td>
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<tr>
<td>$k_r$</td>
<td>rate of radiative decay</td>
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Chapter 1

Introduction

Organoboranes are attracting tremendous research interest in an effort to exploit their remarkable photochemical and optoelectronic properties\textsuperscript{1,2} as well as their capacity to act as Lewis acid catalysts,\textsuperscript{3} small molecule activators,\textsuperscript{4} and anion sensors.\textsuperscript{5,6}

This chapter starts with an introduction of the concepts of photophysical and photochemical processes, followed by a review of applications of organoboranes in optoelectronics. This is followed by a review of the literature on the photoreactions of organoboranes and recent research progress regarding the photochromic organoboranes will be presented.

1.1 Photophysical Processes

Molecular photophysics refers to the series of radiative and radiationless processes (Figure 1.1) that occur within molecules following light excitation to an excited state and returning back to the ground state. The molecule remains in the same ground state geometry as that before light irradiation. Molecular absorption (process 1) in the UV-Vis electromagnetic radiation region results in the change of electronic states with the same spin multiplicity, rather than to a higher vibrational state in a same electronic state. Following light absorption, the excess energy can be dissipated radiatively as fluorescence (process 6) returning to ground state, or quickly go through an isoenergetic radiationless transition, which often results in a vibrationally excited molecular entity in the lower electronic state. When the spin multiplicity remains the same, it is defined as internal conversion (process 2). When the spin multiplicity changes, it is defined as intersystem crossing, which can be either from singlet to triplet (process 3) or triplet to singlet crossing.
(process 4). Since singlet-triplet transitions are spin-forbidden via light excitation, triplet excited states can be populated only via intersystem crossing from the singlet-excited states.

**Figure 1.1** Jablonski energy diagram.

(Reproduced from “Photochemistry of Organic Compounds: From concepts to Practice” Petr Klán and Jakob Wirz Copyright © 2009 P. Klán and J. Wirz)

**Table 1-1** Summary of photophysical processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Name</th>
<th>Time scale (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Absorption</td>
<td>$10^{-15}$</td>
</tr>
<tr>
<td>2</td>
<td>Internal conversion</td>
<td>$10^{-12} - 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>Intersystem crossing (S - T)</td>
<td>$10^{-12} - 10^{-6}$</td>
</tr>
<tr>
<td>4</td>
<td>Intersystem crossing (T - S)</td>
<td>$10^{-9} - 10^{1}$</td>
</tr>
<tr>
<td>5</td>
<td>Vibrational relaxation</td>
<td>$10^{-13} - 10^{-12}$</td>
</tr>
<tr>
<td>6</td>
<td>Fluorescence</td>
<td>$10^{-9} - 10^{-7}$</td>
</tr>
<tr>
<td>7</td>
<td>Phosphorescence</td>
<td>$10^{-6} - 10^{0}$</td>
</tr>
</tbody>
</table>
Vibrational relaxation, or vibrational cooling (process 5) is a very fast radiationless process ($10^{-13} - 10^{-12}$ s), which refers to the deactivation of the molecular entity from its vibrationally excited state to the lowest vibrational level within the same electronic state. It primarily occurs when molecules collide with each other to dissipate the excited state energy.

Besides fluorescence, phosphorescence (process 7) is another form of radiative decay, which is typically from the first excited triplet state to the ground state and requires a change in the spin multiplicity. The lifetime of phosphorescence can range from microseconds to seconds, which is much longer than the fluorescence lifetime.

1.2 Photochemical Processes

Photochemistry is the study of chemical reactions (bond breaking or isomerization) that proceed with the absorption of light by molecules. After light absorption, a molecule can undergo radiative and radiationless processes back to the ground state. Radiative processes include the emission of photons, i.e. fluorescence, phosphorescence. Radiationless processes are those which consist of two types: photophysical and photochemical. Photochemical radiationless processes refer to the situation in which molecules undergo chemical reactions (bond breaking or isomerization) and return to the ground state with different structures. In the excited states, photochemical and photophysical processes are competitive pathways (Figure 1.1), thus the photophysical lifetimes listed in Table 1-1 are of paramount importance.

Photochemistry can be characterized by the point along the reaction coordinate from which the molecule transitions from the excited potential energy surface to the product ground state. There are four main categories: (a) hot ground state reaction; (b) adiabatic reaction; (c) diabatic reaction; (d) reaction via intermediate. A schematic presentation is shown in Figure 1.2.
Figure 1.2 Two-dimensional cross-sections of an excited-state and a ground-state potential energy surface along a reaction coordinate leading from reactant A to product B in four different classes of photoreactions.

(a) Hot ground state reaction. As shown in Figure 1.1, upon excitation, the molecule can go through intersystem crossing to be vibrationally excited in the electronic ground state. However, vibrational relaxation occurs within a few picoseconds in solution, formation of product B with different coordinates cannot compete with the vibrational cooling to A with same coordinates. Thus, hot ground state reactions are more likely to occur in gaseous molecules at low pressure and low temperature.

(b) Adiabatic reaction. The molecule forms the excited state of product B along the excited state potential energy surface before returning to the product’s ground state. Most adiabatic reactions occur through triplet excited state, in which the competing photophysical processes are relatively slow, allowing the molecule to overcome the excited triplet state barrier. Adiabatic reactions occurring through singlet excited state are usually associated with only minor structural changes with very low barrier, such as valence isomerization, geometric isomerization and hydrogen or proton transfer.
(c) Diabatic reactions. The photochemical process proceeds directly from the excited state to the ground state at the point where the two energy surfaces cross geometrically.

(d) Reactions via intermediates. This photochemical process involves the formation of intermediates, which are reactive, but with low-lying excited states. Commonly observed intermediates include carbenes, diradicals and zwitterions.

Photochromism is a subdivision of photochemistry. Photochromic compounds are defined as molecules that are capable of undergoing a reversible transformation between two structural forms with a distinct color change when excited at least in one pathway by light. Because of the rapid and often instant change of the physical and electronic properties such as color, luminescence, conductivity, refractive index, etc., photochromic materials have potential applications in optical memory devices, molecular switches, smart windows, ophthalmic glasses, etc. Many examples of organic photochromic compounds have been extensively investigated including fulgide, azobenzenes, diarylethenes (DTEs), spiropyans, etc.

1.3 The Performance of Organoboranes in Optoelectronics

Metal-oxide semiconductors, such as transistors, light emitting diodes, have greatly benefited our daily lives in the past half-century. Compared to their inorganic counterparts, electronic materials based on organic compounds are much cheaper, more environmentally friendly and have greater flexibility. The \( \pi \)-conjugated electrons in organic compounds are the primary functioning units. Incorporation of main group elements into the \( \pi \)-conjugated framework has proven to be an effective way to tune the electronic properties.

Organoboranes are defined as organic molecules incorporating a boron atom into the carbon skeleton. With a boron atom embedded in the carbon \( \pi \) conjugated skeleton, organoboron
compounds have demonstrated unique photophysical properties compared to their counterparts with a full carbon skeleton. Organoboranes have been widely utilized as luminescent, hole/electron transporting, host materials in the optoelectronics area.

This section begins with a brief introduction about the structure of OLEDs and their working principles, and is followed by a discussion of why organoboranes are suitable for use in this area.

1.3.1 Organic Light Emitting Diodes

Luminescence is the energy release in the form of photons. Molecules can be excited to a higher energy electronic state upon light irradiation, chemical reaction, or electricity. Organic Light Emitting Diodes (OLEDs) are devices that convert electrical energy to light using organic materials as the emissive center. They are made of typically three layers as shown in Figure 1.3, where the luminescent molecule (emitter) is sandwiched between a hole transport layer (HTL) and an electron transport layer (ETL). When an electrical current is applied to the OLED, the electrons and holes injected from cathode and anode recombine in the emissive layer, and then relax to the ground state by releasing photons. This technology has been widely applied to a variety of portable electronic devices, such as smart phones, light flat-panel displays and solid-state lighting.

In 1987, Tang and co-workers reported the first low driving voltage OLED utilizing an aromatic diamine as HTL and Alq\(_3\) (q=hydroxyquinolate) as EML and ETL. However, the application of Alq\(_3\) in OLEDs was limited by its green emission color and the poor device stability. The relatively large electronegativity difference between aluminum and carbon, oxygen, nitrogen in Alq\(_3\) analogues makes the molecules electrochemically reactive, resulting in the short device operational lifetimes. In contrast, the greater covalent bond character in the B-O, B-N, B-C
bonds confers organoboranes better chemical stability and superior performances in OLEDs devices.

Figure 1.3 An OLED structure.

Figure 1.4 lists some commonly used materials as host or charge transporting layers in OLEDs devices: Alq₃: tris(8-quinolinolato)aluminum; TPD: N,N’-bis(3-methylphenyl)-N,N’-diphenylbenzidine; CBP: 4,4’-N,N’-dicarbazole-biphenyl; TPBi: 1,3,5-tris(N-phenyl-benzimidazole-2-yl)benzene.

Figure 1.4 Structure of some materials commonly used as hosts or charge-carrier layers in OLEDs devices.

1.3.2 Triarylboron Compounds As Electron Transporting Layers

To increase the OLEDs device efficiency, an electron-transporting layer, which can facilitate the electron injection from the cathode to the organic emitting layers and lower the
cathodic working function, is of paramount importance. Triarylboryl moieties with an empty $p_z$ orbital exhibiting a high electron affinity have been widely exploited as electron-transporting materials in organic electronics area. However, the electronically unsaturated nature from a vacant $p_z$ orbital makes organoboranes easily attacked by most donor molecules, such as water. In order to be successfully incorporated into practical devices, the boron center has to be protected by bulky substituents, such as a mesityl moiety.

Early work from Shirota and co-workers firstly demonstrated the excellent performance of organoboranes as electron-transporting materials in OLEDs. With Alq$_3$ as the emissive layer, the OLED device incorporating 1.1-nT (n=2, 3) as the electron-transporting layer exhibited 1.6-1.8 times higher maximum luminance than the OLED without the 1.1-nT layer. Taking advantage of the highly blue fluorescent property of 1.1-2T ($\Phi = 0.86$ in THF), later work from Shirota also successfully incorporated 1.1-2T as a bifunctional layer in blue-emitting EL device.

Figure 1.5 Representative examples of triarylboranes as ETL from Shirota.

To further increase the electron affinity of the electron-transporting layer, molecular designing strategies combining boryl functionalization with electron deficient heterocycles, such as pyridine and triazine, have also been implemented. Representative examples from the literature are shown in Figure 1.6. The electron affinity ($E_a$) for 1.2 and 1.3 was estimated to be 3.32 and 3.25 eV, respectively. Moreover, due to the steric congestions imposed by the mesityl groups,
The π conjugation along the groups pendant to the central core is partially interrupted, leading to a large HOMO-LUMO energy gap and high triplet energy level. Carrier transport materials with high triplet energy level are highly beneficial to phosphorescent OLEDs due to their ability to suppress the triplet excited energy transfer from phosphorescent emitters to the adjacent carrier layer.\(^{17}\)

![Figure 1.6](image)

**Figure 1.6** Representative examples of triarylboran es as ETL from Kido and Wang.

### 1.3.3 Triarylboron Compounds As Emissive Layers

For ideal applications in OLEDs, emitting materials should meet the following criteria: 1. intense fluorescence; 2. energy levels matching the charge carrier injection to accept both holes and electrons; 3. the ability to form homogeneous thin films to eliminate grain boundaries; 4. high thermal and chemical stabilities. Compared to organic luminescent counterparts, organoborane compounds retain their own uniqueness in this field. The intramolecular charge transfer process from the π conjugated backbone to the vacant p\(_z\) orbital on the boron center confers a large Stokes shift, ensuring significant decrease of the intramolecular fluorescence self-quenching. Moreover, the bulky mesityl protecting group not only protects the boron center from degradation by moisture, but also prevents intermolecular stacking and interaction in the solid state, leading to intense solid-state emission. The non-planar structure also facilitates the formation of amorphous
With oligothiophenes,\textsuperscript{19} phenylenes\textsuperscript{20,21} as the $\pi$-conjugated central bridging unit, electron-donating groups such as the triarylamino moiety are often incorporated into the other end of $\pi$-conjugated system to enhance intramolecular charge transfer to the electron-deficient boron center. The variation of the type and length in the central $\pi$-conjugated units significantly affects the HOMO-LUMO energy gaps. Phenylene bridging units tend to have larger HOMO-LUMO energy gaps relative to oligothiophenes and the elongation of the $\pi$-conjugated units decreases the HOMO-LUMO energy gaps. Representative bright emitters in this catalogue from Shirota and Wang are shown in Figure 1.7.

\begin{align*}
\textbf{Figure 1.7} & \text{ Representative examples of triarylboranes as emitters from Shirota and Wang.}\textsuperscript{19,20} \\
\end{align*}

\textbf{1.4a} derivatives exhibit bright luminescence of $\lambda_{\text{max}}$ ranging from 505-582 nm ($\Phi = 50$ - 14\% in THF) with the elongation of bridging thienyl units. Molecule \textbf{1.4b} shows bright blue emission with $\lambda_{\text{max}} = 451$ nm ($\Phi = 95\%$ in THF solution, 31\% in the solid state). The fabricated devices with a series of \textbf{1.4a} compounds as emissive layers all exhibited high performance.\textsuperscript{19} The bipolar character of accepting both electrons and holes is also responsible for their abilities to serve as good host materials for emissive dopants.\textsuperscript{19} High efficiency OLEDs incorporating \textbf{1.4b} in different device structures further extended their potential to act as a trifunctional molecule,
namely electron transport layer, blue emitter and hole transport layer.\textsuperscript{20}

With the introduction of the bulky dimesitylboryl groups on the side of the $\pi$-conjugated framework, variation of the electron-donating $\pi$ skeleton could achieve bright, full color emission, as demonstrated by 3-borylbithiophene and its derivatives from Yamaguchi’s group (Figure 1.8).\textsuperscript{22}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Molecular structures of 3-borylbithiophene derivatives and a picture depicting their intense fluorescence in solid state and THF solution.\textsuperscript{22}}
\end{figure}

\subsection{1.3.4 Triarylboron Functionalized Compounds for Phosphorescent OLEDs (PhOLEDs)}

In a typical electroluminescent device, the combination of charge carriers generates both singlet and triplet excitons. The fraction of singlet excitons is 25\% due to the 1:3 degeneracies of the singlet and triplet states. In most organic emitters at room temperature, the direct relaxation from triplet states back to ground state is spin-forbidden, thus phosphorescence is rarely observed and the non-radiative process dominates. As a consequence, with organic molecules as emitters in EL devices, 75\% of the excitons generated via electric energy are wasted through non-radiative decay. In contrast, the radiative decay of triplet states can be greatly promoted in molecules containing heavy atoms, owing to the fact that the efficient high spin-orbital coupling of heavy atoms can effectively facilitate the intersystem crossing process and shorten the radiative decay lifetime. Thus lots of molecules containing heavy metal atoms are highly phosphorescent. By incorporating phosphorescent compounds as the emissive layer in EL devices, emission can occur
from both singlet and triplet excitons, and 100% internal EL quantum efficiency can potentially be achieved.

Highly emissive phosphors based on transition metals such as Os(II), Ru(II), Ir (III) and Pt(II) with cyclometalating ligands have been extensively studied.\textsuperscript{23} Pt(II) complexes with a large ligand field splitting energy are of particular interest here.

![Energy profile of Pt(II) complexes.](image)

(Thick arrow indicates light absorption; blue arrow indicates thermal population of d-d state via $^3$LC excited-state; red arrow indicates radiative decay pathway.)

Pt(II) complexes adopt square planar geometry with an unoccupied dx\textsuperscript{2}-y\textsuperscript{2} orbital. As shown in Figure 1.9, the lowest electronic transition is predominately ligand-based $\pi$-$\pi^*$ mixed with $^1$MLCT (metal-to-ligand charge transfer) process. If the triplet ligand centered ($^3$LC) excited state is close in energy to the empty d orbital, the population from the $^3$LC excited state to the d orbital is thermally accessible at the isoenergetic crossing point on the potential energy surface, which leads to a non-radiative d-d transition back to the ground state.

To ensure high luminescent efficiency of Pt(II) complexes, incorporation of aromatic cyclometalates with a strong ligand field is an effective strategy.\textsuperscript{24} Cyclometallation refers to the
binding of polydentate ligand to a metal via a covalent bond (metal-carbon anion, nitrogen anion), with the remaining heteroatoms such as nitrogen, phosphorus forming dative bonds. The structural rigidity offered by polydentate ligands generally favors luminescence over non-radiative decay pathways. More importantly, the anionic strong sigma donor offers the metal center a very strong ligand-field and large d-d energy gap, which effectively suppresses the thermally accessible population from $^3$LC orbital to the d orbital. On the other hand, increasing the mixing of the $^1$MLCT to the $^3$LC low-lying excited state could also increase the luminescent efficiency, owing to that increased metal participation in the excited state can enhance spin-orbital coupling and shorten the radiative decay lifetime.

Since the lowest electronic transition is mainly $^3$LC based $\pi$ to $\pi^*$ transition, the emission color can be easily tuned via manipulating the $\pi$ electron system with functional groups on the cyclometalating ligand. Consequently, ancillary ligands on the Pt center normally won’t affect the emission energy. However, not to be neglected, ancillary ligands with strong ligand field can greatly further increase the luminescent efficiency of the metal complexes as evidenced by the shortened radiative decay lifetime.$^{25}$

Taking into account of the above-mentioned tactics, to further improve the EL device performance based on phosphorescent emitters, decorating the cyclometalating ligands with triarylboron group seems an elegant approach. Utilizing the intrinsic electron deficiency of the boron center, triarylboron group functionalized Pt(II) complexes exhibit increased phosphorescent quantum efficiency due to the enhanced mixing of $^1$MLCT with $^3$LC based excited state. Secondly, Pt(II) complexes with triarylboron group demonstrated improved electron mobility during the device operation. Since holes in general have faster mobility compared to electrons in EL devices, the better-balanced charge carrier mobility in the presence of triarylboron
group greatly improves the device performance. Thirdly, the steric bulkiness provided by the triarylboron group can prevent the intermolecular Pt-Pt stacking and self-quenching.²⁶

Pt(II) complexes based on three types of cyclometalating ligands (phenylpyridine,²⁷ phenyl-NHC,²⁸ phenyl-1,2,3-triazole²⁵) with triarylboron group have been studied and evaluated in EL device performance. Selected examples are shown in Figure 1.10.

![Figure 1.10](image.jpg)  
**Figure 1.10** Representative triarylboryl functionalized Pt(II) emitters.

Compound 1.6²⁷ displays bright green luminescence (527 nm) both in solution and solid state, with solution quantum efficiency almost approaching 100%. OLED device structure as [ITO/NPB (45 nm)/CBP (5 nm)/15% 1.6 : CBP (15 nm)/TPBI (30 nm)/LiF (1 nm)/Al (100 nm)] gave peak current and power efficiency of 34.5 cdA⁻¹ and 29.8 lmW⁻¹, and a maximum luminance of 31510 cdm⁻² at 9.8 V. Bipolar compound 1.7²⁹ incorporating both donor (amine) and acceptor (boron) moieties on the ligand backbone showed bright orange electrophosphorescence with peak current and power efficiency of 35.0 cdA⁻¹ and 36.6 lmW⁻¹ and a maximum external quantum efficiency of 10.6%.

For phenylpyridine cyclometalating ligand, even electron-withdrawing substituent, such as fluorine, were introduced on the phenyl ring, the emission color of its Pt(II) complex remained greenish.²⁷ To obtain blue phosphorescence and enlarge the HOMO-LUMO band gap, NHC with strong carbene sigma donor can result in a significant increase of the LUMO energy. Compound
based on phenyl-NHC ligand indeed displayed sky-blue emission at 462 nm in CH$_2$Cl$_2$ solution at room temperature. Notably, phenyl-triazole ligand is also effective in achieving blue phosphorescent Pt(II) compounds. This might be owing to the weakening of the $\pi$-conjugation in the phenyl-triazolyl backbone, which also leads to an increase in energy of the LUMO level. Compared to 1.8, compound 1.9 exhibited an even greater blue-shifted emission at 450 nm in Me-THF solution at room temperature.

1.3.5 Optoelectronic Application of Four-Coordinate Organoboron Compounds

In the past decade, tremendous research progress has been achieved in $\pi$-conjugated four-coordinate boron area, with various applications including emitters, electron-transporting materials, host/hole-blocking materials for OLEDs, sensory and biological imaging materials. The general structure of compounds with a four-coordinate boron nesting in a $\pi$-conjugated chelate site is shown in Figure 1.11.

![Figure 1.11](image)

Figure 1.11 General structure of four-coordinate boron compounds.

Organoborane compounds normally incorporate mono-anionic chelate ligands such as hydroxylquinolate, 7-azaindolyl, phenylpyridyl to achieve a charge neutral boron center. The negative charge on the ligand can dissipate to the boron center via a covalent bond formation in between them. As a consequence, the lowest unoccupied molecular orbital (LUMO) of such four-coordinate boron compounds is normally localized on the $\pi^*$ orbitals of the chelation
backbone, while the highest occupied molecular orbital (HOMO) is localized on the \(\pi\)-conjugated backbone or substituted R groups on the boron center. The attainment of greater \(\pi\) conjugation via chelation lowers the LUMO energy level and increases the electron affinity, ensuring four-coordinate organoboron compounds can act as electron-transporting materials. The \(\pi\) to \(\pi^*\) electronic transition on the chelate backbone or charge transfer process from the R substituents to the chelate backbone confer four-coordinate organoboranes bright luminescence. Based on the chelate donor atoms, four-coordinate organoboranes can be catalogued as N,O-, N,N-, N,C-, C,C-, C,O-, and O,O-chelate, which will be reviewed in the following subsections.

1.3.5.1 N,O-Chelate Compounds

Three types of N,O-chelate boron compounds have been studied for OLEDs applications so far, such as 8-hydroxyquinolinate, 2-pyridylnphenolate and oxazolylphenolate.

8-Hydroxyquinolinate. The luminescent properties of 8-hydroxyquinolinate based boron compounds with the general formula of BR\(_2\)q (1.10), where R = ethyl, phenyl, 1-naphthyl and 2-naphthyl, were reported in 2000 by our group.\(^{30}\) These organoborane compounds exhibited greenish blue emission (490-500 nm) originating from the similar \(\pi\) (ph-O) to \(\pi^*\)(py) electronic transition as those in the Alq\(_3\) analogues. Double- or triple-layer devices with either N,N’-diphenyl-N,N’-bis(1-naphthyl)-1,1’-biphenyl-4,4-diamine (NPB) or N,N’-bis(3-methylphenyl)-N,N’-diphenylbenzidine (TD) as a HTL and the boron compound as an emitter/ETL were fabricated. However, these devices are not efficient with an apparent exciplex emission at the interface of the charger carrier layers and emissive layer. Further functionalization by 5-aryl groups (phenyl, naphthyl, benzothienyl) (1.11) were found to greatly red shift the emission color (530 – 565 nm in CH\(_2\)Cl\(_2\)).\(^{31}\) Jäkle’s group also examined the substitution effect by donor and acceptor groups at the 5 position on the emission properties of B(p-Ph-t-Bu)\(_2\)(5-R-q) (1.12).\(^{32}\)
Through the variation of electron withdrawing or donating substituents, full color emissions ranging from 456-625 nm were achieved.

**Figure 1.12** Molecular structures of selected hydroxyquinolinate N,O-chelate organoboranes.

**2-Pyridylenolate.** Compared to the hydroxyquinolinate chelate, the extent of π conjugation is lessened in pyridylenolate, resulting in both an increase of the emission energy and HOMO-LUMO energy gap. Considering these merits, in the past decade a series of these compounds have been developed for stable blue emitters for OLEDs\(^{33,34}\) and effective hole blocking materials in phosphorescent OLEDs.\(^{35}\) Both the terdentate (1.13)\(^{33,34}\) and bidentate (1.15)\(^{36}\) chelate boron containing molecules are blue emitters with \(\lambda_{\text{em}} = 445-481\) nm, attributed to the intraligand π-π* electronic transition. Wang and his coworkers also developed a bipolar emitter (1.14) with an electron-donating substituent on the boron center.\(^{37}\) This compound has a HOMO energy level similar to that of the commonly used hole transport layer NPB, and a LUMO energy level similar to the electron transport layer Alq\(_3\). A single-layer EL device using only compound 1.14 was therefore fabricated with impressive performance of a maximum 2654 cd m\(^{-2}\) brightness and 5.2 cd A\(^{-1}\) efficiency.
Figure 1.13 Molecular structures of selected pyridylphenolate N,O-chelate organoboranes.

**Oxazolylphenolate.** With further reduced conjugation in oxazolylphenolate chelate, Kang and coworkers have recently reported a class of these boron compounds (1.16)\(^38\). Modulating the substituents at the 4-position of oxazolylphenolate from electron withdrawing to donating nature, the HOMO energy levels were increased and the emission color can be systematically tuned from 420 to 520 nm in chloroform solution.

### 1.3.5.2 N, N-Chelate Compounds

Compared to hydroxylquinolinate based boron compounds, N, N-chelate compounds are less prone to the irreversible oxidation induced degradation in devices. Our group initiated blue-luminescent boron compounds based on 7-azaindolyl chromophore more than a decade ago. Compound 1.17 (R = Et)\(^39\) is a bright purple-blue emitter with \(\lambda_{em} = 419\) nm (422 nm in the solid state) and \(\Phi = 0.47\) in toluene, with great stability toward air and high thermal stability. A bright-blue EL device using NPB (doped by 1% 9,10-diphenylnanthracene) as a HTL; compound 1.17 (R = Ph, \(\lambda_{em} = 450\) nm)\(^40\) as the emitter; and Alq\(_3\) as an ETL was achieved. This device has a turn-on voltage of approximately 7 V and a luminance of 1024 cd m\(^{-2}\) at 14 V.
Further molecular modifications and the following device applications as emitter and electron transporting layers in OLEDs were developed in Wang and Chi’s group. The molecular structures of some representative examples (1.18 – 1.21) are shown here. In general, the boron atom binds to the negatively charged N atom of the chelate ligand (indoly1, azaindoly1, aniliny1, benzimidazoly1, pyrroly1), and a neutral N donor atom on the other part of chelate ligand (pyridyl, thiazolyl, quinolyl, pyrazolyl) forming N, N-chelate four-coordinate boron compounds. The HOMO is mainly localized on the negatively charged N heterocycles of the chelate ligand, while the LUMO is mainly localized on the neutral N-heterocycles.

1.3.5.3 Other Types of Chelate Organoboranes

N,C-chelate. In the literature, the nitrogen-containing subunits in this type of chelation normally involve N-heteroaryl rings, imine moiety. Yamaguchi’s group reported the first example of N, C-chelate dimesitylboration compounds in 2006. The conjugated diboron compound (1.22) demonstrated a good electron mobility of $\mu = 1.5 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ according to preliminary time-
of-flight carrier mobility measurements on its vacuum-deposited film. A low-lying LUMO level resulting from the extended π conjugation and the boron chelation endowed the good electron mobility. The solid-state intermolecular electrostatic interaction between electron rich thiophene moiety and electron poor thiazole moiety also played an indispensable role.

![Molecular structures of N,C-chelate organoboranes.]

**Figure 1.15** Molecular structures of N,C-chelate organoboranes.

Kawashima, Gabbai, and Yamaguchi have reported a series of imine-coordinating organoboron compounds. Compounds (1.23) with C₆F₅ substituents on the boron center exhibit higher luminescent quantum yield relative to that of mesityl substituents. In mesityl substituted organoboranes, the charge transfer from mesityl moiety to the π-conjugated backbone dominates the lowest electronic transition, the lowest electronic transition in the C₆F₅ substituted organoboranes is more of a π (substituent on the imine nitrogen) to π* (benzylideneamine moiety) character. The rigidity of the molecular structure via boron coordination greatly enhanced the luminescent efficiency of this class of molecules.

**C,C-chelate.** In 2008, Yamaguchi and co-workers reported a new class of phosphonium and borate-bridged zwitterionic ladder stilbenes, which displayed narrow HOMO-LUMO energy gap and highly electron-accepting character. The lowest-energy transition is from the negatively charged benzoborole moiety (HOMO) to the positively charged benzophosphole
moiety (LUMO). Compound 1.24 with an extended structure exhibited bright fluorescent emission at 614 nm in THF, with a quantum yield of 40%.

![Figure 1.16 Molecular structures of N,N-, O, O-chelate organoboranes.](image)

**O,O-chelate.** O, O-chelate boron compounds have the general structure of 1.25. With substituents such as F and C₆F₅ on the boron center, this class of compounds in general exhibits bright fluorescence with easily tunable colors, owing to π to π* electronic transitions localized on the diketone backbone. In addition to those attractive linear properties, several BF₂ derivatives possess large cross section for two-photon absorption. The introduction of a polymer chain to one of the aryl groups on the diketone of the BF₂ compounds was found to induce unusual and highly oxygen-sensitive solid-state phosphorescence, extending their usage as oxygen sensors/tumor hypoxia imaging reagents.

**1.4 The Photochemistry of Organoboron Compounds**

The photochemistry of organic compounds plays an indispensable role in the living organism, such as the synthesis of vitamin D with sunlight. Trivalent boron is isoelectronic and isostructural to the carbon cation, while boron anion is isoelectronic, isostructural to the carbon atom. In contrast to the extensive research work on the photochemistry of organic compounds, the photochemistry of organoboron compounds remains a less explored area. In the literature hitherto, the photochemistry of organoboron compounds retain some similar traits to their full
carbon analog, while standing out due to its rich chemical reactivity. This section starts with a brief review of the photoreactivity of organoborates, followed by a discussion of the discovery of photochromic organoboron compounds, and the recent research progress in this area.

1.4.1 Early Work On the Photoreactions of Organoborates

Williams and co-workers were the first to carry out the systematic work on photochemistry of sodium tetraphenyl borates in the 70s. The seminal work in the late 80s by Schuster showed that irradiation of sodium tetraphenylborate salt (1.26) initiates a process related to the well-known di-π-methane rearrangement of hydrocarbons (Figure 1.17). The structure of the photo-produced boranorcaradiene (1.26a) was confirmed by X-ray crystallography. Notably, the C-C coupling in tetraaryl borate system are not selective when different aryl groups are present in the same molecule. For instance, irradiation of (p-biphenylyl)triphenylborate (1.27) in acetonitrile resulted in a mixture of products from phenyl to phenyl coupling and biphenylyl to phenyl coupling (Figure 1.18).

![Figure 1.17 Photochemistry sodium tetraphenylborate salt.](image-url)
In the meantime, Schuster investigated the photochemistry of alkynyl- (1.28), alkenyl (1.29), and cyclopropyl- (1.30) substituted borate salts, which also underwent di-π and cyclopropyl-π-borate rearrangements (Figure 1.19). Eisch also demonstrated that under UV
irradiation in a donor solvent dimesityl(mesitylethynyl)borane (1.30, Figure 1.20) also rearranged to trimesitylborirene in a similar fashion to the di-π-methane rearrangement.\textsuperscript{63}

![Diagram](image)

**Figure 1.20** Photochemistry of dimesityl(mesitylethynyl)borane from Eisch.\textsuperscript{63}

### 1.4.2 Photochromism of Organoboranes

#### 1.4.2.1 Photochromic N,C-chelate Organoboron Compounds

In 2008, intrigued by the report of Yamaguchi and co-workers on the congested 2-thienylthiazolyl N,C-chelate four-coordinate boron compounds (1.22), we decided to investigate the related 2-phenylpyridyl N,C-chelate dimesitylboron (1.32) shown in Figure 1.21.\textsuperscript{64} Despite the steric congestion around the boron center, this compound is fairly stable in both solution and solid state. The N, C-chelation site remains intact even in the presence of small anion fluoride, which readily forms adduct with triarylboranes. However, upon UV light (365 nm) irradiation, this compound was found to change color rapidly from colorless to dark blue and lose its fluorescence ($\lambda_{em}=458$ nm and $\Phi=0.15$ in toluene) completely. The photo-induced transformation was quantitative and the whole process was fully thermally reversible with an activation barrier of 110 kJmol\textsuperscript{-1} and $t_{1/2} = \sim 7.7$ h at 323 K. Solution NMR data and complementary computational modeling suggest that compound 1.32 underwent an intramolecular C-C bond breaking/formation with the dearomatization of one mesityl group to form the new isomer 1.32a. Photoisomerization from 1.32 to 1.32a was found to be very efficient with a quantum yield of $\sim 0.85$ at 365 nm.
Exposure of $1.32a$ to oxygen resulted in the two B-C bonds cleaving in the boracyclopropane three-member ring and the formation of the final product ($1.32b$) with the mesityl ring coupled to the ppy chelate backbone.

**Figure 1.21** Photoisomerization of N,C-chelate dimesitylboranes.

Considering that the light-induced transformation of $1.32$ exhibited high resemblance to that of tetraaryl borate anions, the mechanism of this transformation might also be similar to the di-$\pi$-methane rearrangement, followed by a sigmatropic shift. Notably, in contrast to that C-C coupling between two aryl groups in BAr$_4$ anions under UV irradiation that is not selective when two different aryl groups are present in the molecule, the C-C coupling in compound $1.32$ occurs exclusively between a mesityl group and the phenyl group on the ppy ligand. The HOMO and LUMO levels of compound $1.32$ are located predominantly on one mesityl group and the chelate backbone, respectively. Thus, the lowest excited state of $1.32$ can be described as a mesityl group to the chelate charge transfer, which is believed to play a key role in promoting its highly selective C-C coupling.

However, in contrast to tetraphenyl borate ($1.26$)’s isomerization upon UV light irradiation, B(2-phenylpyridyl)Ph$_2$ ($1.33$) was found to be photo-stable. Therefore, the steric congestion imposed by the mesityl groups in compound $1.32$ appears to be indispensible for the occurrence of photoisomerization in N,C-chelate boron compounds. The average of B-N and B-Cppy bond
lengths for 1.32 and its derivatives are 1.65(1) and 1.63(1) Å, respectively, while the corresponding ones for 1.33 are 1.62(1) and 1.63(1) Å, respectively. The B-C<sub>Mes</sub> bond length is 1.65(1) Å for 1.32, much longer than that of B-C<sub>Ph</sub> of 1.33 [1.61(1) Å]. Furthermore, the arrangement of the two mesityl groups in 1.32 is much less symmetric than the two phenyl groups in 1.33, with one mesityl group being much closer to the ppy-C atom (~2.58 Å) than the phenyl in 1.33 (2.64 Å), as shown in Figure 1.22. This, along with the relatively weak B-C<sub>Mes</sub> bonds in 1.32, was believed to be the key driving force for its facile photoisomerization.

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**Figure 1.22** Structural comparison between N,C-chelate dimesityl and diphenyl boranes.

*Chelation Impact.* In phenylpyridyl-chelate dimesitylboranes, varying substituents (trimethylsilyl, dimesitylboron, phenylalkynyl) on the 5-position of pyridyl ring doesn’t impede the photochromic process. However, an increased π-conjugation on the chelation backbone can lower the photoisomerization quantum efficiency, as demonstrated in the case of 5-phenylalkynyl substituted pyridyl ring. When a heterocyclic group such as benzofuryl or N-phenylindolyl replaces the phenyl group of ppy chelation, the resulting N,C-chelate BMes<sub>2</sub> compounds isomerize in the same manner as compound 1.32 does upon UV irradiation. The first crystal structure of dark isomer (as shown in Figure 1.23) was obtained with 2-(N-phenylindolyl)pyridine as the chelation backbone.
**Figure 1.23** The first crystal structure of dark isomer from “2-(N-phenylindolyl)pyridyl BMes₂” with 30% ellipsoid.

Important bond length (Å) and angles (°): B(1)-C(1) = 1.626(7), B(1)-C(2) = 1.602(7), B(1)-C(10) = 1.593(5), B(1)-N(1) = 1.592(5), C(1)-C(2) = 1.574(7); C(10)-B(1)-C(1) = 126.7(6), C(2)-B(1)-C(10) = 121.9(7), C(1)-B(1)-C(2) = 58.4(3), C(10)-B(1)-N(1) = 110.8(6), C(1)-B(1)-N(1) = 112.3(6).

**Involvement of a triplet excited state.** Recent work in our group reported a number of compounds incorporating aromatic π acceptors of different triplet energy into a photochromic boryl chromophore via a non-conjugated dimethylsilyl linker.⁶⁸

**Figure 1.24** Molecules integrating boryl moiety and π acceptors via a dimethylsilyl linker.
The photoisomerization quantum efficiency was found to be 0.12 for \textbf{1.34a} and 0.03 for \textbf{1.34b}, while compound \textbf{1.34c} is photo-stable. This could be attributed to the involvement of a triplet photoactive state in the photoisomerization process. The \textpi acceptors all have much higher singlet levels (> 3 eV) relative to compounds \textbf{1.34a} – \textbf{1.34c}’s first singlet energy (2.77 eV), which is centered on the boron chromophore. In contrast, according to TD-DFT calculations, the lowest triplet state localized on the boryl unit was found to lie at 2.13 eV for compounds \textbf{1.34a} – \textbf{1.34c}, while the triplet energies of the acceptors vary considerably, lying at 2.55, 2.10 and 1.77 eV, respectively, for \textbf{1.34a}, \textbf{1.34b}, and \textbf{1.34c}. Energy transfer from the triplet excited state of the boryl unit to that of the acceptor would be expected to be negligible in \textbf{1.34a}, weak in \textbf{1.34b}, and dominant in \textbf{1.34c}. The absence of energy transfer from the triplet boryl unit to the \textpi acceptor resulted in much more efficient photoisomerization for compounds \textbf{1.34a} and \textbf{1.34b}.

\textbf{1.4.2.2 Competitive Isomerization Pathways in Poly-N,C-chelate Dimesitylborane Systems}

\textit{Olefin Substitution.} Photo-induced cis-trans isomerism in alkene or stilbene system has long been a subject of intense research, both experimentally and theoretically.\textsuperscript{69} Incorporation of photoactive olefin functional groups into photochromic organoborane systems adds another competitive excited state pathway. Previous work in our group has demonstrated that in olefin-substituted N,C-chelate dimesitylborane system (\textbf{1.35}),\textsuperscript{65} the photoisomerization pathway around the boron center is completely shut off by the olefinic bond isomerization. This is due to the fact that the presence of the cis-trans isomerism on olefinic bond provides an alternative excited-state energy dissipation pathway for olefin substituted N,C-chelate dimesitylboron chromophore, thus stabilizing the molecule toward photochromism. Meanwhile, in the polyolefinic substituted N,C-chelate dimesitylborane system (\textbf{1.36}), only one olefinic bond isomerization is observed.
Figure 1.25 Olefin substituted photoactive organoboranes.

**Polyboryl System.** In a polyboryl system, with a phenyl group as the core and an alkyne unit as the bridging linker, only one boryl unit was found to undergo photoisomerization upon irradiation at 365 nm. This is due to the fact that the photoisomerization pathway cannot compete with the much faster energy transfer to the low-energy absorption of the isomerized boryl unit. The same phenomenon was also observed in polyboranes with a non-conjugated linker of a dimethylsilyl moiety.

Figure 1.26 A polyboryl system with alkyne linkages.
1.4.2.3 Impact of Transition-Metal on Photochromic System

**General.** Photo-responsive materials that integrate transition metal coordination and a photochromic organic moiety into one molecular system can combine together and coordinate the unique electronic state of each component.\textsuperscript{71,72} For most organic photochromic systems, high-energy UV irradiation is in general required to excite the organic molecules and initiate the photo-reactivity. However, long-term exposure to UV light results in the degradation of organic materials. For photo-pharmacological applications, using high-energy UV light as the molecular switch trigger would cause cell damage. On the other hand, transition metal complexes in general have a low-lying energy MLCT band that absorbs in visible light region, which is not destructive. Hybrid metal-organic photochromic systems have the potential to utilize metal-sensitized population of the triplet manifold to initiate the isomerization on the organic chromophores’ triplet states via energy transfer.\textsuperscript{71,72}

One of the most studied systems is the metal-coordination complex with photo-switchable dithienylethene (DTE). Dithienylethene (DTE) has the general structure and transformation as shown in Figure 1.27. DTE system undergoes reversible ring-opening/closing reactions between two isomers, with each exhibiting remarkably different optical and electronic properties.\textsuperscript{73,74}

![Figure 1.27 Photochromic dithienylethene.](image)

To date, transition metal ions such as Re(I),\textsuperscript{75,76} Ir(III),\textsuperscript{77} Pt(II),\textsuperscript{78,79} Ru(II)\textsuperscript{80} have been incorporated into DTE systems with a π-conjugated linker in between. Besides the photocyclization of DTE occurring upon irradiation with UV light absorbed by the ligand-centered
moiety, all these metal complexes also successfully demonstrated the feasibility of using lower-
energy light absorbed by the MLCT band to sensitize the ring-closing process localized on triplet
intraligand state ($^3$IL). A scheme showing the energy-transfer sensitizing mechanism is given in
Figure 1.28.\textsuperscript{75,76} Some representative molecules are listed in Figure 1.29.\textsuperscript{75,77,78}

![Energetic scheme for photosensitized photocyclization by MLCT excitation.](image1)

**Figure 1.28** Energetic scheme for photosensitized photocyclization by MLCT excitation.

![Representative examples of transition-metal sensitized DTE systems.](image2)

**Figure 1.29** Representative examples of transition-metal sensitized DTE systems.

In contrast, the photochromic behavior of organoboron systems incorporating transition
metals is completely quenched or severely impeded. While the $\pi$ to $\pi^*$ intraligand excited states
result in the photoisomerization in DTE systems, the intramolecular charge-transfer from the mesityl moiety to the chelation backbone is responsible for the photoisomerization of N,C-chelate dimesitylboranes.

A series of N,C-chelate organoboron compounds with a metal-acetylide unit investigated by the Wang group are shown in Figure 1.30.81 Among them, the photoisomerization of the boryl moiety in Re(I) complex (1.38) is completely quenched, because both the lowest singlet and triplet electronic transitions are dominated by the low lying intraligand charge transfer/MLCT of the Re(I) unit, rather than the mesityl-to-chelation charge transfer on the boryl moiety. The Au(I) complex (1.39) displayed a similar photoisomerization quantum efficiency compared to the free ligand, while the Pt(II) complex (1.40) showed much less efficient photoisomerization.

![Figure 1.30](image_url)

*Figure 1.30* N,C-chelate organoboron compounds with a metal-acetylide unit.

TD-DFT calculations suggested that the first singlet state ($S_1$) in both compounds 1.39 and 1.40 is a typical mesityl-to-alkyne-chelate charge-transfer transition, while the first triplet state ($T_1$) involves a significant contribution from a $\pi$ to $\pi^*$ transition on the conjugated backbone. The $T_1$ state in Au(I) complex (1.39) has 50% of $\pi$ to $\pi^*$ transition mixed with 34% of mesityl-
chelate charge transfer transition, while $T_1$ in the Pt(II) complex (1.40) is dominated by the $\pi$ to $\pi^*$ transition with notable contributions from the d orbitals of the Pt(II) atom. Though the calculated energy of $T_1$ in Au(I) (3.66 eV) and Pt(II) (3.50 eV) complexes are much higher than their free ligand (2.56 eV), the incorporation of metal atoms effectively enhances the population of triplet $\pi$ to $\pi^*$ ligand-centered states, but is futile in terms of enhancing the triplet mesityl-to-chelate charge transfer transition. Especially along with the extended $\pi$ conjugation in the chelate backbone, the $\pi$ to $\pi^*$ transition becomes the more competitive lowest excited state compared to the mesityl-to-chelate charge transfer, which is responsible for the ineffectiveness of the metal ions in these compounds to enhance the photoisomerization quantum efficiency.

Another series of photochromic organoboron compounds incorporating Pt(II) metal in a phenylpyridyl cyclometallation are shown in Figure 1.31. The ancillary ligand on the Pt(II) center was also found to have an impact on the boryl photoisomerization efficiency.

![Figure 1.31](image)

**Figure 1.31** N,C-chelate organoboron compounds with a cyclometallating Pt(II) unit.

The extended $\pi$ conjugation and the Pt(II) coordination on the chelation backbone of 1.42 - 1.44 significantly lowered the photoisomerization quantum efficiency around the boron center. Under 365 nm irradiation, the photoisomerization quantum yield ($\Phi_{\text{isomerization}}$) is 0.85 for
compound 1.32, while the $\Phi_{\text{isomerization}}$ is 0.03 for ligand 1.41, $\sim$0.0015 for 1.42, $<$0.0001 for 1.43, and $\sim$0.0005 for 1.44, respectively. All these metal complexes (1.42-1.44) exhibit bright yellow phosphorescence with $\lambda_{\text{max}} = 550$ nm. The phosphorescent quantum yield ($\Phi$) and lifetime ($\tau$) are $\Phi = 0.16, \tau = 14.67(2) \mu$s for 1.42, $\Phi = 0.13, \tau = 9.64(5) \mu$s for 1.43 and $\Phi = 0.45, \tau = 14.5(1) \mu$s for 1.44, respectively.

Complex 1.43 with ancillary ligand of 4-$t$-butylpyridine exhibited the lowest photoisomerization efficiency and shortest phosphorescent lifetime. $t$-Butylpyridine, which is more strongly donating than DMSO, can help to ensure a significant metal character in the HOMO and facilitate the radiative decay, thus the photoisomerization pathway is greatly suppressed. Compared to 1.42, complex 1.44 with acetylacetonate ancillary ligand retains the molecule in a more rigid geometry and enhances its luminescence efficiency. Consequently, the photoisomerization efficiency in 1.44 is inhibited to a greater extent relative to 1.42.

In summary, several key factors are believed to explain why the metal-sensitized photoisomerization in general is ineffective in the N,C-chelate dimesitylborane system, namely: 1. the increased $\pi$-conjugation in the chelation backbone due to metal coordination; 2. enhanced triplet $\pi$ to $\pi^*$ transition and efficient radiative decay due to the strong spin-orbital coupling intrinsic to heavy atoms. The photoisomerization of N,C-chelate dimesitylborane requires the charge-transfer (CT) from mesityl-to-chelate backbone to be the dominant lowest electronic transition. It also involves a larger conformational change than the DTE system, thus, a relatively long-lived triplet CT state is crucial in the organoborane system for its photoisomerization.

1.4.3 Other Types of Photochromic Organoboranes

Recently, Braunschweig and co-workers reported a different photochromic four-coordinate boron system based on a pentaphenylborole-2,6-lutidine adduct (1.45).\textsuperscript{83} Irradiation of the toluene
solution of 1.45 at −50 °C results a significant color change from yellow to dark green. NMR spectroscopic study suggests a clean conversion of 1.45 into 1.45a, namely, a shift of the base from boron to the adjacent carbon atom with the formation of a B=C bond.

![Figure 1.32](image1.jpg)

Figure 1.32 Photochromism based on a pentaphenylborole-2,6-lutidine adduct.

![Figure 1.33](image2.jpg)

Figure 1.33 A dimesitylboryl borepin based photochromism.

While the photochemistry discussed so far mainly involves a four-coordinate boron center, Yamaguchi and co-workers recently reported an interesting photochromic phenomenon with three-coordinate boron as the active unit. Upon UV irradiation at 320 nm, a dimesitylboryl borepin (1.46) exhibited dramatic photochromic behavior with a color change from colorless to deep blue. A new C-C bond formed between the mesityl aryl carbon and the adjacent allylic carbon in a stereospecific manner, resulted in the deep blue product (1.46a). The product in THF solution can be thermally reverted to the starting borepin at room temperature overnight. The
photo-cyclization in 1.46 is similar to Nazarov cyclization, in which a 4π-electrocyclic reaction of a dialkenylketone forms a cyclopentenyl cation. The B/C\(^+\) isosterism in 1.46 is believed to be the cause for its new reactivity.

### 1.4.4 Photoelimination of B, N-Heterocycles

Wang and co-workers recently disclosed another type of B, N-heterocycles (1.47, 1.48) that underwent photoelimination to generate azaborine derivatives.\(^{85}\) Compared to the multi-step synthesis needed to obtain the azaborine,\(^{86}\) photochemistry offers an effective shortcut to achieve this goal elaborately.

![Figure 1.34 Photoelimination of B, N-heterocycles.](image-url)
1.5 Scope of this Thesis

The work described in this thesis focuses on smart materials based on organoboron compounds, aiming at the following areas: a continuing search for highly efficient phosphors in OLEDs and solid-state lighting; to address the problem of certain types of charge carrier layers towards photo-degradation; further exploration and expansion of the photo-responsive materials and investigation into their serendipitous photochemical reactivity.

Chapter 2 outlines a series of new phosphorescent Pt(II) compounds based on dimesitylboron (BMes₂)-functionalized 2-phenylpyridyl (ppy) N,C-chelate ligands and an acetylacetonato ancillary ligand. This work demonstrated that the location of the BMes₂ group on the ppy has a dramatic impact on the phosphorescent energy, and BMes₂ substitution on the dipyridylbenzene N,C,N-chelate ligand can greatly enhance the performance of the EL devices.

Chapter 3 illustrates the impact of a dithienyl unit on photo-stability of N,C-chelate boron compounds. Dithienyl unit in a N,C-chelate monoboryl compound has been found to completely stabilize a N,C-chelate boryl chromophore toward photoisomerization.

Chapter 4 illustrates the reactivity and electronic properties of a ferrocene molecule bearing an N,C-Chelate BMes₂ unit. The B–N bond was found to undergo a dynamic dissociation-association process in solution. Upon oxidation, a notable spin delocalization occurred through space from the Fe(III) center to a flanking mesityl group.

Chapter 5 details a new type of C,C-chelate BMes₂ compounds containing an N-heterocyclic carbene (NHC) donor, which underwent photoisomerization in the same manner as N,C-chelate BMes₂ compounds do, but also exhibited a second-step photoisomerization resulting in an intramolecular C–H insertion product via a borylene intermediate.

Chapter 6 details a series of benzoazolyl N, C-chelate BMes₂ compounds which underwent
a cascade of multi-structural transformations upon light irradiation or heating, namely, intramolecular H-atom transfer, 1,3-shift of a boron atom and a spiropyran-type ring-opening/closure process. Each reaction has the potential to be an important basis for finding a new reaction and photo-function of organoboron compounds.

Chapter 7 details two imidazolyl N, C-chelate BMes₂ compounds, which demonstrated consecutive photochromic phenomenon, with initially a typical rearrangement to the boratanorcaradiene moiety, then a continuous transformation to a borata-alkene moiety.
1.6 References


(49) Garcia-Hernández, Z.; Gabbaï, F. P. Z. Naturforsch **2009**, 64b, 1381.


Chapter 2

Bluish-Green BMes$_2$-Functionalized Pt(II) Complexes for High Efficiency PhOLEDs: Impact of the BMes$_2$ Location on Emission Color

2.1 Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs), which can harvest both singlet and triplet excitons to afford superior device efficiency, are promising technologies for next-generation flat-panel displays and solid-state lighting devices.$^{1,2}$ The key challenge in PhOLEDs research is the development of phosphorescent metal complexes with high quantum efficiency, especially blue phosphors. Most earlier and current research efforts on phosphorescent materials for OLEDs focus on 2-phenylpyridine (Hppy)-based Ir(III) complexes and their derivatives because of their high photo-luminescent quantum efficiencies.$^{3,4,5}$ Although highly efficient PhOLEDs based on Ir(III) emitters have been achieved, stable blue PhOLEDs based on Ir(III) compounds remain elusive.$^{6,7,8,9}$ Due to the often strong intermolecular π-π stacking interactions caused by the square-planar geometry, Pt(II) compounds are prone to excimer formation, resulting in the decrease of emission quantum efficiency and color purity in the solid state.$^{10,11,12}$ The square-planar geometry of Pt(II) may have one advantage over Ir(III), namely the access to a higher triplet state, due to the greater ligand field splitting that greatly increases the energy of the d–d state, for a given set of chelate ligands. This may be evident from the emission energy (538 nm) of PtBppy and that (605 nm) of the Ir(III) analogue (Figure 2.1). Thus, Pt(II) compounds are good candidates for the development of blue phosphorescent emitters, when the issues like low emission efficiency and intermolecular interaction can be addressed.
Several examples of green, orange or red phosphorescent Pt(II) compounds have demonstrated successful usage in PhOLEDs recently,\textsuperscript{13-19} while blue PhOLEDs based on Pt(II) compounds remain rare and only a few examples are known in the literature.\textsuperscript{20-26} Among them, dimesitylboron (BMes\textsubscript{2}) functionalized Pt(ppy)(acac) and derivative compounds have been applied in high efficiency green and orange PhOLEDs with external quantum efficiency as high as 20\%.\textsuperscript{17,19,27} The introduction of the BMes\textsubscript{2} group to the N,C-chelate backbone offers several advantages, such as the increased photoluminescence efficiency, inhibition of the excimer formations and facilitating the electron injection into the emissive layer/dopant, which all attribute to the improved device performance based on Pt(II) emitters.

For BMes\textsubscript{2} functionalized Ir-ppy compounds, Park,\textsuperscript{28} Wong and Marder\textsuperscript{29} et al., have demonstrated that the location of the BMes\textsubscript{2} group has a great impact on emission energy. As shown in Figure 2.1, placing the BMes\textsubscript{2} group on the phenyl ring, trans to the Ir(III) atom, significantly widens the HOMO–LUMO gap and blue-shifts the emission energy. In the previously studied BMes\textsubscript{2}-functionalized Pt(ppy)(acac) and its derivative compounds, the BMes\textsubscript{2} group was placed either at the pyridyl ring or the phenyl ring, meta to the Pt atom (Figure 2.1).\textsuperscript{27}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.1.png}
\caption{Literature example of BMes\textsubscript{2} functionalized Ir(III), Pt(II) complexes.}
\end{figure}

This chapter introduces three new boron-functionalized 2-phenylpyridine chelate Pt(II)
complexes (2.1-2.3), where the location of BMes₂ group on the phenyl ring is *para* to Pt(II), aiming to study the impact of the location of BMes₂ group on emission color. Secondly, a BMes₂-functionalized 3,5-dipyridylbenzene (dpb) N,C,N-chelate Pt(II) compound (2.4) was evaluated in terms of its PhOLEDs performance, since several N,C,N-chelate Pt(II) compounds have been shown previously to be very promising blue-green phosphorescent emitters for OLEDs.²²–²⁴

2.2 Experimental

2.2.1 General Procedures

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques unless otherwise noted. Solvents were dried using activated alumina column system, PURE SOLV, purchased from Innovative Technology Inc. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. NMR spectra were recorded on Bruker Avance 400, 500 or 600 MHz spectrometers. NMR Chemical shift values are reported relative to that of reference compound of tetramethyldisilane (TMS) for nuclei ¹³C and ¹H; BF₃.OEt₂ for nucleus ¹¹B. UV-Vis spectra were obtained on a Varian Cary 50 UV/Vis spectrometer. Elemental analyses were performed by the Laboratoire d’Analyse Élémentaire de l’Université de Montréal, Montreal, Quebec. Photoluminescent measurements were performed on Photon Technology International spectrometers. All solutions for photophysical experiments were degassed with nitrogen. Phosphorescence quantum yields were obtained relative to Ir(ppy)₃ in degassed CH₂Cl₂ at 298 K. Cyclic voltammetry was performed on a BAS CV-50W voltammetric analyzer with scan rates of either 50 or 100 mVs⁻¹ and with NBu₄PF₆ (0.10 M) as supporting electrolyte. The electrolytic cell used was a conventional three-compartment cell, with a Pt working electrode, Pt wire auxiliary electrode, and Ag/AgCl reference electrode. The ferrocenium/ferrocene couple (E₁/₂ = 0.55 V) was used as the internal standard.

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2.2.2 Synthesis of Ligands

2-(5’-Dimesitylboryl-6’-fluorophenyl)pyridine (2.7): n-Butyllithium (0.63 mL, 1.60 M in hexane, 1.00 mmol) was slowly added to a solution of 2-(2-fluoro-3-bromophenyl)pyridine (0.25 g, 1.00 mmol) (2.7) in THF at -78°C. The solution was then stirred for 1 h at -78°C before BMes₂F (0.30 g, 1.10 mmol) was added. The resulting solution was maintained at -78°C for an additional hour, then slowly warmed to room temperature and stirred overnight. The concentration of the solution under vacuum and further purification by chromatography on silica gel afforded the desired product in 80% yield. \(^1\text{H NMR (400 MHz, CD}_2\text{Cl}_2, 25°C, ppm): 8.76 (d, } J = 4.5 \text{ Hz, 1 H), 8.19 (t, } J = 8.0 \text{ Hz, 1 H), 7.79 (d, } J = 8.5 \text{ Hz, 1 H), 7.68 (t, } J = 7.0 \text{ Hz, 1 H), 7.39 (t, } J = 7.0 \text{ Hz, 1 H), 7.32 (t, } J = 7.5 \text{ Hz, 1 H), 7.23 (t, } J = 6.0 \text{ Hz, 1 H), 6.80 (s, 4 H), 2.36 (s, 6 H), 2.16 (s, 12 H).\]

The starting materials, (3-bromophenyl)dimesitylborationne and 2-(2’-(dimesitylboryl)phenyl)pyridine (2.9) were synthesized according to a literature procedure.\(^{28}\)

2-Bromo-6-dimesitylboryltoluene (2.10): A solution of n-butyllithium (6.00 mL, 1.60 M solution in hexane, 9.6 mmol) was added dropwise to a solution of 2,6-dibromotoluene (2.00 g, 8.00 mmol) in Et₂O (30 mL) at -78°C. The reaction mixture was maintained at this temperature for an additional hour, and then BMes₂F (2.57 g, 9.60 mmol) in Et₂O (50 mL) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred, overnight. The reaction mixture was quenched with water, and then extracted with CH₂Cl₂. The organic layers were combined and washed with water, dried over MgSO₄, and then filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica column chromatography by using hexane to give the product in 75% yield as a white solid. \(^1\text{H NMR (300 MHz, CDCl}_3, 25°C, ppm): 7.63 (d, } J = 7.8 \text{ Hz, 1 H), 7.05–7.15 (m, 2 H), 6.83 (s, 4 H), 2.32 (s, 6 H), 2.24 (s, 3}}
2-(5′-Dimesitylboryl-6′-methylphenyl)pyridine (2,6): A Schlenk flask was charged with 2-bromopyridine (0.87 g, 5.50 mmol) and dry THF (15 mL). This solution was cooled to -78°C, then n-butyllithium (4.1 mL, 1.60 M solution in hexane, 6.56 mmol) was added dropwise via syringe. The resulting solution was stirred at -78°C for 1 h. ZnCl$_2$(tmeda) (1.60 g, 6.60 mmol) in THF (66 mL) was added slowly at the same temperature via cannula. After 30 min at -78°C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Pd(PPh$_3$)$_4$ (0.32 g, 5 mol%) and (3-bromo-2-methylphenyl)dimesitylborane (2.32 g, 5.5 mmol) in THF (20 mL) were added to the reaction mixture. The reaction mixture was refluxed, overnight, and then cooled to room temperature. All volatiles were removed under reduced pressure, and the residue was then extracted with CH$_2$Cl$_2$. Organic layers were combined and washed with water, dried over MgSO$_4$, and then filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica column chromatography by using ethylacetate/hexane (1:3 v/v) to give the product in 50% yield as a white solid. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C, ppm): 8.68 (d, $J$ = 3.9 Hz, 1 H), 7.76 (td, $J$ = 7.8 Hz, $J$ = 1.8 Hz, 1 H), 7.44 (dd, $J$ = 6.0 Hz, $J$ = 2.7 Hz, 1 H), 7.38 (d, $J$ = 7.8 Hz, 1 H), 7.25 (m, 3 H), 6.84 (s, 4 H), 2.32 (s, 6 H), 2.20 (s, 3 H), 1.99 (s, 12 H).

1-Dimesitylboryl-3,5-dibromobenzene (2,12): A solution of n-butyllithium (2.0 mL; 1.60 M in hexane, 3.20 mmol) was slowly added to a solution of 1,3,5-tribromobenzene (1.00 g, 3.20 mmol) in THF at -78°C. The solution was then stirred for 1 h at -78°C before BMes$_2$F (0.94 g, 3.50 mmol) was added. The resulting solution was maintained at -78°C for an additional hour, then slowly warmed to room temperature and stirred, overnight. The concentration of the solution under vacuum and further purification by chromatography on silica gel gave a white solid. Recrystallization produced the product in 45% yield. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C, ppm):
7.82 (t, $J = 1.5$ Hz, 1 H), 7.53 (d, $J = 1.5$ Hz, 2 H), 6.83 (s, 4 H), 2.36 (s, 6 H), 2.02 (s, 12 H).

1-Dimesitylboryl-3,5-diprydylbenzene (2.8): Excess 2-(tributylstannyl)-pyridine (1.82 mL, 4.80 mmol), LiCl (0.40 g, 9.50 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.055 g, 0.08 mmol) were added to the toluene solution of 1-dimesitylboryl-3,5-dibromobenzene (0.95 mmol). The solution was then stirred and refluxed for 3 days under nitrogen. Purification through column chromatography by using CH$_2$Cl$_2$/hexanes afforded a white solid of Bdpb (2.8) (0.14 g, 30%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 8.91 (s, $J = 1.5$ Hz, 1 H), 8.72 (d, $J = 3.5$ Hz, 2 H), 8.20 (d, $J = 1.5$ Hz, 2 H), 7.80 (m, 4 H), 7.29 (t, $J = 1.5$ Hz, 2 H), 6.93 (s, 4 H), 2.38 (s, 6 H), 2.10 (s, 12 H).

2.2.3 Synthesis of Pt(acac) Complexes

BMe$_2$-functionalized Pt(acac) compounds were synthesized by the general procedure similar to the one reported recently for N,C-chelate Pt(acac) compounds.$^{31}$ A typical procedure is given below. [PtMe$_2$(SMe)$_2$]$_2$ and corresponding BMe$_2$-functionalized phenylpyridine were dissolved in THF (~5 mL) and then this mixture was stirred for 1 h at ambient temperature. Trifluoromethanesulfonic acid (TfOH) in THF was added slowly to this solution. After 30 min, Na(acac)·H$_2$O in methanol was added and stirred for 1 to 2 hours. The pale yellow precipitate formed was filtered and washed with Et$_2$O. An analytically pure BMe$_2$-functionalized Pt(ppy)(acac) was isolated in the range of 80~90% yield.

Synthesis of 2.1: Yield: 92%; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 9.24 (d, sat, $^3J = 5.6$ Hz, $J_{Pt-H} = 36$ Hz, 1 H), 7.81 (td, $J = 8.0$ Hz, $J = 1.6$ Hz, 1 H), 7.65–7.53 (m, 3 H), 7.28 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 1 H), 7.18 (td, $J = 6.4$ Hz, $J = 1.2$ Hz, 1 H), 6.87 (s, 4 H), 5.55 (s, 1 H), 2.35 (s, 6 H), 2.07 (s, 12 H), 2.06 (s, 3 H), 2.02 (s, 3 H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 186.2, 184.4, 167.9, 147.9, 147.2, 144.9, 140.7, 138.2, 131.2, 130.3, 128.2, 128.1, 121.5, 118.6, 102.3, 27.9, 26.9, 23.2, 20.9; elemental analysis calcd (%) for C$_{33}$H$_{35}$BNO$_2$Pt: C 57.99, H 5.16, N
Synthesis of Pt-Bmppy (2.2): Yield: 89%; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 9.10 (dd, sat, $J = 5.6$ Hz, $J = 1.2$ Hz, $J_{Pt-H} = 42$ Hz, 1 H), 7.79–7.74 (m, 2 H), 7.45 (d, sat, $J = 7.7$ Hz, $J_{Pt-H} = 28$ Hz, 1 H), 7.05 (td, $J = 7.2$ Hz, $J = 1.2$ Hz, 1 H), 6.84 (d, $J = 7.6$ Hz, 1 H), 6.70 (s, 4 H), 5.41 (s, 1 H), 2.40 (s, 3 H), 2.20 (s, 6 H), 1.93 (s, 12 H), 1.87 (s, 3 H), 1.45 (s, 3 H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 186.3, 184.4, 168.4, 147.8, 146.2, 143.8, 143.4, 140.2, 138.5, 137.9, 134.8, 128.2, 128.0, 123.2, 120.8, 102.2, 28.0, 26.9, 22.8, 20.9 ppm; elemental analysis calcd (%) for C$_{34}$H$_{37}$BNO$_2$Pt: C 58.54, H 5.35, N 2.01; found: C 58.52, H 5.38, N 2.05.

Synthesis of Pt-Bfppy (2.3): The Pt complex was synthesized the same way as indicated in the literature.$^{13}$ Bright yellow crystals were obtained after recrystallization from DCM/hexane. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 9.11 (d, $J = 0.5$ Hz, 1 H), 8.02 (d, $J = 8.5$ Hz, 1 H), 7.86 (t, $J = 8.0$ Hz, 1 H), 7.45 (d, $J = 8.5$ Hz, 1 H), 7.20 (t, $J = 7.5$ Hz, 1 H), 7.06 (t, $J = 7.5$ Hz, 1 H), 6.85 (s, 4 H), 5.54 (s, 1 H), 2.33 (s, 6 H), 2.10 (s, 12 H), 1.75 (s, 3 H), 1.15 (s, 3 H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 186.4, 184.5, 147.4, 140.2, 138.8, 138.5, 137.6, 137.5, 128.1, 126.4, 123.4, 123.2, 121.6, 102.4, 27.9, 26.8, 22.8, 20.9 ppm; elemental analysis calcd (%) for C$_{34}$H$_{35}$BFNO$_2$Pt: C 57.15, H 4.94, N 1.96; found: C 56.97, H 4.95, N 1.87.

Synthesis of Pt-(Bdpb)Cl (2.4): compound 2.8 (0.029 g, 0.06 mmol) and K$_2$PtCl$_4$ (0.028 g, 0.066 mmol) were stirred in degassed an acetonitrile and water (3:1; 5 mL) mixture at 90 °C, overnight. After removal of the solvent and further recrystallization from hexane/CH$_2$Cl$_2$, orange crystals of the complex 2.4 were obtained (0.04 g, 94%). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, ppm): 9.40 (d, sat, $J = 1.0$ Hz, $J_{Pt-H} = 60$ Hz, 1 H), 7.92 (td, $J = 10$ Hz, $J = 1.5$ Hz, 2 H), 7.65 (d, $J = 10$ Hz, 2 H), 7.61 (s, 2 H), 7.31 (td, $J = 8.0$ Hz, $J = 1.5$ Hz, 2 H), 6.87 (s, 4 H), 2.36 (s, 6 H), 2.07 (s, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C, ppm): 168.4, 167.2, 152.2, 141.6, 141.0,
140.8, 139.2, 138.7, 132.5, 128.3, 123.2, 119.6, 23.6, 21.3; elemental analysis calcd (%) for C34H32BClN2Pt: C 57.52, H 4.54, N 3.95; found: C 57.02, H 4.37, N 3.85.

2.2.4 EL Device Fabrication

Devices were fabricated in a Kurt J. Lesker LUMINOS® cluster tool with a base pressure of approximately 10^{-8} Torr without breaking vacuum. The ITO anode is commercially patterned and coated on glass substrates 50×50 mm^2 with a sheet resistance less than 15 Ω. Substrates were ultrasonically cleaned with a standard regiment of Alconox®, acetone, and methanol followed by UV ozone treatment for 15 min. The active area for all devices was 2 mm^2. The film thicknesses were monitored by a calibrated quartz crystal microbalance and were further verified for single-carrier devices by using capacitance-voltage measurements (Agilent 4294A). I-V characteristics were measured by using a HP4140B picoammeter in ambient air. Luminance measurements and EL spectra were taken by using a Minolta LS-110 luminance meter and an Ocean Optics USB200 spectrometer with bare fiber, respectively. The external quantum efficiency of EL devices was calculated following the standard procedure. After deposition, single carrier devices were transferred to a homebuilt variable temperature cryostat for measurement at 298 K. Additional details regarding device fabrication, and characterization have been described elsewhere.

2.2.5 X-ray Crystallography Analysis

Single crystals were mounted on glass fibers and were collected on a Bruker Apex II single crystal X-ray diffractometer with graphite monochromated Mo Kα radiation, operating at 50 kV and 30 mA and at 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package (version 6.14) and corrected for absorption effects. All non-hydrogen atoms were refined anisotropically. CCDC 875462 (2.1), 875463 (2.2), 875464 (2.4) and 875465 (2.3) contain the supplementary crystallographic data, which can be obtained free of
charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2.6 DFT Calculations

DFT calculations were performed using Gaussian 03 software at the theory level of B3LYP functional with basis set of 6-31G* for all atoms except Pt, for which LANL2DZ was used.

2.3 Results and Discussion

2.3.1 Synthesis

Figure 2.2 Synthetic routes for ligands 2.1, 2.2, 2.3 and 2.4.

Reagents and conditions: a) n-BuLi/Et₂O, B(Mes)₂F, -78 °C, then room temperature, overnight; b) 2-Br-pyridine, n-BuLi, ZnCl₂(tmeda)₂, Pd(PPh₃)₄, THF, reflux, overnight; c) 2-Br-pyridine, K₂CO₃, THF, Pd(PPh₃)₄, 70 °C, 7 h; d) n-BuLi/Et₂O, BMes₂F, -78°C, then room temperature, overnight; e) [PtMe₂(SMe₂)]₂, CF₃SO₂H, Na(acac)-H₂O, room temperature, 1 to 2 h; f) (2-Bu₃Sn)pyridine, LiCl, Pd(PPh₃)₂Cl₂, toluene, reflux, 3 days; g) K₂PtCl₄, CH₃CN/H₂O (3:1), 90 °C, overnight.
Pt complexes, 2.1–2.3 were obtained in high yields (80–90%) involving a one-pot reaction of the appropriate ligand (2.5–2.7) with [PtMe₂(SMe₂)]₂, without isolation of any intermediates. The synthesis of the BMe₅₂-functionalized N,C,N-chelate ligand 1-dimesitylboryl-3,5-dipyridylbenzene (2.8) was accomplished by Stille coupling of excess 2-(tributylstannyl)pyridine with 3,5-dibromophenyldimesitylborane using Pd(PPh₃)₂Cl₂ as the catalyst. Compound 2.4 was synthesized and isolated in 94% yield from the treatment of 2.8 with K₂PtCl₄ in a mixed solvent of CH₃CN and water at 90 °C. All compounds are stable in air and soluble in common organic solvents but not in pentane, hexane and methanol.

2.3.2 Crystal Structure

The structures of compounds 2.1-2.4 are shown in 2.3. Important bond distances and angles are shown in Table 2.1.

![Crystal structures of 2.1, 2.2, 2.3 and 2.4](image)

**Figure 2.3** Crystal structures of 2.1, 2.2, 2.3 and 2.4 (from left to right) with 50% thermal ellipsoids and labels of key atoms. Hydrogen atoms are omitted for clarity.

For compound 2.1, three independent molecules are located in the asymmetric unit with similar bond distances and angles. For 2.4, two independent molecules are located in the asymmetric unit with similar bond distances and angles. Despite the variation of the R group in structures of 2.1–2.3, the bond lengths and bond angles around the Pt(II) atoms are similar. The
dihedral angle between the BC₂(mesityl) plane and the phenyl ring of the ppy chelate for these three compounds are also similar (21.4°, 22.0° and 24.6° in 2.1; 23.6° in 2.2; and 23.7° in 2.3); this indicates that the change of the R group from H atom to a methyl group does not have a significant impact on the conjugation of the BMes₂ group with the phenyl ring of the ppy chelate. The dihedral angles between the phenyl and the pyridyl ring of the ppy ligand are 5.9(5)°, 4.4(5)° and 3.0(5)° for 2.1, 12.5(7)° for 2.2 and 3.0(3)° for 2.3, respectively. The increase of this dihedral angle from 2.1 to 2.2 is clearly caused by the steric effect of the methyl substitution in 2.2. Interestingly, however, this dihedral angle for compound 2.3 is close to those of 2.1 and much less than that of 2.2, which appears to be the result of strong intramolecular hydrogen bonding between fluorine and hydrogen atoms of both mesityl and pyridine ring. These small dihedral angles prove the presence of effective π conjugation of the ppy chelate in all three compounds. For compounds 2.1–2.3, the Pt-O bond trans to the Pt-C bond is slightly longer than that trans to the Pt-N bond, attributable to the greater trans effect exerted by the carbon atom.

<table>
<thead>
<tr>
<th>Table 2-1 Selected bond lengths (Å) and angles (°) for compounds 2.1–2.4.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 2.1</td>
</tr>
<tr>
<td>Pt(1)-N(1)                                      1.992 (9)</td>
</tr>
<tr>
<td>Pt(1)-O(1)                                      1.992 (9)</td>
</tr>
<tr>
<td>C(1)-Pt(1)-O(1)                                  175.8 (4)</td>
</tr>
<tr>
<td>Compound 2.2</td>
</tr>
<tr>
<td>Pt(1)-N(1)                                      1.990 (9)</td>
</tr>
<tr>
<td>Pt(1)-O(1)                                      2.015 (8)</td>
</tr>
<tr>
<td>C(1)-Pt(1)-O(2)                                  174.8 (4)</td>
</tr>
<tr>
<td>Compound 2.3</td>
</tr>
<tr>
<td>Pt(1)-N(1)                                      1.986 (4)</td>
</tr>
<tr>
<td>Pt(1)-O(1)                                      1.998 (3)</td>
</tr>
<tr>
<td>C(1)-Pt(1)-O(2)                                  175.08 (16)</td>
</tr>
<tr>
<td>Compound 2.4</td>
</tr>
<tr>
<td>Pt(1)-N(1)                                      2.024 (3)</td>
</tr>
<tr>
<td>Pt(1)-C(11)                                     1.905 (4)</td>
</tr>
<tr>
<td>N(1)-Pt(1)-N(2)                                  161.10 (13)</td>
</tr>
</tbody>
</table>

54
Complex 2.1 forms a stacked dimer in the solid state with the pyridyl ring being directly above the Pt-acac chelate. The shortest Pt⋯C$_{py}$ separation distances in the dimer of 2.1 are found to be 3.64–3.67 Å and the Pt⋯Pt separation distances to be 4.64–4.67 Å (Figure 2.4).

![Packing diagram showing the intermolecular interactions of 2.1.](image)

(C-H⋯π interactions are indicated as dashed line, with distances of H84⋯Cg$_1$ 2.89 Å; H96A⋯Cg$_2$ 3.00 Å, respectively. Cg$_1$ and Cg$_2$ mean the centroids of aromatic rings).

Complex 2.2 also forms a similar stacked dimer with Pt⋯C$_{py}$ separation distance of 3.64 Å and a Pt⋯Pt separation of 4.64 Å (Figure 2.5). For complexes 2.1 and 2.2 the stacking intermolecular interactions are limited to the discrete dimer and no extended stacking was observed in the crystal lattice.
Figure 2.5 Packing diagram showing the intermolecular interactions of 2.2.

(C-H⋯π interactions are indicated as dashed line, with distances of H30B⋯Cg1 3.04 Å; H21B⋯Cg2 3.04 Å; H9⋯Cg1 2.82 Å; H29C⋯Cg2 3.13 Å respectively. Cg1 and Cg2 mean the centroids of aromatic rings).

Complex 2.3 (Figure 2.6) forms a stacked dimer but with a much shorter Pt⋯C\textsubscript{py} separation distance (3.38 Å) and a Pt⋯Pt separation of 4.70 Å similar to those of 2.1 and 2.2. Furthermore, the molecules of 2.3 display extended stacking with short interdimer C\textsubscript{py}⋯C\textsubscript{py} separation distance of approximately 3.26 Å and a long Pt⋯Pt separation of 6.87 Å.

Figure 2.6. Packing diagram showing the intermolecular interactions of 2.3 (Pt⋯Pt separation of 4.70 Å).
Thus, among N,C-chelate complexes 2.1–2.3, the fluoro-substituted compound is most prone to intermolecular stacking interactions. This is consistent with our earlier observation for the fluoro derivative of PtppyB (Figure 2.1) that dimerizes with a short Pt⋯Pt separation distance of 3.404(1) Å.\textsuperscript{27} However, compared to PtppyB, PtBppy (Figure 2.1) and their derivatives, which have the tendency to form dimers that stack directly along the Pt⋯Pt vector, leading to very short Pt⋯Pt separation distances and strong Pt⋯Pt interactions, none of compounds 2.1–2.3 shows similar Pt⋯Pt interactions. In fact, all intermolecular interactions in 2.1–2.3 are between the pyridyl ring and the Pt center.

![Packing diagram showing the intermolecular interactions of 2.4.](image)

(Intermolecular C-H⋯Cl interactions are indicated as dashed line with distances around 2.81-2.91 Å)

As shown in Figure 2.7, the N,C,N-chelate complex 2.4 also forms a stacked dimer in the crystal lattice with the pyridyl ring being located directly above the Pt atom. A short interdimer Pt⋯Cpy separation distance of 3.64 Å and a short C⋯C separation distance of 3.55 Å between the py ring and the central phenyl ring are observed. The Pt⋯Pt separation distance in the dimer of 2.4 is very long (5.70 Å) and no further extended stacking interactions are evident. The lack of
direct Pt···Pt interactions in these new BMes₂-functionalized Pt(II) compounds can be attributed to the presence of the bulky boron group at the 5'-position, which inhibits the formation of excimer in either solid state or thin film.

2.3.3 Thermal Property

Due to the fact that small molecule-based OLEDs are fabricated by vacuum deposition at elevated temperature, it is critical for materials used in OLEDs to have a high thermal stability. Differential scanning calorimetric diagrams were recorded for complexes 2.1–2.3 to investigate their thermal properties. Although none of the compounds show glass transitions in both the first and second heating/cooling cycles, they do display a high thermal stability with a crystallization temperature at approximately 250 °C (with the order of 2.1>2.2>2.3). As shown in Figure 2.8, these compounds are thermally stable up to their melting points (>300 °C).

![Figure 2.8](image)

**Figure 2.8** Differential scanning calorimetric data of 2.1, 2.2, and 2.3.

2.3.4 Photophysical and Electrochemical Properties

Complexes 2.1-2.3 all display a distinct but weak absorption band around 350-450 nm (Figure 2.9), which may be attributed MLCT transitions. Compound 2.4 has a well-resolved absorption band with a moderate intensity at 387 nm, which may be assigned to intraligand
charge transfer transition. The main absorption band at approximately 330 nm for \textbf{2.1-2.3}, which is attributed to \(\pi-\pi^*\) transitions of the N,C-chelate ligands, is similar to that observed in \textbf{PtBppy}. Similar to compounds \textbf{PtBppy}, compounds \textbf{2.1-2.3} exhibit bright luminescence with quantum efficiencies ranging from 0.43–0.26 in solution and 0.35 to 0.21 in the solid state. In contrast, the quantum efficiency of the non-borylated Pt(ppy)(acac) compound is only 0.15.\textsuperscript{35} The phosphorescent decay lifetimes of \textbf{2.1-2.3} are similar to that of \textbf{PtBppy}.

![Absorption and emission spectra of \textbf{2.1-2.4} in CH\textsubscript{2}Cl\textsubscript{2} at 298 K.](image1)

\textbf{Figure 2.9} Absorption and emission spectra of \textbf{2.1-2.4} in CH\textsubscript{2}Cl\textsubscript{2} at 298 K.

![Emission spectra of \textbf{2.1-2.4} in the solid state at 298 K (10% wt PMMA film).](image2)

\textbf{Figure 2.10} Left: emission spectra of \textbf{2.1-2.4} in the solid state at 298 K (10% wt PMMA film). Right: photos showing the emission color of \textbf{2.1-2.4} in CH\textsubscript{2}Cl\textsubscript{2} (top) and in PMMA film (10 wt\%, bottom) under 365 nm irradiation.
However, compared to PtBppy with emission maximum at 538 nm, the emission energy of 2.1-2.3 is significantly blue-shifted with the emission maximum at 478, 485 and 470 nm, respectively (Figure 2.8 and Table 2.2). The impact of the BMes₂ position on the emission energy of the Pt(II) compounds follows the same trend as that observed for the Ir(III) compounds. Furthermore, the emission colors of 2.1–2.3 do not change significantly from solution to the solid state (Table 2.2 and Figure 2.10), which indicates that the intermolecular interactions observed in the crystal structures do not have any significant impacts on the luminescence of these complexes. Among compounds 2.1–2.3 the fluoro-substituted compound 2.3 has the shortest emission wavelength whereas the methyl-substituted compound 2.1 has the longest emission wavelength, differing by approximately 15 nm.

<table>
<thead>
<tr>
<th></th>
<th>Absorption ( \lambda_{\text{max}} [\text{nm}] ), ( \varepsilon [10^4 \text{M}^{-1} \text{cm}^{-1}] )</th>
<th>Emission, 298K, Solution / Solid</th>
<th>Emission, 77K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>271 (1.85), 327 (3.01), 344 (2.13)</td>
<td>481/476, 8.7(2)/9.5(3)</td>
<td>478, 9.4(1)</td>
</tr>
<tr>
<td>2.2</td>
<td>282 (2.40), 328 (3.33), 349 (2.56)</td>
<td>492/487, 8.7(2)/8.7(1)</td>
<td>485, 12.2(2)</td>
</tr>
<tr>
<td>2.3</td>
<td>274 (2.10), 331 (3.56), 343 (2.71)</td>
<td>475/472, 9.6(2)/7.2(2)</td>
<td>470, 10.2(7)</td>
</tr>
<tr>
<td>2.4</td>
<td>283(3.10), 334(3.20), 387(0.87)</td>
<td>485/489, 8.9(2)/6.6(2)</td>
<td>490, 9.5(1)</td>
</tr>
</tbody>
</table>

- The absorption spectra were measured in degassed CH₂Cl₂ solution; [M]=8.0 \( \times 10^{-5} \). Doped into PMMA at 10 wt%.
- Phosphorescence quantum efficiency measured in CH₂Cl₂, relative to Ir(ppy)₃ (Φ = 1.0). Solid state quantum efficiency was measured using an integration sphere (error range ±10% of the reported value).
- In frozen CH₂Cl₂ glass.
- The reduction potentials of all compounds were measured in DMF with 0.10 M NBu₄PF₆ at a scan rate of either 50 mVs⁻¹ or 100 mVs⁻¹ (vs. FeCp₂⁺⁻⁻).
The emission spectrum of 2.4 closely resembles that of the non-borylated Pt(dpb)Cl parent molecule, as shown by Figure 2.11, indicating that the phosphorescence of these two molecules share a common origin, which is most likely a mixed ligand-centered π-π* and MLCT transitions, as established previously for Pt(dpb)Cl.\textsuperscript{35} Compared to Pt(dpb)Cl, the emission maximum of 2.4 is blue-shifted by a few nanometers with a significantly enhanced emission efficiency (0.70 in solution, versus 0.60 of Pt(dpb)Cl). Furthermore, unlike Pt(dpb)Cl, which has a very poor solubility in common organic solvents and a strong tendency to produce excimer emission in both concentrated solution and the solid state due to strong intermolecular interactions,\textsuperscript{36} the emission of 2.4 does not change significantly with concentration in solution or from the solution to the solid state. The bulky BMes\textsubscript{2} clearly plays a role in minimizing intermolecular interactions of 2.4.

![Absorption and emission spectra](image)

**Figure 2.11** Absorption (left) and emission (right) spectra of compound 2.4 and Pt(dpb)Cl in CH\textsubscript{2}Cl\textsubscript{2}, recorded under the same conditions.

Using the following two equations (eq. 1 and 2), the values for the radiative ($k_r$) and non-radiative ($k_{nr}$) decay rates for all four new Pt(II) compounds were determined and compared in Figure 2.12.
\[ \Phi_{PL} = k_r / (k_r + k_{nr}) \quad (1) \]
\[ 1/\tau = k_r + k_{nr} \quad (2) \]

While the \( k_r \) values are comparable to one another for 2.1, 2.2 and 2.3, the \( k_{nr} \) value of the highly emissive 2.4 is considerably smaller than those of 2.1, 2.2 and 2.3. Thus, the high \( \Phi_{PL} \) value for 2.4 can be attributable to the suppression of the non-radiative decay processes. Interestingly, the \( k_r \) values of 2.1 - 2.3 are similar with that of Pt(ppy)(acac) (5.7 \times 10^4 \text{ s}^{-1}), while the \( k_{nr} \) values of 2.1-2.3 are almost 5 times smaller than that of Pt(ppy)(acac) (3.2 \times 10^5 \text{ s}^{-1}).[13], [15] These results strongly indicate that the BMes_2 unit introduced into the ppy ligand significantly retards the non-radiative decay process, leading to improved PL efficiency.

![Figure 2.12 Rate constants of \( k_r \) and \( k_{nr} \) for 2.1, 2.2, 2.3 and 2.4.](image)

To understand the origin of the phosphorescence blue shift and the substitution effect observed in compounds 2.1-2.4, electrochemical properties of these compounds were examined by cyclic voltammetry. All four compounds display a reversible reduction peak at \( E_{1/2}^{\text{red}} = -2.34, -2.36, -2.27 \) for 2.1-2.3, respectively, relative to FeCp_2\(^+\)/0 (4.8 eV below vacuum). Using the reduction potentials and the energy of the absorption edge, HOMO and LUMO energies for compounds 2.1-2.4 were estimated and shown in Table 2.3.
The impact of the BMes$_2$ substitution and location can be illustrated by comparing compound **2.1, PtBppy** (HOMO = -5.45 eV, LUMO = -2.78 eV)$^{[7a]}$ and Pt(ppy)(acac) (HOMO = -5.31 eV, LUMO = -2.41 eV)$^{[13]}$. The attachment of BMes$_2$ to the ppy chelate leads to the decrease of both LUMO and HOMO levels as shown by Figure 2.13. However, the decrease of the LUMO level of **PtBppy** is much more pronounced than that of **2.1**, thus supporting that BMes$_2$ substitution at the 4’-position of the phenyl ring is more effective to achieve high phosphorescence energy. Among compounds **2.1 – 2.3**, the electron-withdrawing fluoro group significantly stabilizes the HOMO level and the LUMO level as well in **2.3** albeit to less a degree, leading to the highest emission energy. In contrast, the electron-donating methyl group in **2.2** destabilizes the HOMO level but does not change the LUMO level significantly, resulting in the lowest emission energy among the three compounds. The influence of the fluoro and the methyl group on HOMO and LUMO energies may be attributed to the electronic induction effect. These data support that the introduction of a BMes$_2$ group at the 4’-position of the ppy ligand is an effective approach in shifting the emission energy of phosphorescent Pt(II) compounds toward blue.

![Figure 2.13](image.png)

**Figure 2.13** Comparison of experimental HOMO and LUMO energy levels of **2.1 – 2.3** with Pt(ppy)(acac) and PtBppy.
Table 2-3 Experimental data of HOMO/LUMO energy and DFT calculation results.

<table>
<thead>
<tr>
<th>Complex</th>
<th>HOMO (eV)(^a)</th>
<th>LUMO (eV)(^b)</th>
<th>(E_g) (eV)</th>
<th>HOMO (eV)(^c)</th>
<th>LUMO (eV)(^c)</th>
<th>HOMO-LUMO gap (eV)</th>
<th>%HOMO (\rightarrow) LUMO ((S_0 \rightarrow S_1))</th>
<th>Oscillator strength ((S_0 \rightarrow S_1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>-5.49</td>
<td>-2.57</td>
<td>2.92</td>
<td>-5.54</td>
<td>-1.67</td>
<td>3.87</td>
<td>78</td>
<td>0.0414</td>
</tr>
<tr>
<td>2.2</td>
<td>-5.36</td>
<td>-2.54</td>
<td>2.82</td>
<td>-5.42</td>
<td>-1.64</td>
<td>3.78</td>
<td>79</td>
<td>0.0314</td>
</tr>
<tr>
<td>2.3</td>
<td>-5.61</td>
<td>-2.64</td>
<td>2.97</td>
<td>-5.62</td>
<td>-1.73</td>
<td>3.89</td>
<td>85</td>
<td>0.0239</td>
</tr>
<tr>
<td>2.4</td>
<td>-5.60</td>
<td>-2.82</td>
<td>2.78</td>
<td>-5.56</td>
<td>-1.98</td>
<td>3.58</td>
<td>86</td>
<td>0.0283</td>
</tr>
</tbody>
</table>

\(^a\)Calculated using the reduction potential and the optical energy gap \((E_g)\); \(E_g\) was determined from absorption edge. \(^b\)Estimated using the reduction potential. \(^c\)HOMO and LUMO energies were determined by DFT calculation.

For compound 2.4, the reduction potential is at -2.09 V, slightly more positive than that\(^{14}\) of the non-borylated Pt(dpb)Cl (-2.14 V). Because the HOMO-LUMO gaps of 2.4 and Pt(dpb)Cl are similar, the addition of the BMes\(_2\) group to the N,C,N-chelate must decrease both the LUMO and the HOMO level, thus maintaining the same HOMO-LUMO gap.

To further understand the photophysical properties of these materials, TD-DFT calculations were performed to provide an insight into their electronic structures.\(^{16}\) The computational results show that the \(S_0 \rightarrow S_1\) transitions arise predominantly from the HOMO and LUMO with reasonable oscillator strengths (Table 2.3). Hence, the discussion herein will focus on these orbitals (Figure 2.14). The trends in the calculated and observed energy gaps are in reasonably good agreement. The HOMO levels of 2.1-2.3 have significant contributions from the \(d\) orbital of the Pt atom, some minor contributions from the acac ligand and major contributions from the phenyl ring of the ppy chelate. It should be noted that there is a large contribution by the carbon atom at the 4’ \((para\) to Pt) position of the phenyl ring at the HOMO level. In contrast, at the LUMO level, the contribution from the 4’-carbon atom is very small. Thus, substitution by an electron-withdrawing BMes\(_2\) group at this position should be very effective in stabilizing the
HOMO level via both induction effect and $\pi$-conjugation while minimizing the impact on the LUMO level. This explains the observed increase of the HOMO-LUMO gap and emission energy of compounds 2.1-2.3, compared to Pt(ppy)(acac). In contrast, the impact of BMes$_2$ substitution at the 5’-position of the phenyl ring to the HOMO level is much less due to the small orbital/electron density contribution at the 5’-position while the LUMO level can be significantly stabilized by the boron center due to the large contribution at the 5’-position in the LUMO level.

<table>
<thead>
<tr>
<th></th>
<th>2.1</th>
<th>2.2</th>
<th>2.3</th>
<th>2.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO</td>
<td><img src="image1" alt="Image 360x275 to 450x371" /></td>
<td><img src="image2" alt="Image 360x275 to 450x371" /></td>
<td><img src="image3" alt="Image 360x275 to 450x371" /></td>
<td><img src="image4" alt="Image 360x275 to 450x371" /></td>
</tr>
<tr>
<td>Energy</td>
<td>-1.67 eV</td>
<td>-1.64 eV</td>
<td>-1.73 eV</td>
<td>-1.98 eV</td>
</tr>
<tr>
<td>HOMO</td>
<td><img src="image5" alt="Image 360x275 to 450x371" /></td>
<td><img src="image6" alt="Image 360x275 to 450x371" /></td>
<td><img src="image7" alt="Image 360x275 to 450x371" /></td>
<td><img src="image8" alt="Image 360x275 to 450x371" /></td>
</tr>
<tr>
<td>Energy</td>
<td>-5.54 eV</td>
<td>-5.42 eV</td>
<td>-5.62 eV</td>
<td>-5.56 eV</td>
</tr>
</tbody>
</table>

**Figure 2.14** Diagrams showing the surfaces and energies of frontier orbitals for 2.1-2.4 plotted with an isocontour value of 0.02.
For 2.4, the LUMO level is dominated by the empty $p$ orbital of the boron atom and the $\pi^*$ orbital of the N,C,N-chelate while the HOMO level has major contributions from the central benzene ring, the Pt atom and the chloro ligand. Thus, the electronic transition of the first excited state of compound 2.4 may be considered as a mixture of intra-ligand charge transfer, metal-to-ligand charge transfer and $\pi$ to $\pi^*$ transition of the chelate ligand. The carbon atom at the 4’-position of the benzene ring in 2.4 has a very large contribution to the HOMO level but has no contributions at all to the LUMO level. The influence of the BMes$_2$ group to the LUMO level is therefore limited to induction effect. It can, however, effectively stabilize the HOMO level via both induction effect and $\pi$-orbital overlap with the carbon atom at 4’-position of the benzene ring. Based on this analysis, the slight widening of the HOMO-LUMO gap in 2.4 relative to that of Pt(dpb)Cl is caused mainly by the stabilization of the HOMO level through the boron atom.

2.3.5 Electroluminescence

Complexes 2.1, 2.3 and 2.4 were selected for the evaluation of performance in electroluminescent devices due to their relatively high phosphorescence energy and efficiency. The devices we fabricated have a double-layer structure with CBP (4,4’-N,N’-dicarbazolebiphenyl) as hole-transport layer (HTL) and host and TPBI (1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene) as the electron-transport layer (ETL) as shown in Figure 2.15. This device structure has been used successfully recently for green Pt(II) phosphorescent emitters by the Lu group.$^{17}$ A transition metal oxide hole injection layer, such as MoO$_3$, raises the work function of the ITO anode sufficiently so as to allow direct charge injection into the host material, eliminating the need for a discrete hole-transport layer (HTL).$^{37}$
Using the double-layer device structure design, a series of EL devices were fabricated with varying doping levels of the Pt(II) compound in the CBP layer at 2%, 4%, 8% and 12%, respectively. No excimer emission was observed for any of the devices. For compounds 2.3 and 2.4 the best performance was achieved at a doping level of 12% while for 2.1 the device has slightly better performance at a doping level of 8% than that of 12%. For comparison purpose, the performances of EL devices at the 12% doping level for all three emitters are summarized in Table 2.4. The EL spectra of these devices ($\lambda_{\text{max}} = 483$ nm for device with 2.1 as dopant, 478nm...
with 2.3 and 493 nm with 2.4) are shown in Figure 2.16, which match very well with the PL spectra of complexes 2.1, 2.3 and 2.4.

![Figure 2.16](image)

**Figure 2.16** Left: EL spectra of devices with Pt compounds 2.1, 2.3, and 2.4 as the phosphorescent dopant, respectively. Right: The J-L-V characteristics of devices.

![Figure 2.17](image)

**Figure 2.17** The external quantum efficiencies of EL devices versus luminance (left) and current density (right).

As shown by Figure 2.17, the EL devices based on compounds 2.1, 2.3 and 2.4 have impressive performance. For 2.1 and 2.3, the turn-on voltage of the devices is about 3.5 V while for 2.4 it is 2.8 V with maximum brightness reaching 3025 cd/m$^2$ and 2765 cd/m$^2$, respectively.
At the 12% doping level, the external quantum efficiencies of devices 2.1 and 2.3 at 100 cd/m$^2$ are 4.7% and 6.5%, respectively. At the 8% doping level, the EQE of the EL device of 2.1 is 5.7% at 100 cd/m$^2$ with a maximum brightness of 3340 cd/m$^2$. Although the device efficiencies of 2.1 and 2.3 are lower than the green PhOLEDs based on PtBppy our group reported previously,$^27$ it is certainly among the most efficient bluish-green PhOLEDs based on Pt(acac) compounds. The relatively low external quantum efficiencies of EL devices of 2.1 and 2.3 can be attributed to the relatively low photoluminescent quantum efficiencies of 2.1 and 2.3, compared to that of Pt(BppyA)(acac) (0.98 in CH$_2$Cl$_2$). In fact, taking the photoluminescent quantum efficiency (0.25 in CH$_2$Cl$_2$) of 2.3 into consideration, the EQE of EL device 2.3 is close to the commonly accepted theoretical limit for typical OLEDs.$^{38-40}$ Most significant is that the EL devices based on 2.1 and 2.3 maintain the high efficiency at high brightness and high current density and show little tendency of high current “roll-off” often observed in OLEDs.

The EL devices based on compound 2.4 have the most impressive performance as shown by Figure 2.16 and Table 2.4. At the 12% doping level, the device EQE is 15.3% at 10 cd/m$^2$ luminance and 13.4 cd/m$^2$ at 100 cd/m$^2$ luminance with a brightness of 2417 cd/m$^2$ at 9 V. At the 8% doping level, the device performance remains impressive with EQE of 16.1% at 10 cd/m$^2$ luminance and 10.6 cd/m$^2$ at 100 cd/m$^2$ luminance, respectively, and a brightness of 2242 cd/m$^2$ at 9.2 V. Efficient blue-green and green PhOLEDs based on Pt(dpb)Cl and its derivatives have been demonstrated previously by Williams and others.$^{12,22-24,36}$ Compared to the previously reported Pt-N,C,N compounds-doped EL devices, the performance of the EL devices based on compound 2.4 is certainly much better in terms of device efficiency, thus demonstrating that the BMes$_2$ group is also highly effective in enhancing the performance of N,C,N-chelate Pt(II) compounds.
2.4 Conclusion

This chapter has demonstrated that substitution by a BMes$_2$ group in a ppy chelate ligand is a highly effective strategy to enhance the phosphorescent efficiency of the corresponding Pt(acac) compounds. The location of the BMes$_2$ group on the ppy has a dramatic impact on the phosphorescent energy. Substitution at the 4’ position of the phenyl ring of ppy by BMes$_2$ has been found to effectively shift the phosphorescent emission energy of the Pt(II) compound to the blue-green region, which can be further tuned by a substituent at the 3’ position. BMes$_2$ substitution on the dipyridylbenzene N,C,N-chelate ligand does not significantly change the phosphorescent energy of the Pt(II) compound, it does however increase phosphorescent quantum efficiency, minimize excimer emission and greatly enhance the performance of the EL devices. High performance bluish-green EL devices using a simple double-layer structure and compounds 2.1, 2.3 and 2.4 as the dopants have been achieved, demonstrating once again the important role played by the BMes$_2$ group in achieving high efficiency PhOLEDs.
2.5 Notes and References

The work outlined in this chapter has been published as:


References:


Chapter 3

Impact of a Bisthienyl Unit on the Photostability of N,C-Chelating Boron Compounds

3.1 Introduction

π-Conjugated organoboron compounds have been widely used as electron transporting/emitting materials in OLEDs and optoelectronics devices. Yamaguchi and co-workers have demonstrated that the chelation of a BAr₂ group to a π-conjugated backbone can greatly improve the electron transporting property of the conjugated material. Nonetheless, dimesitylboron (BMes₂) compounds with a N,C-chelate conjugated backbone are highly prone to photoisomerization, triggered by a charge transfer transition from the BMes₂ moiety to the chelate backbone. Such a photoisomerization phenomenon may find use in photochromic applications but is certainly not desirable if the boron containing compounds are intended for use as either charge transport or emissive materials in optoelectronic devices. As discussed in Chapter 1.4.2, the efficiency of the photoisomerization process is highly dependent on the extent of π-conjugation and the linker in the backbone.

Based on the consideration that oligothiophene units have a low-lying $\pi - \pi^*$ state, which is mainly responsible for their ability to enhance charge mobility and electron transporting property of π-conjugated materials, this chapter reports the synthesis and investigation of monoboryl and diboryl N,C-chelate compounds that contain one or two thienyl units as shown in Figure 3.1 to further understand the impact of π-conjugated linkers.
3.2 Experimental

3.2.1 General Procedures

Experimental techniques for synthesis, the use of instrumentation are as described in Chapter 2.2.1.

3.2.2 Synthesis of 3.1

\( n \)-BuLi (9.6 mL, 6.0 mmol) was added slowly to a solution of 2-(5-(trimethylsilyl)furan-2-yl)pyridine (1.4 g, 6.0 mmol) in THF (50 mL) at \(-78 \, ^\circ\text{C}\), and the resulting solution was stirred for about 1 h at \(-78 \, ^\circ\text{C}\). Then BMes_2F (1.8 g, 6.0 mmol) was added under a stream of nitrogen and the solution was stirred at \(-78 \, ^\circ\text{C}\) for one hour, then warmed up to r.t. overnight. Solvent was removed under reduced pressure and then purified by chromatography (CH_2Cl_2–hexane = 1:4) to give a yellow powder, which was crystallized from CH_2Cl_2–hexane to yield yellow crystals of 3.1 (yield 70%). \(^1\text{H}\) NMR (CD_2Cl_2, 25 °C, ppm): 8.47 (d, \( J = 6.0 \, \text{Hz}, 1 \, \text{H}\)), 7.92 (t, \( J = 7.5 \, \text{Hz}, 1 \, \text{H}\)), 7.62 (d, \( J = 8.0 \, \text{Hz}, 1 \, \text{H}\)), 7.41 (s, 1 H), 7.10 (t, \( J = 6.5 \, \text{Hz}, 1 \, \text{H}\)), 6.69 (s, 4 H), 2.25 (s, 6 H), 1.85
\( \text{H}_{2} \text{Cl}_{2}, 25 ^\circ \text{C}, \text{ppm}: 155.3, 149.9, 146.7, 141.2, 140.5, 139.2, 136.8, 134.2, 129.9, 119.3, 117.6, 24.4, 20.7, -0.04. \) \( ^{11} \text{B} \text{NMR (CD}_{2}\text{Cl}_{2}, 25 ^\circ \text{C, ppm}}: 6.51. \)

HREI-MS (M\(^+\)) m/z: \( \text{Calcd for C}_{30}\text{H}_{36}\text{BNSSi, 481.2431. Found: 481.2445. Anal. Calcd for C}_{30}\text{H}_{36}\text{BNSSi: C, 74.82; H, 7.53; N, 2.91. Found: C, 74.71; H, 7.75; N, 2.88.} \)

### 3.2.3 Synthesis of Bis-3.1

5,5’-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2’-bithiophene was synthesized following the literature procedure.\(^7\) The resulted boronic ester was coupled with 2-bromopyridine to form 5,5’-bis(2-pyridyl)-2,2’-bisthiophene (PTTP) using a standard Suzuki coupling procedure. Purification of PTTP was performed through chromatography using \( \text{CH}_{2}\text{Cl}_{2}-\text{hexane} \) as eluant. \( n\)-BuLi (8 mL, 5 mmol) was added slowly to a solution of PTTP (0.64 g, 2.0 mmol) in diethyl ether (100 mL) at \(-78 \^\circ \text{C, and the resulting solution was stirred for about 1 h at -78 } ^\circ \text{C. Then BMe}_{2}\text{F} (1.5 g, 5.0 mmol) were added under a stream of nitrogen and the solution was stirred at \(-78 \^\circ \text{C for another hour, then warmed up to r.t. overnight. Solvent was removed under reduced pressure and then purified by chromatography (CH}_{2}\text{Cl}_{2}-\text{hexane}} = 1 : 1) to give a bright yellow powder of \text{Bis-3.1} (yield 70%). Anal. Calcd for \( \text{C}_{54}\text{H}_{54}\text{B}_{2}\text{N}_{2}\text{S}_{2}: C, 79.41; H, 6.66; N, 3.43; S, 7.85. \) Found: C, 79.22; H, 6.89; N, 3.44; S, 7.80. \( ^{1} \text{H} \text{NMR (CD}_{2}\text{Cl}_{2}, 25 ^\circ \text{C, ppm}}: 8.42 (d, J = 5.5 \text{Hz, 2 H}), 7.93 (t, J = 8.0 \text{Hz, 2 H}), 7.56 (d, J = 8.5 \text{Hz, 2 H}), 7.35 (s, 2 H), 7.11 (t, J = 6.0 \text{Hz, 2 H}), 6.65 (s, 8 H), 2.18 (s, 12 H), 1.83 (s, 24 H). \)

\( ^{11} \text{B} \text{NMR (CDCl}_{3}, 25 ^\circ \text{C, ppm}}: 2.7. \) \( ^{13} \text{C} \text{NMR cannot be obtained due to the poor solubility of \text{Bis-3.1.}} \)

### 3.2.4 Syntheses of 3.2, Bis-3.2 and Bis-3.3

2-Bromo-5-(thiophen-2-yl)-thiophene was synthesized through a standard Suzuki coupling procedure between 2-bromo-5-iodothiophene and 2-thienylboronic acid in THF–\( \text{H}_{2}\text{O} \) mixture. Compound B(2-(5-ethynylpyridin-2-yl)phenyl)Me_{2} (\text{A}) was prepared according to a
published method. Compounds 3.2, Bis-3.2 and Bis-3.3 were obtained through Sonogashira coupling between their corresponding brominated precursors with B(2-(5-ethynylpyridin-2-yl)phenyl)Mes$_2$ (A).

*General procedure for Sonogashira coupling.* Compound A, Pd(PPh$_3$)$_4$ (5%), CuI (10%), triethylamine and precursors 2-bromothiophene; or 2-bromo-5(thiophen-2-yl)thiophene; or 2-bromo-5-(5-bromothiophen-2-yl)thiophene, respectively, were refluxed in degassed THF overnight. The solution was then extracted with acetyl acetate and water mixture, dried over MgSO$_4$, and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography using silica gel (CH$_2$Cl$_2$-hexane as the eluent) and recrystallized if necessary to afford the desired product S3.2, Bis-3.2 and Bis-3.3.

**3.2:** Compound A (200 mg, 0.5 mmol), 2-bromothiophene (80 mg, 0.5 mmol), Pd(PPh$_3$)$_4$ (30 mg, 0.025 mmol), CuI (9.7 mg, 0.05 mmol) and triethylamine (3 mL) in 30 mL of THF were treated using general procedures for Sonogashira coupling. Light yellow crystals of 3.2 were obtained from CH$_2$Cl$_2$–hexane mixture (yield, 45%). $^1$H NMR (CD$_2$Cl$_2$, 25 °C, ppm): 8.67 (d, $^4$J = 0.8 Hz, 1 H), 8.11 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 1 H), 8.02 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 1 H), 7.91 (dd, $J = 6.4$ Hz, $J = 1.2$ Hz, 1 H), 7.77 (dd, $J = 6.4$ Hz, $J = 1.6$ Hz, 1 H), 7.37 (m, 4 H), 7.08 (dd, $J = 5.2$ Hz, $J = 3.6$ Hz, 1 H), 6.67 (s, 4 H), 2.19 (s, 6 H), 1.81 (s, 12 H). $^{11}$B NMR (CDCl$_3$, 25 °C, ppm): 4.8. $^{13}$C NMR (CD$_2$Cl$_2$, 25 °C, ppm): 158.4, 154.8, 148.3, 145.3, 142.9, 140.2, 134.7, 134.2, 133.6, 131.6, 131.0, 130.1, 129.1, 127.7, 125.7, 122.4, 121.9, 118.2, 118.0, 88.2, 87.8, 25.0, 20.6. Anal. Caled for C$_{35}$H$_{32}$BNS: C, 82.51; H, 6.33; N, 2.75; S, 6.29. Found: C, 81.66; H, 6.90; N, 2.80; S, 6.13. The relative low carbon content is due to trace amount of diethylether left in the sample, which is indicated by the $^1$H NMR spectra. Anal. Caled for C$_{35}$H$_{32}$BNS·1/3C$_4$H$_6$O: C, 81.69; H, 6.67; N, 2.62; S, 6.00.
**Bis-3.2:** Compound A (200 mg, 0.5 mmol), 2-(5-bromothienyl)-2-thiophene (123 mg, 0.5 mmol), Pd(PPh₃)₄ (30 mg, 0.025 mmol), Cul (9.7 mg, 0.05 mmol) and triethylamine (3 mL) in 30 mL of THF were treated using general procedures for Sonogashira coupling. Yellow crystals of **Bis-3.2** were obtained from CH₂Cl₂–hexane mixture (yield, 40%). ¹H NMR (CD₂Cl₂, 25 °C, ppm): 8.69 (d, J = 1.0 Hz, 1 H), 8.13 (dd, J = 8.5 Hz, J = 1.5 Hz, 1 H), 8.05 (d, J = 8.5 Hz, 1 H), 7.93 (d, J = 7.0 Hz, 1 H), 7.80 (d, J = 7.5 Hz, 1 H), 7.35 (m, 5 H), 7.16 (d, J = 9.0 Hz, 1 H) 7.10 (dd, J = 5.0 Hz, J = 3.5 Hz, 1 H), 6.70 (s, 4 H), 2.22 (s, 6 H), 1.83 (s, 12 H). ¹¹B NMR (CDCl₃, 25 °C, ppm): 4.7. ¹³C NMR (CD₂Cl₂, 25 °C, ppm): 158.5, 148.4, 143.0, 140.8, 140.3, 136.6, 134.8, 134.7, 134.4, 131.7, 131.1, 130.3, 128.5, 126.0, 125.9, 125.1, 124.1, 122.5, 120.5, 118.3, 118.1, 89.4, 87.9, 25.1, 20.8. Anal. Calcd for C₃₉H₃₄BNS₂: C, 79.17; H, 5.79; N, 2.37; S, 10.84. Found: C, 79.18; H, 5.85; N, 2.35; S, 10.64.

**Bis-3.3:** Compound A (200 mg, 0.5 mmol), 5,5'-dibromo-2,2'-bithiophene (162 mg, 0.5 mmol), Pd(PPh₃)₄ (30 mg, 0.025 mmol), Cul (9.7 mg, 0.05 mmol) and triethylamine (3 mL) in 30 mL of THF were treated using general procedures for Sonogashira coupling. Bright yellow crystals of **Bis-3.3** were obtained from CH₂Cl₂–hexane mixture (yield, 40%). ¹H NMR (CDCl₃, 25 °C, ppm): 8.72 (d, J = 1.0 Hz, 2 H), 8.03 (dd, J = 8.4 Hz, J = 1.8 Hz, 2 H), 7.97 (d, J = 8.7 Hz, 2 H), 7.82 (m, 4 H), 7.28 (m, 4 H), 7.23 (d, J = 3.6 Hz, 2 H), 7.12 (d, J = 5.2 Hz, 2 H), 6.69 (m, 8 H), 2.21 (s, 12 H), 1.81 (s, 24 H). ¹¹B NMR (CDCl₃, 25 °C, ppm): 4.8. ¹³C NMR could not be obtained due to the poor solubility of **Bis-3.3**. Anal. Calcd for C₇₀H₆₂B₂N₃S₂: C, 82.67; H, 6.14; N, 2.75; S, 6.31. Found: C, 82.28; H, 6.18; N, 2.81; S, 6.63.
3.2.5 Photolysis Procedures

NMR solvent C$_6$D$_6$ was purchased from Cambridge Isotopes and dried over molecular sieves in a glove box. The solvent toluene for UV-Vis spectra measurements was distilled over sodium and then stored over molecular sieves in the dry box.

*Monitoring the photolysis process via $^1$H NMR spectra.* Samples were prepared inside a glove box by dissolving approximately 1–2 mg of desired compound in dry C$_6$D$_6$, this was then subjected to UV irradiation inside a Rayonet photochemical reactor S3, followed by recording the $^1$H NMR spectra at different time intervals.

*Monitoring the photolysis process via UV-Vis absorption spectroscopy.* Substrates were dissolved in toluene in a quartz cuvette ($5 \times 10^{-5}$ M) inside a glove box, and then subjected to irradiation using a handheld UVP UVGL-25 Compact UV lamp (365 nm), with the UV-Vis absorption spectra recorded at different time intervals.

*Photoisomerization quantum yield measurement for 3.1.* All preparation and measurements were done in the dark and with freshly prepared and mixed solutions. Phenanthroline and K$_3$[Fe(C$_2$O$_4$)$_3$]·3H$_2$O are light sensitive and were kept in the dark at all times. The quantum yield of the photoisomerization of 3.1 was determined using potassium ferrioxalate K$_3$[Fe(C$_2$O$_4$)$_3$]·3H$_2$O actinometry based on the Hatchard–Parker method. The absorbance was measured using an Ocean Optics fiber optic spectrophotometer connected to a Quantum Northwest four-way temperature-controlled cuvette holder via 400 µm fiber optic. The irradiation source was a Photon Technologies International 200 W Hg–Xe lamp equipped with a monochromator. This method was not used for 3.2 because its isomerization efficiency is too slow. The photoisomerization quantum efficiency of 3.2 was estimated using 3.1 as an internal reference.
3.2.6 X-ray Diffraction Analysis

X-ray crystallography diffraction data collections were carried out as described in Chapter 2.2.5.

3.2.7 DFT Calculations

The geometrical parameters obtained for Bis-3.3 from X-ray diffraction experiments were used as the starting point for its geometry optimization. The geometries of all compounds were optimized using Gaussian 03 software at the theory level of B3LYP functional with basis set of 6-31G* for all atoms. TD-DFT calculations were performed using the coordinates from the optimized geometry.

3.3 Results and Discussion

3.3.1 Syntheses and Structures

3.1 and Bis-3.1 were synthesized in good yields by mono-lithiation and double-lithiation of the corresponding precursor (5-trimethylsilyl-2-thienyl)-2-pyridine and 6,6-bis(2-thienyl)-3,3’-bipyridine, respectively, followed by the addition of BMes₂F, as shown in Figure 3.2 and 3.3. The precursor 6,6’-bis(2-thienyl)-3,3’-bipyridine was prepared through Suzuki–Miyaura coupling between 5,5’-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2’-bithiophene and 2-bromopyridine.

![Synthetic route of compound 3.1.](image)

**Figure 3.2** Synthetic route of compound 3.1.
Figure 3.3 Synthetic route of compound Bis-3.1.

Compounds 3.2, Bis-3.2 and Bis-3.3 were synthesized in 40–45% yields from a common precursor A via Sonogashira coupling with the appropriate mono- or bis-thiophene bromides, as shown in Figure 3.4.

Figure 3.4 Synthetic routes to compounds 3.2, Bis-3.2, Bis-3.3.

The crystal structures of 3.1 and Bis-3.3 were determined by single-crystal X-ray diffraction analysis, as shown in Figure 3.5 and 3.6, respectively. The molecule of Bis-3.3
possesses a crystallographically imposed inversion center. The B–C and B–N bond lengths of 3.1 are similar to those observed in (py-benzothienyl)BMes₂⁴⁶ while the B–C and B–N bond lengths of Bis-3.3 are similar to those of B(ppy)Mes₂ (1.32 in Chapter 1).⁴² A key feature revealed by the crystal structure is that the chelate backbone of Bis-3.3 is completely flat with extended π-conjugation between the two boron chromophores through the dithienyl and the acetylene linker. Molecules of Bis-3.3 are all aligned along one direction in the crystal lattice with extended intermolecular π-stacking as shown in Fig 3.7. The shortest separation distance between the π-linkers of two neighboring molecules is ∼3.50 Å. The molecular packing pattern displayed by Bis-3.3 resembles those of related diboryl compounds reported by Yamaguchi and co-workers.³

**Figure 3.5** Crystal structure of 3.1 with 50% thermal ellipsoids and labels for key atoms.

Important bond lengths (Å) and angles (°): B(1)–N(1) 1.673(5), B(1)–C(1) 1.633(5), B(1)–C(13) 1.632(5), B(1)–C(22) 1.651(5); C(13)–B(1)–C(22) 114.3(3), C(1)–B(1)–N(1) 94.9(3).
Figure 3.6 Crystal structure of Bis-3.3 with 50% thermal ellipsoids and labels for key atoms. Important bond lengths (Å) and angles (°): B(1)–N(1) 1.676(4), B(1)–C(1) 1.619(4), B(1)–C(18) 1.652(4), B(1)–C(27) 1.646(4), C(12)–C(13) 1.190(5); C(18)–B(1)–C(27) 116.7(2), C(1)–B(1)–N(1) 94.8(2).

Figure 3.7 The stacking of Bis-3.3 in the crystal lattice.

3.3.2 Photophysical and Electrochemical Properties

Absorption and fluorescence data of all compounds are shown in Fig 3.8 and Table 3.1. The diboryl compounds Bis-3.1 and Bis-3.3 have the most red-shifted absorption spectra, compared to all monoboryl compounds, clearly due to the greater extended π-conjugation in these molecules. Extending the π-conjugation by the addition of the second thienyl ring (3.2 to Bis-3.2) also shifts the absorption to a longer wavelength. The fluorescence spectra of the diboryl
compounds **Bis-3.1** and **Bis-3.3** have well-resolved vibrational fine features as shown in Fig 3.8, which suggests that the fluorescence is mostly likely from $\pi^* \rightarrow \pi$ transition of the backbone. In contrast, the fluorescence spectra of all monoboryl compounds are broad and featureless, which may be assigned to a charge transfer transition between the chelate backbone and the mesityl moiety, as previously observed for B(ppy)Mes$_2$ and its derivatives. However, the fluorescence of the dithienyl compound **Bis-3.2** shows little dependence on solvent polarity, in contrast to **3.2** that has a strong dependence on solvent polarity, indicating that its emission is most likely dominated by $\pi^* \rightarrow \pi$ transition of the backbone. The abnormal red-shift of the emission spectrum of **3.2** in THF, relative to **Bis-3.2** and **Bis-3.3**, may be attributed to the charge transfer nature of the emission band of **3.2** and its sensitivity to solvent polarity, as shown in Fig 3.9.

![Figure 3.8](image)

**Figure 3.8** Absorption spectra (left) and fluorescence spectra (right) of all compounds in THF (2 $\times 10^{-5}$ M).
Figure 3.9 Fluorescence spectra of 3.2 and Bis-3.2 in toluene and THF, showing the greater dependence of 3.2 on solvent polarity.

All monoboryl compounds displayed one reversible reduction peak while all diboryl compounds display two reduction peaks, which are characteristic of the boryl unit. Increasing the number of the thienyl unit or the boryl unit lowers the LUMO level somewhat with the most dramatic change being observed between 3.1 and Bis-3.1 (~0.40 eV, see Table 3.1). This is similar to the trend observed in thienylthiazolyl chelate BMes₂ and the corresponding diboryl compounds reported by Yamaguchi and coworkers.⁴

<table>
<thead>
<tr>
<th>Compd</th>
<th>Absorption</th>
<th>ε</th>
<th>Optical Energy Gap</th>
<th>Fluorescence</th>
<th>CV</th>
</tr>
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<tr>
<td></td>
<td>λ₂₁₀,₂₅₀</td>
<td>[nm]</td>
<td>[eV]</td>
<td>λ₉₅₀</td>
<td>[nm]</td>
</tr>
<tr>
<td>3.1</td>
<td>298 374</td>
<td>16500 8000</td>
<td>3.06 3.06</td>
<td>465 465</td>
<td>0.20 0.20</td>
</tr>
<tr>
<td>3.2</td>
<td>330 384</td>
<td>36500 22500</td>
<td>2.95 2.95</td>
<td>497 497</td>
<td>0.31 0.31</td>
</tr>
<tr>
<td>Bis-3.1</td>
<td>436 460</td>
<td>45300 40200</td>
<td>2.50 2.50</td>
<td>482 482 509 509</td>
<td>0.14 0.14</td>
</tr>
<tr>
<td>Bis-3.2</td>
<td>396 416</td>
<td>24300 70700</td>
<td>2.83 2.61 2.61</td>
<td>471 467 496 496</td>
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</tr>
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<td>Bis-3.3</td>
<td>396 416</td>
<td>24300 70700</td>
<td>2.83 2.61 2.61</td>
<td>471 467 496 496</td>
<td>0.41 0.47</td>
</tr>
</tbody>
</table>

⁴in THF. ⁵in DMF with Bu₄NPF₆ as the electrolyte. ⁶determined with 9,10-diphenylanthracene as the standard. ⁷Potentials vs. FeCp₂⁰⁺/⁻.
3.3.3 DFT Calculations

The computational results show that the lowest energy transition of 3.1 and 3.2 is from HOMO to LUMO, mainly a charge transfer transition of the mesityl to the chelate backbone, similar to B(ppy)Mes$_2$. For the dithienyl compound Bis-3.1 the lowest energy transition has nearly equal contributions from HOMO to LUMO and HOMO–2 to LUMO while for Bis-3.2 and Bis-3.3, it involves mainly HOMO to LUMO transition (Table 3.2). The MO diagrams are shown in Figure 3.10 and 3.11.

**Table 3-2** TD-DFT data of the first excited state transition for all compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda$ (nm)</th>
<th>Oscillator strength</th>
<th>Major contributions</th>
</tr>
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<tbody>
<tr>
<td>3.1</td>
<td>427</td>
<td>0.0267</td>
<td>HOMO→LUMO (96%)</td>
</tr>
<tr>
<td>3.2</td>
<td>468</td>
<td>0.0467</td>
<td>HOMO→LUMO (96%)</td>
</tr>
<tr>
<td>Bis-3.1</td>
<td>477</td>
<td>0.1704</td>
<td>HOMO–2→LUMO (42%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HOMO→LUMO (49%)</td>
</tr>
<tr>
<td>Bis-3.2</td>
<td>482</td>
<td>0.1304</td>
<td>HOMO→LUMO (88%)</td>
</tr>
<tr>
<td>Bis-3.3</td>
<td>527</td>
<td>0.9908</td>
<td>HOMO→LUMO (89%)</td>
</tr>
</tbody>
</table>

A careful examination of the frontier orbitals involved in the first excited state revealed that the lowest energy transition for Bis-3.1, Bis-3.2, and Bis-3.3, in addition to the charge transfer transition, has large contributions from the $\pi\rightarrow\pi^*$ transition of the chelate backbone. For the diboryl compounds Bis-3.1 and Bis-3.3, the $\pi\rightarrow\pi^*$ contribution to the first excited state is greater than 50%. As shown by the HOMO and LUMO diagrams of 3.2, Bis-3.2 and Bis-3.3 in Fig 3.10, increasing the number of thiényl units and the number of boryl units increases the $\pi\rightarrow\pi^*$ transition contributions to the lowest excited state. The trend is in agreement with absorption and luminescence data.
Figure 3.10 MO diagrams of 3.1 and Bis-3.1, plotted with an isocontour value of 0.01.

Figure 3.11 MO diagrams of compounds 3.2, Bis-3.2 and Bis-3.3, plotted with an isocontour value of 0.01. Energy unit is Hartree.

3.3.4 Photoisomerization

Upon irradiation at 365 nm, compound 3.1 underwent photoisomerization rapidly, accompanied by a color change to deep blue. $^1$H, $^1$H $^1$H NOESY and $^1$H$^{13}$C HMBC NMR data confirmed that the boryl unit of the blue isomer 3.1a (Figure 3.12) has a similar structure as that of the dark isomer of B(ppy)Mes$_2$ (1.32). The excerpted regions of $^1$H$^1$H NOESY and $^1$H$^{13}$C HMBC spectra of 3.1a are shown in Figure 3.14 and Figure 3.15.
Figure 3.12 Left: a scheme showing the structural change of 3.1 and 3.1a. Right: absorption spectral change of 3.1 in toluene (∼1×10⁻⁵ M) upon irradiation at 365 nm with a handheld UV lamp with 1 s time intervals (the photolysis is completed in ∼20 s).

The photoisomerization quantum efficiency of 3.1 was determined to be 0.77, using ferrioxalate actinometry. This efficient photoisomerization of 3.1 resembles the behavior of B(ppy)Mes₂ (Φ_photoisomerization: 0.85). As shown in Figure 3.13, the thienylacetylene functionalized 3.2 also underwent photoisomerization in a similar manner, changing color from light yellow to dark green upon irradiation at 365 nm in toluene but with a much lower quantum efficiency of ∼0.01. The low photoisomerization of 3.2 can be attributed to the greater π-conjugation of the chelate unit, compared to that of B(ppy)Mes₂. The photoisomerizations of both compounds 3.1 and 3.2 were found to be fully thermally reversible, as monitored via ¹H NMR spectra (Fig 3.16).

Figure 3.13 Absorption spectral change of 3.2 under the same conditions (∼1×10⁻⁵ M) with 10 s to 20 s time intervals (the photolysis is completed in ∼150 s).
Figure 3.14 Excerpted region of 3.1a’s $^1$H$^1$H NOESY NMR spectrum in C$_6$D$_6$ showing the characteristic crosspeaks between aromatic and aliphatic protons.

Figure 3.15 Excerpted region of 3.1a’s $^1$H$^{13}$C HMBC NMR spectrum in C$_6$D$_6$ showing the two characteristic quaternary carbon atoms.
Figure 3.16 Stacked $^1$H NMR spectra showing the partial conversion of 3.1 (top) and 3.2 (bottom) (highlighted in green color) to their corresponding dark isomers 3.1a and 3.2a (highlighted in pink color) upon UV irradiation (365 nm) and the thermal reversibility upon heating (80 °C) in C$_6$D$_6$.

In contrast to the photochromism of 3.1 and 3.2, the monoboryl compound Bis-3.2 does not undergo photoisomerization. Similarly, the diboryl compounds Bis-3.1 and Bis-3.3 were also found to be photostable and didn't undergo photoisomerization at all when irradiated at either 365 nm or 420 nm. The high photostability of Bis-3.1 and Bis-3.3 is peculiar because related
polyboryl compounds with alkyne–benzene linkers (1.37 in Figure 3.17) were observed to undergo photoisomerization, albeit involving only one boron center.\textsuperscript{4b,f} The photostability of Bis-3.2 is also in sharp contrast to photoactive compounds that are conjugated to a thienylacetylene group or a phenylpyridyl group shown in Figure 3.17.

![Figure 3.17](image)

**Figure 3.17** Photoactive molecules containing boryl moiety in a conjugated system.

The key difference between compounds Bis-3.1, Bis-3.2, and Bis-3.3 and compounds in Figure 3.17 is the presence of the dithienyl unit. Based on the fluorescence and TD-DFT data, the high photostability of compounds Bis-3.1, Bis-3.2 and Bis-3.3 toward photoisomerization is caused by the low-lying $\pi \rightarrow \pi^*$ transition of the backbone facilitated by the dithienyl unit that effectively quenches or competes with the charge transfer process, leading to the deactivation of photoisomerization.

### 3.4 Conclusions

In summary, the ability of a dithienyl unit in the backbone to completely switch off photoisomerization of N,C-chelate boryl compounds has been demonstrated with several monoboryl and diboryl compounds. The relatively low-lying $\pi \rightarrow \pi^*$ transition state introduced by the dithienyl unit and its effective competition with the charge transfer transition of the boryl unit
is likely the main cause of this unusual phenomenon. The incorporation of a dithienyl unit in \( \pi \)-conjugated compounds that contain a BMes\(_2\) chelate unit is therefore a highly effective way to provide photostability to the materials, preventing it from photodegradation through isomerization.
3.5 Notes and References:

The work outlined in this chapter has been published as:


References:


Chapter 4

Reactivity and Electronic Properties of a Ferrocene Molecule Bearing an N,C-chelate BMes₂ Unit

4.1 Introduction

Photochromic materials, which display distinct physical and electronic properties between two states upon light irradiation, have found wide applications in areas such as optical data storage, molecular switches, chemical or photon sensing.¹ Tremendous research effort has been devoted to incorporating the photoresponsive materials into metal systems with rich electronic, optical and magnetic properties. The two components can mutually benefit from each other, namely, a further modulation of the photochromic properties via the participation of metal moiety or the photo-regulation of many properties intrinsic to the metal moiety.

To further tune the photochromic properties of N,C-chelate BMes₂ compounds, one common strategy is to incorporate transition metal ions such as Au(I), Pt(II) and Re(I) into the chelate backbone.² However, in most instances, the introduction of a metal ion unit greatly inhibited the photoreactivity of the boron unit because of the low-lying metal-to-ligand charge transfer (MLCT) state.³ On the other hand, redox-active transition metal ions have been extensively explored as a stimulus or a control to modulate photochromic systems by influencing the electronic structure of the photo-switch through the oxidation states of the metal ion.⁴ One of the most commonly used metal unit for regulating photoswitching systems is ferrocene.⁵ In addition to influencing the properties of photochromic systems, a ferrocene unit has also been incorporated into a variety of main group systems to create new materials that have unique properties and applications.⁶ In particular, a three-coordinate boryl unit has been found to be very
effective in promoting electronic communication with or between ferrocene units,\textsuperscript{7} which has led to important applications such as electrochemical sensing of anions.\textsuperscript{7f-7h}

To examine the mutual influence of a ferrocene unit and a N,C-chelate BMes\textsubscript{2} unit on their electronic, chemical and photochemical properties, this chapter focuses on a new molecule B(2-ferrocenyl-N-Me-benzimidazolyl)Mes\textsubscript{2} (4.1), in which a four-coordinate boryl moiety is grafted on the ferrocene.

4.2 Experimental

4.2.1 General Procedure

Experimental techniques for synthesis, the use of instrumentation and the collection of X-ray crystallography diffraction data are as described in Chapter 2.2.1.

4.2.2 Synthesis of 4.1

\textit{t}-Butyllithium (1.76 mL, 1.7 M, 3.0 mmol) was added dropwise to (N-methylbenzimidazol-2-yl-ferrocene, 0.79 g, 2.0 mmol) at -78 °C in THF, under nitrogen atmosphere. The solution was then stirred for 1 hour, following which dimesitylboron fluoride (0.86 g, 3.0 mmol) in 5 mL THF solution was added dropwise. The reaction mixture was then warmed up to room temperature and stirred overnight. The compound was purified as a reddish solid (0.7 g, yield: \(\sim 60\%\)) by column chromatography on silica gel using hexane:CH\textsubscript{2}Cl\textsubscript{2} (50\%:50\% v/v) as the eluent. \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 25 °C, ppm), \(\delta\): 7.43 (d, 1 H, \(J = 8.5\) Hz), 7.38 (d, 1 H, \(J = 8.0\) Hz), 7.29 (t, 1 H, \(J = 8.0\) Hz, \(J = 1.0\) Hz), 7.21 (t, 1 H, \(J = 8.5\) Hz, \(J = 1.5\) Hz), 6.84 (s, 1 H), 6.70 (s, 1 H), 6.61 (s, 1 H), 6.43 (s, 1 H), 4.81 (d, 1 H, \(J = 2.5\) Hz), 4.75 (d, 1 H, \(J = 2.5\) Hz), 4.58 (t, 1 H, \(J = 2.5\) Hz), 3.95 (s, 3 H), 3.72 (s, 5 H), 2.25 (s, 3 H), 2.21 (s, 3 H), 2.13 (s, 3 H), 2.11 (s, 3 H), 1.92 (s, 3 H), 1.26 (s, 3 H). \textsuperscript{13}C NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 25 °C,
ppm): 161.1, 142.9, 141.6, 141.0, 137.2, 137.0, 136.5, 133.8, 132.3, 129.7, 129.4, 128.9, 128.7, 123.9, 122.5, 115.7, 110.3, 74.5, 73.3, 72.3, 69.0, 59.2, 30.9, 26.4, 24.8, 24.3, 23.7, 20.3. 11B NMR (160 MHz, CD2Cl2, 25 °C, ppm): 0.6. HRMS (TOF MS EI+): Calcd, 564.2421; Observed, 564.2399.

4.2.3 Synthesis of 4.2

Compound 4.2 could be obtained from the hydrolysis of 4.1 in solution under ambient condition after several weeks. 1H NMR (400 MHz, CD2Cl2, 25 °C, ppm), δ: 13.8 (s, 1 H), 7.79 (m, 1 H), 7.46 (m, 1 H), 7.36 (m, 2 H), 6.86 (s, 2H), 5.23 (dd, 1 H, J = 2.4 Hz, J = 1.2 Hz), 4.67 (t, 1 H, J = 2.4 Hz), 4.21 (m, 6 H), 4.03 (s, 3 H), 2.33 (s, broad, 9 H). 13C NMR (100 MHz, CD2Cl2, 25 °C, ppm): 139.3, 136.8, 127.0, 122.7, 122.6, 118.1, 109.4, 79.8, 72.8, 72.4, 70.6, 32.3, 22.3, 20.8. 11B NMR (160 MHz, CD2Cl2, 25 °C, ppm): 48.6. HRMS (TOF MS EI+): Calcd, 462.1566; Observed, 462.1583.

4.2.4 Synthesis of 4.3

A solution of iodine (128 mg, 0.5 mmol) in dichloromethane (5 mL) was added to a stirred solution of 4.1 (200 mg, 0.34 mmol) in 5 mL CH2Cl2 at r.t. Dark brown precipitates of 4.3 were then collected after the solution was left standing overnight, followed by washing with hexane. 1H NMR (600 MHz, CD3CN, 25 °C, ppm), δ: 28.1 (s, broad, 4.3 H), 26.0 (s, broad, 3 H), 16.7 (s, 2.6 H), 12.4 (s, 1 H), 9.22 (s, 1 H), 8.46 (s, broad, 2.7 H), 8.2 (s, 1 H), 7.22 (d, 1 H, J = 5.4 Hz), 6.93 (s, 1 H), 6.60 (s, 1 H), 5.52 (s, 1 H), 3.48 (s, 3 H), 2.35 (s, 1 H), -0.56 (s, 2.4 H), -5.53 (s, 1.7 H), -7.47 (s, 1.5 H). Due to the presence of Fe3+ paramagnetic center, the 1H integrations are not accurate when peaks are far away from the spectrum center. Anal. Calcd for C36H17BFeN3I3 · 0.1CH2Cl2: C, 45.47; H, 3.93; N, 2.94. Found: C, 45.19; H, 3.82; N, 2.87. (the
residue CH₂Cl₂ left inside the sample could not be removed even after overnight under vacuum at r.t, which is evidenced by the ¹H NMR peaks of CH₂Cl₂ in the CD₃CN solution of 4.3.

4.2.5 DFT Calculations

All calculations were performed with the Gaussian 09 Software.¹⁶a For compounds 4.1 and 4.2, DFT and TD-DFT calculations were performed at the B3LYP level of theory,¹⁶b,c basis set of LanL2DZ for Fe,¹⁶d,e 6-31G(d) for other atoms. For cation 4.3, DFT calculation is performed at the theory level of BP86 function, basis set of def2SVP for Fe,¹⁶f 6-31G(d) for other atoms. The geometric parameters obtained from crystal structure data were used as the initial points for geometry optimization calculations.

4.2.6 X-ray Crystallographic Analysis

X-ray crystallography diffraction data collection protocols follow those described in Chapter 2.2.5. The crystal data of 4.1, 4.2 and 4.3 have been deposited at the Cambridge Crystallographic Data Center (CCDC 983808, 983809, and 983810 for 4.1, 4.2 and 4.3, respectively).

4.2.7 NOESY/EXSY Experiments

The “EXSYCalc” software that is offered free on the web from MestRec was used to determine the exchange rate constants. Stacked variable temperature ¹H NMR spectra of 4.1 are shown in Figure 4.1. To avoid integration overlap, the NOESY/EXSY NMR experiments were done at 273K to obtain well-separated o-protons peaks (Figure 4.2). The exchange in 4.1 was treated as a four-site exchange and the o-protons from the mesityl groups were used to determine the exchange rate. As shown in Figure 4.3, the exchange at three mixing time (70 ms, 150ms, 400ms) were determined and the same resulted were obtained. The exchange rate between
different mesityl groups is 0.79 to 0.89 s$^{-1}$, which provides Gibbs free energy $\Delta G^\circ = \sim 67$ kJ/mol. The exchange rate between the $o$-protons on the same mesityl ring is 0.21 to 0.24 s$^{-1}$, which provides Gibbs free energy $\Delta G^\circ = \sim 70$ kJ/mol.

Figure 4.1 Stacked $^1$H NMR spectra of 4.1 at variable temperatures.

Figure 4.2 Protons peaks of 4.1 used for EXSY experiments calculation. A and C refer to the $o$-protons from the same mesityl ring (determined via 2D COSY data), similarly, B and D are from the other mesityl ring.

Figure 4.3 Excerpted regions of the EXSY spectra of 4.1 in CD$_2$Cl$_2$ at 273K with different mixing time: 70 ms (left); 150 ms (middle); 400 ms (right).
4.3 Results and Discussion

4.3.1 Synthesis and Structural Properties

The key starting material, N-methylbenzimidazol-2-yl-ferrocene (4.4) was obtained by a modified procedure reported previously. The benzimidazolyl directed ortho-lithiation of (N-methylbenzimidazol-2-yl-ferrocene, followed by addition of 1 eq dimesitylboron fluoride, led to the formation of compound 4.1, which was isolated in ~60% yield (Figure 4.5). Compound 4.1 is a reddish solid. The $^{11}$B NMR spectrum has a peak at 0.60 ppm that is characteristic of four-coordinate boron. The four aryl protons and the six methyls on the two mesityl groups display well resolved and distinct peaks in the $^1$H NMR spectrum of 4.1 that is in agreement with the asymmetric nature of the molecule and the highly congested environment around the boron center.
Figure 4.5 Synthetic route of 4.1.

Figure 4.6 The proposed mechanism for the interconversion between the two mesityls in 4.1.

Variable temperature \(^1\)H NMR (Figure 4.1) and 2D NOESY NMR (Figure 4.2) spectra showed the existence of a dynamic exchange between the two mesityls and between the two aryl protons on the same mesityl ring.\(^9a\) From NOSEY/EXSY experiments, the Gibbs free energy for the exchange between two mesityl groups was determined to be 67.0 kJ/mol at 273 K, while that for the exchange between two aryl protons of the same mesityl is 70.0 kJ/mol. The proton chemical shift exchange within the same mesityl ring is due to the rotation around the B-C bond. The dynamic exchange between the two mesityl groups is most likely caused by the dissociation of the B-N bond forming the intermediate A,\(^9b\) followed by the rotation of B-C\(_{Cp}\) bond and the reformation of the B-N bond, as shown in Figure 4.6. This is quite unusual since a similar phenomenon was not observed in previously reported N,C-chelate BMes\(_2\) compounds involving phenyl-benzimidazolyl and related phenyl-azolyl chelate ligands. The greater steric congestion imposed by the ferrocene unit in 4.1, compared to the previously reported non-ferroocene-
containing N,C-chelate BMes₂ compounds, may be one of the causes responsible for the unusual B-N bond dissociation/re-association process of 4.1.

The crystal structure of 4.1 was examined by a single-crystal X-ray analysis, which confirmed the congested nature of 4.1 as shown in Figure 4.7. There are two independent molecules in the asymmetric unit of 4.1. Selected bond lengths and angles for one of them are shown in Table 4.1. The B-N bond length (1.658(3) Å, 1.644(3) Å) in 4.1 is indeed much longer than those observed in phenyl-azolyl chelate BMes₂ compounds (1.620-1.635 Å) while the B-C_Cp and B-C_Mes bonds are also longer (by ~0.01 Å) than the typical B-C bond lengths observed in previously reported N,C-chelate BMes₂ compounds. The Fe-C bonds on the Cp ring bound to the boron atom vary significantly as shown in Table 4.1. The Fe-C(2) bond (2.125(2) Å) is ~ 0.1 Å longer than the other Fe-C bonds, clearly because of the binding of C(2) to the bulky BMes₂ unit. The two Cp rings are nearly parallel to each other, with a tilted angle of 8.7° and 4.8°, respectively for the two independent molecules in the asymmetric unit.

Figure 4.7 Crystal structure of 4.1 (left) (one of the independent molecules in the asymmetric unit) and crystal structure of 4.2 (right) with 50% thermal ellipsoids.
Table 4-1 Selected bond lengths (Å) and angles (°) of compound 4.1, 4.2 and 4.3.

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4.3.2 Chemical and Photochemical Reactivity of 4.1

Under ambient condition, we observed that the solution color of 4.1 slowly changed from red to yellow-orange. NMR spectra indicated that 4.1 was converted to a new species 4.2 (Figure 4.8) quantitatively over a period of a few weeks if the solvent used was not dried rigorously. NMR and single-crystal X-ray diffraction analyses established that 4.2 is a ring-opened, hydrolyzed product of 4.1. As shown by the crystal structure of in Figure 4.7, the boron atom is no longer bound to the imidazolyl nitrogen atom and a hydroxyl group replaces one of the
mesityls bonded to boron. The geometry of the boron atom changed from a tetrahedron to a trigonal plane. The B-O bond length (1.351(4) Å) is characteristic of a B=O bond, while the B-C$_{Cp}$ and B-C$_{Mes}$ are much shorter than those in 4.1 due to the much reduced congestion. Furthermore, the Fe-C(6) bond length (2.052(3) Å) in 4.1 is also much shorter than the corresponding one (Fe-C(2)) in 4.2 and is similar to other Fe-C bonds. These provide further support to the steric congestion being the main cause that is responsible for the long Fe-C and B-N bonds in 4.1. As a consequence, the tilt angle between the two Cp rings in 4.2 also becomes much smaller (2.9°). The H atom of the OH group in 4.2 was located in the difference Fourier map and refined successfully. It forms a fairly strong intramolecular hydrogen bond with the imidazolyl N atom, as indicated by the O(1)···N(1) distance (2.686(7) Å). The chemical shift of this H atom appears at 14 ppm in $^1$H NMR spectrum of 4.2, which is in agreement with the hydrogen bond formation. The chemical shift of the boron atom in 4.2 appears as a broad peak at 48.6 ppm in the $^{11}$B NMR spectrum, consistent with a three-coordinated boron center.

![Figure 4.8](image)

**Figure 4.8** The proposed mechanism for the formation of 4.2.

The formation of the hydrolyzed product 4.2 is consistent with the proposed B-N bond dissociation process of 4.1 shown in Figure 4.8. After B-N bond dissociation (intermediate A), external donor molecules such as H$_2$O can compete with the internal nitrogen donor atom for
binding to the boron center. An intramolecular H bond between the H₂O and the N atom would stabilize the intermediate \( \text{B} \), making the hydrolysis a highly competitive pathway, compared to the reformation of the B-N bond. Elimination of a mesitylene molecule from \( \text{B} \) can lead to the product 4.2. The fact that the addition of excess H₂O to the solution of 4.1 did not accelerate the hydrolysis process made us to suggest that the formation of the intermediate A is likely the rate determining step. The facile hydrolysis of 4.1 is in sharp contrast with previously reported N,C-chelate BMes₂ compounds, which did not exhibit the same behavior at all. Again, the greater steric congestion in 4.1 is believed to be the main cause of this phenomenon.

In addition, similar hydrolysis was not observed for a related Fe(Cp)[(Cp-3,5-dimethylpyridyl)BMes₂] compound in which, instead of a benzimidazolyl ring, a pyridyl ring is bound to the BMes₂ unit.¹¹ Since N-methylbenzimidazole has a donor strength which is comparable to that of 3,5-dimethylpyridine and the steric environment around the boron atom in 4.1 is similar to that in Fe(Cp)[(Cp-3,5-dimethylpyridyl)BMes₂], the greater hydrolysis tendency by 4.1 is likely caused by the more strained chelation to the boron atom by the two five-membered rings in 4.1, in comparison to that by a five-membered and a six-membered ring in Fe(Cp)[(Cp-3,5-dimethylpyridyl)BMes₂]. The greater chelation strain in 4.1 may also be a key factor in the dynamic exchange between the two mesityl groups.

Compound 4.1 can be oxidized readily by a mild oxidant such as I₂, generating a dark brown species \([4.1]^+\)I₃⁻ (4.3) (Figure 4.9) quantitatively. The crystal structure of 4.3 is shown in Figure 4.9.
Figure 4.9 Left: oxidation of 4.1 by I\textsubscript{2} to form 4.3. Right: Crystal structure of 4.3 with 50% thermal ellipsoids.

Compared to those of 4.1, the Fe-C bonds in 4.3 are much longer, which is in agreement with the trend reported in the literature for ferrocenium cations and can be attributed to the decreased π-back bonding between the Fe(III) ion and the Cp rings\textsuperscript{12}. As observed in the structure of 4.1, one of the mesityls (the C(28) ring) is on the same side with the Fe(III) center, thus very close to the Fe atom (Fe(1)···C(28) = 3.52(1) Å). Significantly, The Fe-C bonds that are close to the C(28) mesityl ring are all longer than other Fe-C bonds (Fe(1)-C(1) (2.200(7) Å), Fe(1)-C(5) (2.148(7) Å), Fe(1)-C(6) bond (2.129(9) Å) Fe(1)-C(7) bond (2.116(8) Å). Furthermore, the two Cp rings in 4.3 have a much greater titled angle (13.7º) and are much more open toward the C(28) mesityl ring than that observed in 4.1.

Despite the high degree of steric congestion, compound 4.1 is fairly stable toward irradiation by light. No change was observed when the dry C\textsubscript{6}D\textsubscript{6} solution of 4.1 was irradiated under nitrogen at 365 nm or using white light for several hours. Detailed explanation for 4.1’s photo-stability is presented in Section 4.3.4.
4.3.3 Electrochemical Properties of 4.1 and 4.2

Both compounds displayed the characteristic reversible 1e oxidation peak at \( E_{1/2} = -67 \) mV and 205 mV for 4.1 and 4.2, respectively, relative to FeCp\(^+\)/FeCp\(_2\), as shown in the CV diagrams in Figure 4.10.

![CV diagram of 4.1 and 4.2 showing the oxidation wave (vs Fc/Fc\(^+\)) at a 75 mV/s scan rate with [Bu\(_4\)N][PF\(_6\)] (0.1 M) as the electrolyte in CH\(_3\)CN.](image)

The fact that the oxidation potential of 4.1 is more negative than ferrocene is consistent with the four-coordinate boron unit being an electron donating group, thus putting more electron density on the Fe(II) center.\(^7\) The 270 mV increase of the oxidation potential from 4.1 to 4.2 indicates a considerable decrease of the electron density on the Fe(II) center, which may be attributed to the BMes(OH) unit, since the same trend was observed in the previously reported ferrocene compounds functionalized by an electron-deficient three-coordinate boron unit.\(^7\) The loss of chelation between the Cp and the benzimidazolyl ring is believed to be another key factor in the higher oxidation potential of 4.2. The oxidation potential of the non-borylated precursor compound 4.4 was found to be more positive than that of ferrocene (\( E^{1/2} = 128 \) mV, relative to Fe/Fe\(^+\)), albeit to a lesser degree compared to that of 4.2.
4.3.4 Electronic Properties and TD-DFT data of 4.1 and 4.2

Compounds 4.1 and 4.2 have distinct electronic properties. As shown in Figure 4.11, the characteristic low energy absorption band of ferrocene appears at ~490 nm for 4.1 and at ~450 nm for 4.2 with ε = ~1200 M⁻¹cm⁻¹, which accounts for the distinct colors of these two compounds. The 450 nm absorption band of 4.2 in fact is very similar to that of non-substituted ferrocene.

![UV-Vis absorption spectra of 4.1 and 4.2 in CH₂Cl₂.](image)

**Figure 4.11** UV-Vis absorption spectra of 4.1 and 4.2 in CH₂Cl₂.

TD-DFT data (Table 4.2 and Figure 4.12) suggests that the weak absorption band of 4.1 at ~490 nm is mainly from d → π*(Cp–benzimidazolyl) and d → π*(Cp) transitions (MLCT) with a small contribution from a Mes → π*(Cp) transition. The BMes₂ unit in 4.1 lowers the π* energy by enhancing the π conjugation of the Cp–benzimidazolyl unit via chelation and raises the filled d orbital energy via σ donation (as evidenced by the oxidation potential of 4.1), which leads to the relatively low energy MLCT band. Well-defined MLCT transitions in borylated ferrocenes have been observed previously.¹³

Although the HOMO level of 4.1 has appreciable contributions from a mesityl and the LUMO has a large contribution from the π* orbital of the benzimidazolyl–Cp chelate, the HOMO
The LUMO transition contributes very little to the first five excited states, which are dominated by d-d and MLCT transitions. Thus, the inactivity of the boron unit in 4.1 toward photoisomerization can be explained by the presence of the low-lying electronic states involving the ferrocene unit that effectively quench the photoisomerization pathway by trapping the excitons.

![Figure 4.12 MO diagrams of 4.1, displayed with an isocontour value at 0.003.](image)

**Table 4-2** The calculated first four singlet electronic transitions in 4.1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Wavelength (nm)</th>
<th>Osc. Strength</th>
<th>Major contribs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>655.2</td>
<td>0.0008</td>
<td>H-2-&gt;LUMO (11%), H-1-&gt;L+1 (23%), HOMO-&gt;LUMO (20%), HOMO-&gt;L+2 (15%)</td>
</tr>
<tr>
<td>2</td>
<td>643.2</td>
<td>0.0013</td>
<td>H-2-&gt;L+1 (13%), H-1-&gt;LUMO (22%), H-1-&gt;L+2 (17%), HOMO-&gt;L+1 (25%)</td>
</tr>
<tr>
<td>3</td>
<td>515.7</td>
<td>0.0046</td>
<td>H-8-&gt;LUMO (11%), H-8-&gt;L+1 (14%), H-2-&gt;L+1 (10%), H-1-&gt;LUMO (13%), HOMO-&gt;L+1 (14%)</td>
</tr>
<tr>
<td>4</td>
<td>510.1</td>
<td>0.0001</td>
<td>H-8-&gt;L+1 (12%), H-1-&gt;L+1 (32%)</td>
</tr>
</tbody>
</table>
For compound 4.2, the key contributions to the lowest absorption band at ~ 450 nm were found to involve mainly d→π*(Cp-B) and d→π* (benzimidazolyl-B) transitions (MLCT), as shown in the calculated MO diagrams in Figure 4.13 and TD-DFT data in Table 4.3. The boron center in 4.2 has a significant contribution to the π* level, which should lower the π* energy. This is, however, offset by the loss of the chelation between the Cp and the benzimidazolyl ring in compound 4.2. Thus, the higher MLCT energy of 4.2 relative to that of 4.1 is mainly caused by the decreased electron density (or the stabilization of the filled d orbitals) on the Fe(II) center induced by the unsaturated boron unit.

![MO diagrams](image)

**Figure 4.13** MO diagrams of 4.2, displayed with an isocontour value at 0.003.

**Table 4-3** The calculated first four singlet electronic transitions in 4.2.

<table>
<thead>
<tr>
<th>No.</th>
<th>λ(nm)</th>
<th>Osc. Strength</th>
<th>Major contributions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>603.8</td>
<td>0.0004</td>
<td>H-1→LUMO (14%), H-1→L+1 (19%), H-1→L+2 (17%), HOMO→L+1 (20%), HOMO→L+2 (12%)</td>
</tr>
<tr>
<td>2</td>
<td>603.7</td>
<td>0.0017</td>
<td>H-1→L+1 (23%), H-1→L+2 (14%), HOMO→LUMO (12%), HOMO-&gt;L+1 (16%), HOMO-&gt;L+2 (14%)</td>
</tr>
</tbody>
</table>
4.3.5 Electronic and Chemical Properties of 4.3

To examine the electronic structures of 4.3, the UV-Vis-NIR absorption spectra of [4.1+] generated in situ using a stoichiometric amount of tris(4-bromophenyl)ammoniumyl hexachloroantimonate and iodine, respectively, were recorded. As shown in Figure 4.14, upon addition of the oxidant, a broad band covering the range of 600-1300 nm appeared, with the peak at ~950 nm ($\varepsilon = 400 \text{ M}^{-1}\text{cm}^{-1}$), which matches well with that observed for the isolated pure compound 4.3. This low energy band may be assigned to a ligand-to-metal charge transfer transition ($^{2}E_{2g} \rightarrow ^{2}E_{1u}$), according to the well documented work for ferrocenium ions in the literature (~ 617 nm, $\varepsilon = 390 \text{ M}^{-1}\text{cm}^{-1}$ for non-substituted ferrocenium at 300 K). Due to the proximity of the C(28) mesityl (Figure 4.9) to the Fe(III) center, this band most likely involves a mesityl→Fe(III) charge transfer transition.

![Figure 4.14](image)

**Figure 4.14** UV-Vis-NIR absorption spectra change of 4.1 upon the addition of an oxidant: [N(4-Br-C₆H₄)]₂[SbCl₆] (left) and I₂ (right) in CH₂Cl₂.

The EPR spectrum of 4.3 was recorded at 21 K and 9 K, respectively. At both temperatures, a highly anisotropic EPR signal with an axial character was observed at $g_{//} = 3.11$ and $g_{\perp} = 1.94$ (Figure 7), which is characteristic of ferrocenium cations. Nonetheless, the much smaller $g_{//}$ value compared to that (~3.8) of a non-substituted ferrocenium indicates that the spin density extends partially over to the organic substituent. Moreover, the spin density distribution obtained from DFT calculation of $[4.1^+]$ corroborated the EPR results. The tilted angle of the two Cp rings from optimized geometry of $[4.1^+]$ is 13°, similar to that observed in the crystal structure. As shown in Figure 4.15, the calculated spin density in $[4.1^+]$ is mainly localized on the ferrocenium center with notable delocalization to the flanking mesityl group (the C(28) ring).

![Figure 4.15](image)

**Figure 4.15** Left: the EPR spectrum of 4.3 recorded at 21 K. Inset: The spin density distribution diagram of $[4.1^+]$ from DFT calculation. Right: the crystal structure of 4.3 without the counterion, in which the C(28) ring is highlighted with red color.

The NMR spectrum of 4.3 in CD$_3$CN was recorded to further examine the influence of the paramagnetic Fe(III) center on the surrounding organic ligands. The $^{11}$B NMR signal of 4.3 appears at -30 ppm, ~30 ppm upfield shift relative to that of 4.1. As shown in Figure 4.16, the $^1$H chemical shifts of the aromatic protons on benzimidazole moiety in 4.3 are similar to those in 4.1.
The chemical shifts of seven methyls are distinct and spread over the range of 26 ppm to -8 ppm. Assignments for some of the chemical shifts of 4.3 were possible with the aid of 2D $^1$H$^1$H COSY and $^1$H$^1$H NOESY data. The chemical shifts for two of the methyls and the two aryl H atoms on the C(19) mesityl ring that is far away from the Fe(III) center were assigned without ambiguity. Because the difference of the chemical shifts of these protons compared to those in 4.1 are small (< 2 ppm), the influence of the Fe(III) center on this mesityl ring is small. In contrast, the methyl and the aryl H atoms on the C(28) mesityl ring experience a much greater shift. For example, the chemical shifts of the two aryl H atoms on the C(28) mesityl ring appear at 12.4 ppm and 2.3 ppm, respectively, which are more than 3 ppm shifted, compared to those of 4.1. These data further support the greater influence of the unpaired electron of the Fe(III) center and the partial through-space spin delocalization to the C(28) mesityl ring. The greater tilting of the two Cp rings in 4.3 is likely a consequence of the spin delocalization/electronic interaction between the Fe(III) center and the flanking mesityl ring.

Figure 4.16 $^1$H NMR spectra of 4.3 in CD$_3$CN at 298 K (the asterisks indicate all the methyl groups).
2D $^1$H$^1$H NOESY data (Figure 4.17) indicated that there is a similar dynamic exchange between the two mesityl groups in 4.3 as observed in compound 4.1, which is likely through the same B-N bond dissociation process as proposed for 4.1. In Figure 4.17, the diagonal peaks are phased “up” (red color), NOE cross peak are phased “down” (blue color), and chemical exchange cross peak are phased “up” (red color).

![Figure 4.17 $^1$H$^1$H NOESY spectrum of 4.3 in CD$_3$CN at 298K.](image)

Compound 4.3 is stable in the solid state under ambient condition for months. However, it can be quickly reduced back to compound 4.1 in solution by weak donor solvent molecules such as DMSO. This is not surprising since a similar phenomenon was known for some of the previously reported ferrocenium compounds.\textsuperscript{17} The tilted Cp rings and the dynamic B-N bond dissociation could make the Fe center in 4.3 more vulnerable toward chemical reduction. Compound 4.3 was found to be sensitive toward light in solution and rapidly decomposed to unidentified species upon exposure to light and no evidence of photoisomerization of the boron unit was observed.
4.4 Conclusion

Using the N,C-chelate BMes₂-functionalized ferrocene compound 4.1, this chapter has illustrated the great mutual influence by the boron unit and the ferrocene unit on the electronic, photochemical, and chemical properties of the molecule. The low-lying electronic states of the ferrocene unit prohibit the photoisomerization of the boron unit. In addition, the steric congestion imposed by the ferrocene unit and the chelate strain by Cp and the N-methylbenzimidazolyl groups are likely responsible for the dissociation of the B–N bond, which leads to an unusual dynamic exchange of the two mesityl rings and the ring-opening hydrolysis of the boron unit. On the other hand, the BMes₂ chelate unit reinforces the MLCT process on the ferrocene unit, providing molecule 4.1 a low-energy MLCT state and a distinct red color. Furthermore, one of the mesityl rings on the boron center has been found to have a notable interaction with the unpaired electron of the Fe(III) ion in 4.3, which leads to a significant delocalization of the spin density through space.
4.5 Notes and References

The work described in this chapter has been published as:


Reference:


(10) Jäkle, F. Personal communication.


Chapter 5

Stepwise Intramolecular Photoisomerization of NHC-Chelate

Dimesitylboron Compounds with C–C Bond Formation and C–H Bond Insertion

5.1 Introduction

N-heterocyclic carbenes (NHCs) are well-known for their ability to stabilize rare main group species such as borylenes, boroles, silylenes, disilylenes, disilynes, germynes, diborenes, P₂, P₄, As₂, and Ga₂ and so forth. Unusual and exciting chemical properties and reactivity have been frequently observed for NHC-stabilized main group compounds, which further drives the intense research interest and activities in NHC-main group chemistry. Nonetheless, much earlier research on main group NHC compounds has focused on monodentate NHC ligands. Main group compounds that contain chelate ligands involving NHC donors have barely been explored, although NHC-containing chelate ligands involving a donor atom such as oxygen or nitrogen are well known and have been extensively explored for transition metal chemistry.

From the perspective of materials applications, aryl-cyclometallating or C,C-chelate NHC ligands containing two strongly σ-donating carbon atoms are capable of acting as new chelating scaffolds to build new main-group π-conjugated materials. Many examples of transition metal complexes with arylcyclometallating NHC ligands have been reported previously and used successfully in catalysis and OLEDs. In contrast, main-group examples especially those with a boron as the central atom remain unexplored. Moreover, the phenylpyridyl N,C-chelate BMes₂ (1.32) and its derivatives have demonstrated unique photochromic phenomenon. The pyridyl
moiety in N,C-chelate ligand plays a vital anchoring role, keeping the boron chromophore intact through the photoisomerization process. NHC ligands are much stronger $\sigma$ donors than pyridyl. Thus, replacing the pyridyl with a NHC donor may afford a new class of photo-responsive organoboron compounds.

With the above considerations, two families of C,C-chelate BMes$_2$ compounds B(2-(3-methylimidazol-2-ylidene)phenyl)Mes$_2$ (5.1) and B(2-(3-methylbenzimidazol-2-ylidene)phenyl)-Mes$_2$ (5.2) were designed. Compounds 5.1 and 5.2 are methylated derivatives of secondary amines 5.3 and 5.4, respectively. The methyl groups are incorporated to avoid the acidic amine protons, thus ensuring an improved stability during photolysis. This chapter will focus on their synthetic routes, structures and the unique photo-responsive properties of 5.1 and 5.2.

\[ \text{Figure 5.1 Molecular structures of 5.1, 5.2, 5.3 and 5.4.} \]

5.2 Experimental

5.2.1 General Procedures

Experimental techniques for synthesis, the use of instrumentation and the collection of X-ray crystallography diffraction data are as described in Chapter 2.2.1.

5.2.2 Synthesis of 5.1

*The non-methylated precursor B((imidazol-2-ylidene)phenyl)Mes$_2$ (5.3).* n-Butyllithium
(2.5 M, 1.7 mL, 4.2 mmol) was slowly added to a solution of 1-phenylimidazole (0.3 g, 2.1 mmol) in Et₂O (100 mL) at −78 °C. The solution was warmed to room temperature and stirred for 3 h. A diethyl ether solution of BMes₂F (0.62 g, 2.1 mmol) was then added dropwise at −78 °C. The resulting solution was slowly warmed to room temperature and stirred overnight. After the addition of excess methanol, the solution was then concentrated under vacuum. Purification by chromatography on silica gel (hexane/CH₂Cl₂) yielded compound 5.3 as a white solid, which was recrystallized from hexane/CH₂Cl₂ (0.40 g, 50%). ¹H NMR (CDCl₃, 25 °C, ppm): 9.02 (s, 1 H), 7.67 (d, 1 H, J = 7.0 Hz), 7.38 (d, 1 H, J = 1.5 Hz), 7.15–7.31 (m, 3 H), 7.87 (d, 1 H, J = 1.5 Hz), 6.70 (s, 4 H), 2.23 (s, 6 H), 1.88 (s, 12 H). ¹³C NMR (CDCl₃, 25 °C, ppm): 140.2, 140.2, 134.7, 133.1, 129.0, 126.7, 124.9, 120.0, 111.6, 110.3, 77.3, 77.0, 76.8, 24.9, 20.7. ¹¹B NMR (CDCl₃, 25 °C, ppm): −9.66 (s). Anal. Calcd for C₂₇H₃₀BN₂: C, 82.44; H, 7.69; N, 7.12. Found: C, 82.58; H, 7.49; N, 7.09.

Compound 5.3 (100 mg, 0.25 mmol) and KOt-Bu (40 mg, 0.35 mmol) were dissolved in 5 mL of THF in a vial; excess CH₃I (0.5 mL) was then added to the solution. The resulting solution was stirred overnight at room temperature, with a white precipitate generated during the progress of the reaction. After filtration of the KI salt and concentration of the filtrate under vacuum, 5.1 was obtained almost quantitatively, which was recrystallized from hexane/CH₂Cl₂. ¹H NMR (CD₂Cl₂, 25 °C, ppm): 7.60 (d, 1 H, J = 7.5 Hz), 7.52 (d, 1 H, J = 1.5 Hz), 7.33 (d, 1 H, J = 7.5 Hz), 7.18 (td, 1 H, J = 7.5 Hz, J = 1.5 Hz), 7.09 (td, 1 H, J = 7.5 Hz, J = 1.5 Hz), 7.00 (d, 1 H, J = 1.5 Hz), 6.66 (s, 4 H), 3.57 (s, 6 H), 2.20 (s, 6 H), 1.83 (s, 12 H). ¹³C NMR (CD₂Cl₂, 25 °C, ppm): 140.4, 140.1, 132.8, 132.6, 129.1, 126.1, 125.3, 124.5, 111.5, 110.8, 35.2, 24.7, 20.4. The carbene carbon could not be observed in ¹³C NMR spectra. In 2D ¹H–¹³C HMBC spectra, the cross peak between the carbene carbon and the protons from N-methyl showed up at
174.5 ppm. $^{11}$B NMR (CD$_2$Cl$_2$, 160 MHz, 25 °C, ppm): $-9.75$ (s). Anal. Caled for C$_{28}$H$_{31}$BN$_2$: 0.17CH$_2$Cl$_2$: C, 80.45; H, 7.51; N, 6.66. Found: C, 80.39; H, 7.79; N, 6.65. The presence of CH$_2$Cl$_2$ (~0.5 per molecule) in the crystal lattice was confirmed by X-ray crystallographic analysis.

5.2.3 Synthesis of 5.2

The non-methylated precursor $B$(benzimidazol-2-ylidene)phenyl)Mes$_2$ (5.4). The ligand 1-phenyl-benzimidazole was synthesized according to a literature procedure.$^{11}$ Compound 5.4 was synthesized and purified in the same manner as described for compound 5.3, and recrystallized from hexane/CH$_2$Cl$_2$ (30% yield) as a colorless solid. $^1$H NMR (CD$_2$Cl$_2$, 25 °C, ppm): 9.69 (s), 8.15 (d, 1H, $J = 10.8$ Hz), 7.84 (d, 1H, $J = 8.4$ Hz), 7.58–7.66 (m, 3H), 7.49 (t, 1H, $J = 10$ Hz), 7.37(t, 1H, $J = 10$ Hz), 7.23(t, 1H, $J = 10$ Hz), 6.87 (s, 4H), 2.21 (s, 6H), 1.92 (s, 12H). $^{13}$C NMR (CD$_2$Cl$_2$, 25 °C, ppm): 141.7, 140.1, 134.9, 134.1, 133.2, 129.0, 128.2, 125.9, 124.8, 113.2, 112.8, 112.1, 25.2, 20.4. $^{11}$B NMR (CD$_2$Cl$_2$, 160 MHz 25 °C, ppm): $-9.65$(s).

HRMS (TOF MS El$^+$): Caled, 442.2580; Observed, 442.2591.

Compound 5.2 was obtained almost quantitatively from precursor 5.4 in the same way as 5.1, and recrystallized from hexane/CH$_2$Cl$_2$. $^1$H NMR (CD$_2$Cl$_2$, 25 °C, ppm): 8.20 (d, 1 H, $J = 7.5$ Hz), 7.81 (d, 1 H, $J = 8.0$ Hz), 7.68 (d, 1 H, $J = 7.5$ Hz), 7.61 (td, 1 H, $^3J = 6.0$ Hz, $^4J = 2.0$ Hz), 7.56–7.60 (m, 2 H), 7.30 (t, 1 H, $J = 7.5$ Hz), 7.13 (t, 1 H, $J = 7.0$ Hz), 6.69 (s, 4 H), 3.57 (s, 6 H), 2.21 (s, 6 H), 1.88 (s, 12 H). $^{13}$C NMR (CD$_2$Cl$_2$, 25 °C, ppm): 140.3, 140.7, 137.2, 133.1, 132.3, 129.2, 128.0, 125.8, 124.9, 124.4, 112.9, 112.4, 111.5, 31.3, 24.9, 20.4. The carbene carbon could not be observed in $^{13}$C NMR spectra. In 2D $^1$H–$^{13}$C HMBC spectra, the cross peak between the carbene carbon and the protons from N-methyl showed up at 183.1 ppm. $^{11}$B NMR (C$_6$D$_6$, 160 MHz, 25 °C, ppm): $-8.98$ (s). Anal. Caled for C$_{32}$H$_{33}$BN$_2$: C, 84.21; H, 7.29; N, 6.14. Found: C, 84.21; H, 7.30; N, 6.28.
5.2.4 Photoisomerization of 5.1/5.2 and Characterization of 5.1/5.2a, 5.1/5.2b

General Procedures. Photoisomerization experiments were carried out in toluene or benzene under nitrogen using a Rayonet Reactor RPR-100. The progress of the photoisomerization was monitored by $^1$H NMR spectroscopy. The photoisomerization quantum efficiencies of 5.1 to 5.1a and 5.2 to 5.2a at 297 nm were determined using ferrioxalate actinometry.\textsuperscript{12}

5.2.4.1 Conversion of 5.1 to 5.1a

Compound 5.1a was obtained quantitatively via irradiation of 5.1 at 300 nm under nitrogen. The photoisomerization quantum efficiency was determined to be $\sim$0.75. On a typical NMR concentration scale (e.g., 1 mg of compound in $\sim$0.5 mL of C$_6$D$_6$), this conversion is completed in less than 0.5 h. Compound 5.1a can be crystallized readily from toluene/hexanes as a yellow crystalline solid. $^1$H NMR (25 °C, 500 MHz, ppm, C$_6$D$_6$): 7.69 (d, 1 H, $J = 10$ Hz), 7.15 (td, 1 H, $J = 10$ Hz, $J = 2.5$ Hz), 7.10 (s, 1 H), 7.06 (m, 2 H), 6.92 (s, 1 H), 6.84 (d, 1 H, $J = 2.5$ Hz), 6.03 (s, 1 H), 5.78 (d, 1 H, $J = 2.5$ Hz), 5.64 (s, 1 H), 3.01 (s, 3 H), 2.73 (s, 3 H), 2.33 (s, 3 H), 2.23 (s, 3 H), 2.07 (s, 3 H), 1.97 (s, 3 H), 0.85 (s, 3 H). $^{11}$B NMR (25 °C, 160 MHz, C$_6$D$_6$): $\sim$25.9 ppm.

5.2.4.2 Conversion of 5.1a to 5.1b

Compound 5.1b was obtained nearly quantitatively via continuous irradiation of 5.1a at 350 nm under nitrogen. The photoisomerization quantum efficiency is $\sim$0.001. 5.1b can be isolated as a colorless crystalline solid from a C$_6$D$_6$/hexanes solution. Because the conversion of 5.1a to 5.1b is very slow and inefficient (taking a few days to reach completion for a solution of
∼1 mg of 5.1a in 0.5 mL of solvent), bulk conversion was not performed. $^1$H NMR (25 °C, 500 MHz, ppm, C$_6$D$_6$): 7.87 (d, 1 H, $J = 7.5$ Hz), 7.32 (t, 1 H, $J = 7.5$ Hz), 7.33 (s, 1 H), 7.01 (d, 1 H, $J = 7.5$ Hz), 6.98 (s, 2 H), 6.97 (s, 1 H), 6.10 (d, 1 H, $J = 2.0$ Hz), 5.58 (d, 1 H, $J = 2.0$ Hz), 3.26 (s, 3 H), 2.63 (s, 3 H), 2.46 (s, 3 H), 2.37 (s, 3 H), 2.32 (s, 3 H), 2.11 (s, 3 H), 1.73 (s, 3 H). The B–H peak was observed in a $^1$H {'$^{11}$B decoupled} NMR spectrum: 4.23 (s, 1 H). $^{11}$B NMR (25 °C, 160 MHz, C$_6$D$_6$): −19.4, ppm, $^{1}J_{B-H} = 85$ Hz. HRMS (TOF MS EI+): calcd, 406.2580; observed, 406.2591.

5.2.4.3 Conversion of 5.2 to 5.2a

Compound 5.2a was obtained quantitatively via irradiation of 5.2 at 300 nm under nitrogen. The photoisomerization quantum efficiency is ∼0.60. Compound 5.2a can be crystallized readily from toluene/hexanes as a orange crystalline solid. 5.2a $^1$H NMR (25 °C, 500 MHz, ppm, C$_6$D$_6$): 7.92 (dd, 1 H, $J = 10$ Hz, $J = 1.0$ Hz), 7.83 (m, $^a$ 1 H), 7.70 (dd, 1 H, $J = 7.5$ Hz, $J = 1.5$ Hz), 7.20 (td, 1 H, $J = 7.0$ Hz, $J = 1.5$ Hz), 7.15 (td, 1 H, $J = 8.0$ Hz, $J = 1.5$ Hz), 7.12 (s, 1 H), 7.00 (m, $^a$ 2 H), 6.86 (s, 1 H), 6.57 (m, $^a$ 1H), 6.08 (s, 1 H), 5.61 (s, 1 H), 3.04 (s, 3 H), 2.97 (s, 3 H), 2.33 (s, 3 H), 2.26 (s, 3 H), 1.95 (s, 3 H), 1.94 (s, 3 H), 0.95 (s, 3 H). $^a$ The coupling constant was not obtained due to the complexity induced by second order coupling. $^{11}$B NMR (25 °C, 160 MHz, C$_6$D$_6$): −24.5 ppm.

5.2.4.4 Conversion of 5.2a to 5.2b

Compound 5.2b was obtained nearly quantitatively via continuous irradiation of 5.2a at 350 nm under nitrogen. The photoisomerization is very inefficient (Q.E. = ∼0.001). As a result, bulk conversion was not performed. Compound 5.2b can be isolated as a colorless crystalline solid. $^1$H NMR (25 °C, 500 MHz, ppm, C$_6$D$_6$): 7.89 (d, 1 H, $J = 7.5$ Hz), 7.37 (s, 1 H), 7.33 (t, 1
H, $J = 7.5$ Hz), 7.06 (d, $J = 7.5$ Hz), 7.02 (s, 1 H), 6.97 (s, 1 H), 6.93 (s, 1 H), 6.85 (m, $^2$ 2 H), 6.51 (m, $^1$ 1 H), 5.58 (m, $^1$ 1 H), 3.30 (s, 3 H), 2.96 (s, 3 H), 2.48 (s, 3 H), 2.39 (s, 3 H), 2.21 (s, 3 H), 2.06 (s, 3 H), 1.78 (s, 3 H). The B–H peak was observed in a $^1$H-$^{11}$B decoupled NMR spectrum: 4.35 (s, 1 H). (*The coupling constant was not obtained due to the complexity induced by second order coupling.*) $^{11}$B NMR (25 °C, 160 MHz, C$_6$D$_6$): −19.7 ppm, doublet, $^1$J$_{B-H} = 85$ Hz. HRMS (TOF MS EI$^+$): calcd, 456.2737; observed, 456.2749.

5.2.5 X-ray Crystallographic Analysis

X-ray crystallography diffraction data collection protocols follow those described in Chapter 2.2.5. The crystal lattice of 5.1a contains disordered solvent molecules that are most likely CH$_2$Cl$_2$ (≈0.5 per molecule of 5.1a). To improve the quality of the structural refinements, solvent contributions were removed by the Squeeze routine of Platon program. The crystals of 5.1b are very small and diffract weakly, resulting in a low ratio of observed reflections versus parameters, despite the 60 s/frame exposure time employed for data collection. Nonetheless, we were able to fully refine the structure of 5.1b. The hydrogen atom bound to the boron atom in 5.1b was located directly from a difference Fourier map and refined successfully. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms other than the one bound to boron were calculated, and their contributions in structural factor calculations were included. Crystal data for all structures have been deposited to the Cambridge Crystallographic Data Center (CCDC 877955–877960).

5.2.6 DFT Calculations

DFT and TD-DFT calculations were performed at the CAM-B3LYP/SVP level of theory. Test calculations demonstrated that this level of theory accurately reproduced the experimentally determined UV–Vis spectrum of a reference compound in the same class as those
considered here. All reactant, product and intermediate structures were optimized without constraints, and characterized as minima on the potential energy surface through frequency calculations. Excited state energies were determined through TD-DFT calculations.

The stationary points were optimized a second time at the B3LYP/6-311++G** level of theory\textsuperscript{15} in order to generate the orbital eigenvalues of the HOMO and LUMO. This was done to be consistent with previous computational work on similar compounds. All calculations were performed with the Gaussian 09 Software.\textsuperscript{16}

5.3 Results and Discussion

5.3.1 Synthesis and Structures of 5.1, 5.2, 5.3 and 5.4

![Synthetic schemes of 5.1, 5.2, 5.3 and 5.4.](image)

Figure 5.2 Synthetic schemes of 5.1, 5.2, 5.3 and 5.4.

The syntheses of compounds 5.3 and 5.4 were accomplished by a straightforward one-pot procedure shown in Figure 5.2. Double deprotonation of N-phenylimidazole or N-phenyl benzimidazole at \(-78\, ^\circ\text{C}\) in diethyl ether, followed by the addition of 1 equivalent of BMes\textsubscript{2}F

...
yielded the lithium salt Li[B(C,C-chelate)Mes₂]. Addition of CH₃OH to the corresponding solution of the lithium salt generated compounds 5.3 and 5.4 in moderate yields (50% for 5.3 and 30% for 5.4). 5.3 and 5.4 can be then converted quantitatively to the methylated derivatives 5.1 and 5.2 by the addition of a base (KO-t-Bu) and CH₃I.

Compounds 5.1, 5.2, 5.3 and 5.4 are colorless, air-stable, and can be purified by column chromatography. They are fully characterized by NMR, single-crystal X-ray diffraction, and elemental analyses. The two key resonance structures of these compounds are also shown in Figure 5.3.

![Figure 5.3 Key resonance structures of 5.1 and 5.2.](image)

Notably, Canac and Chauvin¹⁷ previously carried out a similar reaction, in which a double deprotonation of N-phenylimidazole was followed by the 1 equivalent addition of PPh₂Cl as electrophile. With one ortho position of the phenyl substituent being the most nucleophilic lithiated carbon atom, the reaction yielded product (imidazolylphenyl)diphenylphosphine in 65% yield (Figure 5.4). When the similar reaction was carried out with BMes₂F as nucleophile, monoborylation should also occur at the ortho position of the phenyl substituent in a similar fashion as the monophosphinylation did. However, in the presence of electron-deficient boron moiety, the deprotonated carbon anion on the imidazolyl ring rearranged in situ to a carbene analogue with the extra electron dissipated onto the neighboring nitrogen atoms. This can be attributed to the strong electrostatic attraction between three-coordinate boron and carbene.
Figure 5.4 The double deprotonation and the following monophosphinylation of N-phenylimidazole from Canac and Chauvin.

The crystal structures of 5.1, 5.2, 5.3 and 5.4 are shown in Figure 5.5. The key bond lengths and angles around the boron atom are summarized in Table 5.1. Compounds 5.1, 5.2, 5.3 and 5.4 have structural features similar to those of B(ppy)Mes$_2$ (1.32) and its derivatives. For example, the B–C$_\text{Ph}$ and B–C$_\text{Mes}$ bond lengths are all considerably longer than the typical B–C bonds observed in non-congested four-coordinate boron compounds (e.g., B(ppy)Ph$_2$, 1.33 in Chapter 1) but similar to those in sterically congested four-coordinate boron that contain a BMes$_2$ group. The B–CNHC bond lengths are also all longer than previously reported typical B–CNHC bond lengths in tetrahedral boron compounds. One notable difference is that the B–CNHC bond lengths in the nonmethylated compounds 5.3 and 5.4 (1.672(6) and 1.653(2) Å) are longer than those in the methylated compounds 5.1 and 5.2 (1.644(7) and 1.639(2) Å), which may be attributed to the greater electron donating ability of methyl, compared to a H atom.
Figure 5.5 Crystal structures of 5.1 (top left), 5.2 (top right), 5.3 (bottom left) and 5.4 (bottom right) with 50% thermal ellipsoids and labeling schemes for key atoms.

<table>
<thead>
<tr>
<th>Comp</th>
<th>B-C_{ph}</th>
<th>B-C_{NHC}</th>
<th>B-C_{Mes}</th>
<th>C_{ph}-B-C_{NHC}</th>
<th>C_{Mes}-B-C_{Mes}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>1.653(7)</td>
<td>1.644(7)</td>
<td>1.638(7), 1.646(7)</td>
<td>94.3(3)</td>
<td>115.1(4)</td>
</tr>
<tr>
<td>5.2</td>
<td>1.663(2)</td>
<td>1.639(2)</td>
<td>1.651(2), 1.653(2)</td>
<td>94.2(1)</td>
<td>113.6(1)</td>
</tr>
<tr>
<td>5.3</td>
<td>1.650(7)</td>
<td>1.672(6)</td>
<td>1.657(6), 1.643(7)</td>
<td>92.9(4)</td>
<td>117.5(4)</td>
</tr>
<tr>
<td>5.4</td>
<td>1.638(2)</td>
<td>1.653(2)</td>
<td>1.639(2), 1.666(2)</td>
<td>94.3(2)</td>
<td>116.5(1)</td>
</tr>
</tbody>
</table>
5.3.2 Electronic Properties of 5.1, 5.2, 5.3 and 5.4

Compared to N,C-chelate B(ppy)Mes₂, the new C,C-chelate compounds have a much larger HOMO–LUMO or optical energy gap and do not have any absorption in the visible region at all. Instead, they all have intense absorption bands in the UV region of 250–350 nm, as shown in Figure 5.6. The absorption maxima of 5.1 and 5.3 are about 5–10 nm higher in energy than those of 5.2 and 5.4. The absorption edges (∼ 320 nm) of 5.1 and 5.3 are about 20–30 nm higher in energy than those (∼ 345 nm) of 5.2 and 5.4, which can be attributed to the greater conjugation of the C,C-chelate ligand in 5.2 and 5.4.

Electrochemical data indicate that the narrowing of the HOMO–LUMO gap from 5.1 to 5.2 is mainly caused by the stabilization of the LUMO level (−1.94 to −2.14 eV), which is in agreement with the trend suggested by DFT calculation results (Figure 5.6). Furthermore, electrochemical data support that the large HOMO–LUMO gaps of 5.1 and 5.2, compared to those of B(ppy)Mes₂ (LUMO level = −2.50 eV, determined from CV data), are mainly caused by the high LUMO level of the C,C-chelate compounds.

![Absorption spectra and DFT calculated HOMO/LUMO energy](image)

**Figure 5.6** Left: Absorption spectra of 5.1 and 5.2 in CH₂Cl₂ (1×10⁻⁵ M). Right: DFT calculated HOMO/LUMO energy, and diagrams of 5.1 and 5.2 (isocontour value = 0.02).
5.2 and 5.4 display weak purple blue fluorescence at $\lambda_{\text{max}} = 410$ nm in toluene, which is also much higher in energy than that of B(ppy)Mes$_2$ ($\lambda_{\text{max}} = 480$ nm). The fluorescence quantum efficiency was determined to be 0.11 for 5.2, and 0.10 for 5.4. No appreciable fluorescence was observed for 5.1 and 5.3.

![Emission spectra of 5.2 and 5.4 in toluene (5\times10^{-5} M).](image)

**Figure 5.7** Emission spectra of 5.2 and 5.4 in toluene ($5\times10^{-5}$ M).

TD-DFT computational results confirmed that the transition from the ground state to the first excited state of the C,C-chelate compounds is dominated by the HOMO to LUMO transition, which is a charge transfer from the mesityl to the $\pi^*$ orbital of the C,C-chelate backbone as shown in Figure 5.6. The HOMO–LUMO diagrams of 5.1 and 5.2 bear striking resemblance to those of B(ppy)Mes$_2$. Thus, based on the similarity of molecular and electronic structures of 5.1 and 5.2 with those of B(ppy)Mes$_2$, it is anticipated that the new C,C-chelate BMes$_2$ compounds are very likely to undergo photoisomerization in the same manner as the N,C-chelate compounds.

### 5.3.3 Photoisomerization: 5.1 to 5.1a, 5.2 to 5.2a

Compounds 5.1 and 5.2 are the selected subjects of photo-responsive properties study, based on the consideration that the acidic amine protons in 5.3 and 5.4 might be unstable under
prolonged UV irradiation. The irradiation source is UV light at wavelength of 300 nm. The corresponding changes of 5.1 and 5.2 upon irradiation were monitored by UV-Vis absorption spectra and $^1$H, $^{11}$B NMR spectra.

Upon irradiation at 300 nm, compound 5.1 underwent distinct color changes to a bright yellow isomer 5.1a, with a new low energy absorption band appearing at $\lambda_{\text{max}} = 426$ nm in the UV-Vis absorption spectra (Figure 5.8). Likewise, 5.2 underwent color changes to a new orange isomer 5.2a, with absorption $\lambda_{\text{max}} = 456$ nm.

![Figure 5.8 UV–vis spectra showing the conversion of 5.1 to 5.1a (left) and 5.2 to 5.2a (right), in toluene (5×10$^{-5}$ M) irradiated at 300 nm, recorded with time intervals of a few seconds between each spectrum. Inset: photographs showing the color change of the samples.](image)

$^1$H and $^{11}$B NMR experiments also showed that compounds 5.1 and 5.2 underwent quantitative isomerizations upon irradiation at 300 nm, forming new isomers 5.1a and 5.2a, respectively. As illustrated by the $^1$H NMR spectra in Figure 5.9, the new isomers 5.1a and 5.2a all showed two characteristic olefinic protons peaks consistent with a cyclohexadienyl group. Furthermore, the $^{11}$B NMR spectra changed from $-9.26$ to $-25.86$ ppm for 5.1, and $-8.98$ to $-19.70$ ppm for 5.2.
Figure 5.9 Stacked $^1$H NMR spectra showing 5.1’s conversion to 5.1a (top) and 5.2’s conversion to 5.2a (bottom) in C$_6$D$_6$ with the characteristic olefinic protons highlighted in green bars.

The distinct color changes and appearances of characteristic olefinic protons in the new isomers are similar to those observed for the B(ppy)Mes$_2$(1.32a) shown in Figure 5.10. However, unlike the C–C bond formation in N,C-chelate BMes$_2$ compounds which is restricted to being between a mesityl and the carbon atom of the chelate ligand, the C–C bond formation in the C,C-chelate BMes$_2$ compounds 5.1 and 5.2 could occur at either the phenyl carbon site or the imidazolyl carbon site. To certainly establish the structures of 5.1a and 5.2a, 2D NMR experiments ($^1$H$^1$H COSY, NOESY and $^1$H$^{13}$C HMBC) were performed for both compounds, which confirmed that 5.1a and 5.2a indeed have the structures shown in Figures 5.10. The C–C
bond coupling in 5.1a and 5.2a occurred exclusively at the phenyl site of the C–C chelate in a similar fashion as that of 1.32a, indicating that the NHC-carbon donor atom in these molecules plays a same anchoring role as the pyridyl N donor does in B(ppy)Mes₂.

![Comparison of molecular structural changes in 1.32 to 1.32a, 5.1/5.2 to 5.1a/5.2a.](image)

**Figure 5.10** Comparison of molecular structural changes in 1.32 to 1.32a, 5.1/5.2 to 5.1a/5.2a.

Further evidence supporting the structures of 5.1a and 5.2a were obtained from the single-crystal X-ray diffraction analysis data of 5.2a. The crystal structure of 5.2a is shown in Figure 5.11. Its geometrical parameters are similar to those of a previously reported dark isomer of a N,C-chelate compound, (1-Phenyl-2-(2-Pyridyl)-indolyl)BMes₂ (Figure 1.23 in Chapter 1).

![The crystal structure of 5.2a with 50% thermal ellipsoids and labeling schemes for key atoms (left) and the side view of the structure with H atoms omitted (right).](image)

**Figure 5.11** The crystal structure of 5.2a with 50% thermal ellipsoids and labeling schemes for key atoms (left) and the side view of the structure with H atoms omitted (right).
Table 5.2 Selected bond lengths (Å) and angles (deg) of 5.2a.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(1)–C(7) 1.539(5)</td>
<td>C(7)–B(1)–C(24) 117.3(3)</td>
</tr>
<tr>
<td>B(1)–C(15) 1.684(5)</td>
<td>C(15)–B(1)–C(20) 55.8(2)</td>
</tr>
<tr>
<td>B(1)–C(20) 1.621(5)</td>
<td>B(1)–C(15)–C(20) 60.2(2)</td>
</tr>
<tr>
<td>B(1)–C(24) 1.601(5)</td>
<td>B(1)–C(20–C(15) 64.2(2)</td>
</tr>
</tbody>
</table>

The B(1)–C(7) bond (1.539(5) Å) in 5.2a is much shorter than that of 5.2. The C(15)–C(20) bond (1.548(5) Å) is typical of a C–C single bond while the bond lengths (1.346(5), 1.355(4) Å) of C(16)–C(17) and C(18)–C(19) agree well with typical C=C bonds, thus, confirming that the transformed mesityl group can indeed be described as a cyclohexadienyl. The structural features of the BC2-cyclohexadienyl moiety in 5.2a are also similar to a BC2-naphthyl moiety in boron-carbene compounds reported by Braunschweig and co-workers.2b The C,C-chelate benzene ring and the benzimidazolyl ring are twisted out of coplanarity with a dihedral angle of 19.4°, attributable to the interactions of the two ortho-H atoms.

The photoisomerization of 5.1/5.2 to 5.1a/5.2a is very efficient and the quantum efficiency was found to be ~0.75 for 5.1 to 5.1a, ~0.60 for 5.2 to 5.2a, respectively, in toluene using ferrioxalate actinometry at 297 nm excitation.12

5.3.4 Electronic Properties of 5.1a and 5.2a

Electrochemical analysis data (CV) showed that 5.1a and 5.2a have a distinct low oxidation potential (~0.55 and ~0.41V, vs FeCp2) similar to that of the dark blue isomer B(ppy)Mes2 1.32a (Figure 5.12 and Table 5.3).
**Figure 5.12** Left: CV diagrams showing the appearance and the growth of the oxidation peak of 5.1a with time (t) when the DMF solution of 5.1 is irradiated at 300 nm with a hand-held UV lamp, with NBu₄PF₆ as the electrolyte, and a scan rate of 150 mV s⁻¹. E₁/₂(FeCp₂⁺/0) = 0.55 V.

Right: oxidation peak of 5.2a at the same condition as described for 5.1a.

On the basis of UV–Vis and CV data, the HOMO level of 5.1a and 5.2a is more than 1 eV above that of 5.1 and 5.2 while the LUMO level experiences little change. The color difference between the yellow 5.1a/orange 5.2a and the dark blue 1.32a is therefore caused mainly by the relatively high LUMO level (≈ -2.0 eV) of 5.1a and 5.2a, compared to that of 1.32a (≈ -2.50 eV), leading to a higher S₀→S₁ transition energy. This trend is in good agreement with the DFT computational results shown in Figure 5.13. The electron density distribution in 5.1a and 5.2a was found to be similar to that of 1.32a with the HOMO level being dominated by contributions from the BC₂ triangular ring (Figure 5.13). The computational results also show that 5.1a and 5.2a are about 70–80 kJ/mol less stable than 5.1 and 5.2. This energy difference is much less than that between 1.32 and 1.32a (≈115 kJ/mol), owing to that the carbene donors appear to exert a greater stabilization effect relative to the pyridyl donor.
Figure 5.13 DFT calculated total energy, HOMO/LUMO energy, and diagrams of 5.1, 5.1a and 5.2, 5.2a (isocontour value = 0.02).

5.3.5 Photoconversion of 5.1a/5.2a to 5.1b/5.2b

In sharp contrast to the behavior of B(ppy)Mes$_2$ (1.32a) and its derivative compounds that can thermally reverse back to the more stable colorless or light colored isomers, 5.1a and 5.2a were found to have a very high thermal stability. The $^1$H NMR spectra of 5.1a and 5.2a showed no change at all after being heated at either 110 °C in $d_8$-toluene for hours. However, remarkably, both 5.1a and 5.2a can be sensitized by light. When irradiated at 350 nm, 5.1a and 5.2a gradually lost their color, converting to a new colorless isomer 5.1b and 5.2b, respectively. The whole process was monitored by $^1$H NMR spectra, as shown in Figure 5.14.
Figure 5.14 Stacked $^1$H NMR spectra showing the change of 5.1a (highlight in pink bar) to 5.1b (highlighted in grey bar) in C$_6$D$_6$ upon irradiation at 350 nm.

In the $^1$H{$^1$B decoupled} NMR spectra of 5.1b and 5.2b, a peak at 4.23 and 4.35 ppm, respectively, was observed, which can be assigned to a B–H proton. In the $^{11}$B{$^1$H-coupled} NMR spectra, 5.1b and 5.2b display a distinct doublet at −19.4 and −19.3 ppm, respectively, with a coupling constant of 85 Hz, characteristic of $^1J_{B-H}$ coupling$^{2b,c,e,19,20}$ (see section 5.4). The six-methyl groups on the two mesityls are all resolved in the $^1$H NMR spectra of 5.1b and 5.2b, due to the asymmetric environment around the B atom. Further extensive 2D $^1H^1$H COSY and NOESY NMR spectra led us to establish the structure of 5.1b and 5.2b as shown in Figure 5.15.

5.1b and 5.2b are air-stable and colorless.

Figure 5.15 Conversion scheme of 5.1a/5.2a to 5.1b/5.2b.
Compared to the isomerization of 5.1/5.2 to 5.1a/5.2a, photoconversion of 5.1a/5.2a to 5.1b/5.2b is much less efficient. Full conversion can only be achieved after the samples were irradiated at 350 nm for a few days at the typical NMR concentration scale (∼1 mg sample in 0.5 mL of solvent), while under the same conditions, using 300 nm excitation, the full conversion of 5.1/5.2 to 5.1a/5.2a can be achieved in less than 30 min.

5.3.6 Crystal structure of 5.1b

The crystal structure of 5.1b was determined by single crystal X-ray diffraction analysis, which fully corroborates the structural features established by NMR experiments. As shown in Figure 5.16, the C,C-chelate remains bound to the B atom in 5.1b. In addition, the B atom is bound to one mesityl group and one H atom (located directly from a difference Fourier map) in a distorted tetrahedral geometry.

Figure 5.16 Crystal structure of 5.1b with 50% thermal ellipsoids and labeling for key atoms.

Table 5-3 Selected bond lengths (Å) and angles (deg) of 5.1b.

<table>
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<tr>
<th>Bond Lengths (Å)</th>
<th>Selected Bond Lengths (Å)</th>
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<tr>
<td></td>
<td>B(1)–C(1) 1.621(11)</td>
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<td></td>
<td>B(1)–C(7) 1.618(11)</td>
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<td>B(1)–C(11) 1.609(11)</td>
</tr>
<tr>
<td></td>
<td>B(1)–H(1) 1.20(5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (°)</th>
<th>Selected Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)–B(1)–C(7) 95.3(6)</td>
<td>C(11)–B(1)–H(1) 113(2)</td>
</tr>
<tr>
<td>C(1)–B(1)–C(11) 117.5(7)</td>
<td>C(7)–B(1)–C(11) 117.5(7)</td>
</tr>
</tbody>
</table>
The B(1)–H(1) bond length of 1.20(5) Å is in the range of typical terminal B–H bond lengths reported previously.\textsuperscript{2b,c,e,19,20} The second mesityl group forms a C–C bond with a carbon atom of the phenyl ring with a typical bond length (C(5)–C(20) = 1.488(10) Å). Compared to those of 5.1 and 5.2, the B–C bonds length in 5.1b is considerably shorter, which can be attributed to the reduced steric congestion around the B center.

5.3.7 Electronic structure of 5.1b and 5.2b

The absorption spectra of 5.1b and 5.2b resemble those of 5.1 and 5.2 (Figure 5.17), with the $S_0 \rightarrow S_1$ transition being a charge transfer from a mesityl to the chelate, shown by DFT computational results (Figure 5.17).

![Figure 5.17](image)

**Figure 5.17** Left: Absorption spectra of 5.1, 5.1b and 5.2, 5.2b in CH\textsubscript{2}Cl\textsubscript{2} (1×10\textsuperscript{-5} M). Right: DFT calculated HOMO/LUMO energy, and diagrams of 5.1b and 5.2b (isocontour value = 0.02).

5.3.8 The Photoisomerization Mechanism of 5.1/5.2 $\rightarrow$ 5.1a/5.2a $\rightarrow$ 5.1b/5.2b

Mechanistically, the photoisomerization of the C,C-chelate compound 5.1/5.2 to 5.1a/5.2a likely follows a pathway via a transition state M1, the following photoisomerization of 5.1a/5.2a to 5.1b/5.2b involves a “borylene”-like transient species M2 as shown in Figure 5.18.
5.3.8.1 Mechanism of 5.1→5.1a Studied by DFT Calculation

Our attempts to map out the transition states and calculate the activation barrier for the thermal transformation of 5.1 to 5.1a using DFT methods were unsuccessful. Nonetheless, we have identified an intermediate (5.1-I1) that is similar to that involved in the transformation of B(ppy)Mes₂ 21 but at a much higher energy (∼204 kJmol⁻¹ higher than 5.1, and 130 kJmol⁻¹ than 5.1a), as shown in Figure 5.19. This also suggests that the activation barrier for the reverse transformation of 5.1a to 5.1 is much higher than that of B(ppy)Mes₂ 1.32a to 1.32, in which the activation barrier is determined to be ∼110 kJmol⁻¹ experimentally. This could explain the high thermal stability of 5.1a and 5.2a.

Preliminary computational results on the first excited state indicates that 5.1* to 5.1a* transformation is a downhill process with an energy difference ∼50 kJmol⁻¹, thus, the photoisomerization of 5.1 to 5.1a can occur readily via the excited state.
5.3.8.2 Mechanism of 5.1a→5.1b Studied by DFT Calculation

A computational study of the isomerization 5.1a to 5.1b was also performed. At the ground state, a highly energetic “borylene”-like intermediate 5.1-I2 was identified (∼ 140 kJ mol⁻¹ above 5.1a). Following the “borylene”-like intermediate 5.1-I2 formation, a simple rotation around the N–C bond in 5.1-I2 would bring the ortho-H atom of the benzene ring close to the boron center (5.1-I2), activating the C–H bond (Figure 5.18).

![Energy diagrams showing the relative energies of 5.1, 5.1a, and 5.1b at the ground state (S₀) and at the first excited state (S₁).](image)

The transition state connecting 5.1a and 5.1-I2 could not be located; however, the energy
of the transition state must be higher than that of **5.1-12**, suggesting a large activation energy for the transformation from **5.1a** to **5.1b**, rendering that process inaccessible via a thermal pathway. The formation of **5.1-12** may be described as a cheletropic boron elimination\(^\text{22}\) from **5.1a**. At the first excited state, **5.1b\(^*\)** is less stable than **5.1a** by \(\sim 30 \text{ kJmol}^{-1}\). Thus, in order to convert **5.1a** to **5.1b** via the excited state, **5.1a** needs to be excited above the first excited state.

On the basis of the DFT calculated data, among the three isomers, **5.1b** is the most stable isomer, 75 kJmol\(^{-1}\) below **5.1** and 145 kJmol\(^{-1}\) below **5.1a**. Similarly, the total energy of isomer **5.2b** is 62 kJmol\(^{-1}\) below **5.2**, 151 kJmol\(^{-1}\) below **5.2a**. Thus, the transformation of **5.1a/5.2a** to **5.1b/5.2b** is highly favored thermodynamically.

The possible involvement of a borylene species in intramolecular C–H insertion reaction was proposed in several previously reported organoboron systems, where the proposed “borylene” species was generated in situ via chemical reduction of a borane, followed by C–H insertion.\(^\text{1e,2c,20}\) It is conceivable that in this system, the C,C-chelate ligand stabilizes the “borylene” intermediate **5.1-12** generated through the excited state, leading to C–H bond activation and the isolation of compounds **5.1b** and **5.2b**. The selective activation of an aryl C–H bond over an aliphatic C–H bond (e.g., the methyl group in the mesityl) may be facilitated by the involvement of the \(\pi^*\) orbital of the benzene ring in stabilizing the transition state and the greater stability of the resulting 5-membered ring in **5.1b** (versus the 6-membered ring in methyl activation).
5.4 Conclusion

This Chapter has demonstrated that C,C-chelate BMes₂ compounds with the NHC-donor atom retain structures and electronic properties similar to those of N,C-chelate BMes₂ compounds, and as a result, this class of compounds undergo highly efficient and clean photoisomerization in the same manner as the N,C-chelate BMes₂ compounds do. There are, however, several distinct differences between the N,C-BMes₂ and C,C-BMes₂ compounds. First of all, the carbene donor greatly stabilizes the dark isomers of the C,C-chelate compounds, ensuring their high thermal stability. Second, the dark isomers of the C,C-chelate compounds can undergo further photoisomerization, producing a new isomer that involves intramolecular C–H bond activation. The same phenomenon has not been observed at all in any of the N,C-chelate BMes₂ compounds we investigated previously. The robustness of the C,C-chelate BMes₂ compounds toward photolysis and their ability to undergo clean and stepwise photoisomerization are truly remarkable, opening many new research opportunities in accessing unusual structures/species/reactivity via the excited state.
5.5 Selected NMR data

**Figure 5.20** Stacked $^1$H NMR spectra showing stepwise changes of 5.1 to 5.1a then 5.1b upon irradiation. Insets: all peak are assigned regarding to the molecular structure.

**Figure 5.21** $^{11}$B NMR spectra 5.1b in C$_6$D$_6$. (left): $^{11}$B {$^1$H coupled}; (right): $^{11}$B {$^1$H decoupled}.
Figure 5.22 $^1$H NMR spectra 5.1b in C$_6$D$_6$. (top): $^1$H {${}^{11}$B decoupled}; (bottom): $^1$H {${}^{11}$B coupled}.

Figure 5.23 Stacked $^1$H NMR spectra showing stepwise changes of 5.2 to 5.2a then 5.2b upon irradiation. Insets: all peak are assigned regarding to the molecular structure.
Figure 5.24 $^{11}$B NMR spectra of 5.2b in C$_6$D$_6$. (left): $^{11}$B { $^1$H coupled}; (right): $^{11}$B { $^1$H decoupled}.

Figure 5.25 $^1$H NMR spectra 5.2b in C$_6$D$_6$. (top): $^1$H { $^{11}$B decoupled}; (bottom): $^1$H{ $^{11}$B coupled}. 

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5.6 Notes and References

The work described in this chapter has been published as:


References:


(10) After the submission of this manuscript, we learned that S. Yamaguchi and co-workers also synthesized and investigated related N-thienyl-benzimidazole C,C-chelate BMes_2 at the same time with us, see: Nagura, K.; Saito, S.; Fröhlich, R.; Glorius, F.; Yamaguchi, S. Angew. Chem., Int. Ed. 2012, 51, 7762.


(16) Frisch, M. J. et al.; Gaussian 09, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.

(c) Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5582.


(22) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, **2006**.  
Chapter 6

Photo and Thermal-induced Multi-structural Transformation of 2-ph-azolyl Chelate Boron Compounds

6.1 Introduction

Molecular isomerism is a common phenomenon in the chemical world. It plays an important role in biology, medicine, and the development of advanced materials\textsuperscript{1-4}. The most commonly observed molecular isomerism involves the structural change of two different forms of molecules such as the \textit{cis}, \textit{trans}-isomerization around a double bond\textsuperscript{2}, the inter-conversion of \textit{mer} and \textit{fac}-isomers of octahedral metal complexes\textsuperscript{3}, and the transformation of the ring-opened and ring-closed isomers of dithienylethenes and spiropyans.\textsuperscript{4} Because molecular isomerization can be often controlled by external stimuli such as light, heat or pressure, and the different isomers usually have distinct chemical and physical properties, this phenomenon has been exploited extensively in switching/controlling chemical reactivity, optical, electronic, and physical properties of molecules and materials\textsuperscript{1-4}. Despite the common occurrence of molecular isomerism, molecular systems that display multi-stage isomerization or structural transformation involving more than two isomers in response to heat or light remain rare.

This chapter focuses on an unprecedented example of light-triggered multi-structural transformation based on organoboron molecules. This discovery was made during the investigation on a new class of N,C-chelate organoboron compounds, namely B(2-ph-azolyl)Mes\textsubscript{2} (azolyl = benzothiazolyl, \textit{6.1a}; 4-methylthiazolyl, \textit{6.2a}; benzoxazolyl, \textit{6.3a}; benzoimidazolyl, \textit{6.4a}).
They are analogues of the previously reported N,C-chelate compound B(ppy)Mes$_2$ (1.32) and derivatives. However, unlike compound 1.32 that undergoes facile and efficient photo-thermal isomerization, compounds 6.1a-6.4a undergo sequential and multi-structural transformations in response to irradiation by light or heat. This unusual transformation involves (a) photoisomerization of isomers (b) thermal intramolecular H atom transfer (c) 1,3-shift of the boryl group and (d) diastereomer inter-conversion via a ring opening/closing process. Examples of organoboron compounds that display unusual and unique photo/thermal isomerization phenomena have been reported recently. This work further illustrates the exceptional ability of N,C-chelate boron compounds to transform and adapt in response to light and heat.

6.2 Experimental

6.2.1 General Procedures

Experimental techniques for synthesis, the use of instrumentation and the collection of X-ray crystallography diffraction data are as described in Chapter 2.2.1.
6.2.2 Synthesis of 6.1a, 6.3a

![Synthetic routes of 6.1a and 6.3a.](image)

The ligands 2-(2-bromophenyl)benzothiazole (6.5) and 2-(2-bromophenyl)benzoxazole (6.6) were prepared based on literature procedures, as shown in Figure 6.1.\textsuperscript{5a}

Synthesis and Characterization of 2-(2-(dimesitylboryl)phenyl)benzothiazole (6.1a): n-BuLi (3.2 mL, 5.0 mmol) was added slowly to a solution of 6.5 (1.45 g, 5.0 mmol) in THF (50 mL) at -78 °C and the resulting solution was stirred for about 1 hour at -78 °C. Then, BMes\textsubscript{2}F\textsubscript{2} (1.5 g, 5.0 mmol) was added under nitrogen and the solution was stirred at the same temperature for about 2 hours and then stirred overnight at ambient temperature. Solvents were removed under reduced pressure and the resulting solid was dissolved in 50 mL of CH\textsubscript{2}Cl\textsubscript{2} and quenched with 10 mL of H\textsubscript{2}O. The organic layer was separated and dried over MgSO\textsubscript{4} and filtered. After CH\textsubscript{2}Cl\textsubscript{2} was removed under reduced pressure, the residue was purified over silica gel by flash column chromatography using a CH\textsubscript{2}Cl\textsubscript{2}/hexanes (1:4) mixture, producing a yellow powder of 6.1a (1.4 g, 61%). HREI-MS (M\textsuperscript{+}): m/z Calcd for C\textsubscript{31}H\textsubscript{30}BNS, 459.2192. Found: 459.2209. Anal. Calcd for C\textsubscript{31}H\textsubscript{30}BNS: C, 81.04; H, 6.58; N, 3.05. Found: C, 80.75; H, 6.69; N, 3.02. \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 25 °C, ppm): 7.97-7.92 (m, 2 H), 7.88 (t, 2 H, \textsuperscript{3}J = 7.5 Hz), 7.49-7.40 (m, 3 H), 7.33 (t, 1 H, \textsuperscript{3}J = 7.5 Hz), 6.69 (s, 4 H), 2.20 (s, 6 H), 1.89 (s, 12 H). \textsuperscript{13}C NMR (125.6 MHz,

2-(2-(dimesitylboryl)phenyl)benzoxazole (6.3a): 2-(2-Bromophenyl)benzoxazole (6.6) (1.15 g, 4.19 mmol) in THF (50 mL), n-BuLi (2.63 mL, 4.2 mmol), BMes₂F (1.26 g, 4.2 mmol) were treated according to the same manner as described for 6.1a. Purification by chromatography (CH₂Cl₂:hexane = 1:4) gave a white powder of 6.3a (0.68 g, 41%). HREI-MS (M⁺): m/z Calcd for C₃₁H₃₀BNO, 443.2420. Found: 443.2432. Anal. Calcd for C₃₁H₃₀BNO: C, 83.97; H, 6.82; N, 3.16. Found: C, 83.45; H, 7.06; N, 3.09. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C, ppm): 7.99 (d, 1H, 3J = 7.0 Hz), 7.85 (d, 1H, 3J = 7.5 Hz), 7.76 (d, 1H, 3J = 8.0 Hz), 7.65 (d, 1H, 3J = 7.5 Hz), 7.50-7.37 (m, 4H), 6.69 (s, 4H), 2.19 (s, 6H), 1.91 (s, 12H). ¹³C NMR (125.6 MHz, CD₂Cl₂, 25 °C, ppm): 169.8, 153.2, 134.6, 134.4, 133.4, 131.8, 130.1, 127.1, 126.3, 126.2, 124.1, 123.2, 117.2, 112.8, 111.3, 25.4, 20.8. ¹¹B NMR (128 MHz, CD₂Cl₂, 25 °C, ppm): 3.43.

6.2.3 Synthesis of 6.2a

![Synthetic route of 6.2a.](image)

2-bromo-5-methylthiazole (6.8) was synthesized according to literature procedure⁵b as shown in Figure 6.2. The ligand 6.7 was synthesized using a Suzuki-Miyaura coupling protocol of 2-bromophenylboronic acid (1.2 g, 6.0 mmol) and 2-bromo-5-methyl thiazole (1.0 g, 6 mmol) in THF/H₂O (1:1 v/v 150 mL), with Pd(PPh₃)₄ (0.19 g, 0.15 mmol) as the catalyst and K₂CO₃ (4.5
g, 30 mmol) as the base at 70 °C. $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C, δ, ppm): 7.99 (dd, 1 H, $^3$J = 7.8 Hz, $^4$J = 1.5 Hz), 7.70 (dd, 1 H, $^3$J = 8.0 Hz, $^4$J = 0.9 Hz), 7.63 (s, 1 H), 7.47 (td, 1 H, $^3$J = 7.7 Hz, $^4$J = 1.2 Hz), 7.27 (td, 1 H, $^3$J = 7.7 Hz, $^4$J = 1.2 Hz), 2.56 (s, 3 H).

2-(2-(dimesitylboryl)phenyl)-5-methylthiazole (6.2a): 2-bromophenyl-5-methylthiazole (6.7) (0.48 g, 1.9 mmol) in THF (30 mL), n-BuLi (1.19 mL, 1.9 mmol), BMes$_2$F (0.74 g, 2.0 mmol) were treated according to the same manner as described for 6.1a. Purification by chromatography (CH$_2$Cl$_2$:hexane = 1:4) gave a yellowish powder of 6.2a (0.52 g, 65%). HREI-MS (M)$^+$: m/z Calcd for C$_{28}$H$_{30}$BNS, 423.2192. Found: 423.2209. Anal. Calcd for C$_{28}$H$_{30}$BNS: C, 79.31; H, 7.30; N, 3.30, S, 7.55. Found: C, 79.42; H, 7.14; N, 3.31; S, 7.57. $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 7.89 (d, 1 H, $^3$J = 7.5 Hz), 7.79 (d, 1 H, $^3$J = 8.0 Hz), 7.68 (s, 1 H), 7.47 (t, 1 H, $^3$J = 7.0 Hz), 7.39 (t, 1 H, $^3$J = 7.0 Hz), 6.85 (s, 4 H), 2.56 (s, 3 H), 2.36 (s, 6 H), 2.04 (s, 12 H). $^{13}$C NMR (125.6 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 171.2, 139.8, 134.5, 133.69, 133.65, 132.6, 131.5, 130.5, 129.5, 125.3, 121.6, 24.5, 20.35, 13.0. $^{11}$B NMR (128 MHz, C$_6$D$_6$, 25 °C, ppm): 4.18.

**6.2.4 Synthesis of 6.4a**

![Figure 6.3 Synthetic route of 6.4a.](image_url)

Synthesis of ligand 6.9: Excess methyl iodine (0.25 mL) was added to a stirred THF solution of 2-phenylbenzimidazole (0.7 g, 3.6 mmol) and KO-t-Bu (0.42 g, 3.7 mmol) at r.t under
air. The resulting solution was then further stirred for a few hours. After the removal of the solvent, compound 6.9 were obtained quantitatively.

As shown in Figure 6.3, compound 6.4a was synthesized by using a lithiation procedure according to the literature:\textsuperscript{sc} t-butyllithium (1.5 mL, 1.4 M, 2.1 mmol) was added to 1-methyl-2-phenylbenzimidazol (0.30 g, 1.4 mmol) at -78 °C in THF, under nitrogen atmosphere over a period of 45 minutes. The solution was allowed to stir for 2 hours, following which dimesitylboron fluoride (0.5 g, 1.9 mmol) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The compound was purified as a white crystalline solid (0.44 g, 70%) by column chromatography on silica gel using hexanes:CH₂Cl₂ (70%:30% v/v) as the eluent. HREI-MS (M)\textsuperscript{+}: m/z Calcd for C₃₂H₃₃BN₂, 456.2754. Found: 456.2737. Anal. Calcd for C₃₂H₃₃BN₂: C, 84.12; H, 7.47; N, 6.10. Found: C, 84.21; H, 7.29; N, 6.14. \textsuperscript{1}H NMR (400 MHz, C₆D₆, 25 °C, ppm): 8.20 (d, 1 H, J = 7.7 Hz), 7.92 (d, 1 H, J = 8.2 Hz), 7.36 (d, 1 H, J = 7.7 Hz), 7.15 (dd, 1 H, J = 7.6 Hz, J = 1.0 Hz), 7.01 (td, 1 H, J = 7.6 Hz, J = 1.0 Hz), 6.92 (td, 1 H, J = 8.0, J = 1.0 Hz), 6.85 (td, 1 H, J = 7.7 Hz, J = 1.0 Hz), 6.84 (s, 4 H), 6.58 (d, 1 H, J = 8.0 Hz), 2.84 (s, 3 H), 2.22 (b, 18 H). \textsuperscript{13}C NMR (125.6 MHz, CD₂Cl₂, 25 °C, ppm): 156.6, 140.1, 137.1, 135.4, 133.4, 131.3, 130.8, 129.6, 126.9, 124.9, 124.5, 123.7, 122.3, 116.3, 110.7, 31.6, 24.9, 20.3. \textsuperscript{11}B NMR (128 MHz, C₆D₆, 25 °C, ppm): 1.94.

\textbf{6.2.5 Synthesis and Characterization of 6.1d and 6.1e}

Around 50 mg of 6.1a was dissolved in 100 mL toluene under nitrogen. The solution was then irradiated inside an UV reactor (Rayonet Reactor RPR-100) at 350 nm for a few hours. The resulting dark blue solution was heated at 50 °C overnight. After the solution became colorless, the flask was put under 350 nm irradiation again, then 50 °C for a few hours. This cycle was repeated 2 or 3 times until the solution stopped changing to dark blue color at 350 nm irradiation
(an indication that compound 6.1a has been fully consumed and converted to isomer 6.1d). The solvent was then concentrated under vacuum. Colorless crystals of 6.1d were obtained in high yield. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 7.57 (d, 1 H, $^3$J = 7.0 Hz), 7.53 (t, 1 H, $^3$J = 7.5 Hz), 7.44 (t, 1 H, $^3$J = 7.5 Hz), 7.16 (d, 1 H, $^3$J = 7.5 Hz), 7.10 (d, 1 H, $^3$J = 7.5 Hz), 6.98 (s, 1 H), 6.88 (s, 1 H), 6.86 (t, 1 H, $^3$J = 7.5 Hz), 6.57 (s, 1 H), 6.55 (1 H, overlapped with neighboring singlets), 6.54 (s, 1 H), 6.52 (s, 1 H), 6.13 (d, 1 H, $^3$J = 8.0 Hz), 2.73 (d, 1 H, $^2$J = 11.0 Hz), 2.32 (s, 3 H), 2.29 (s, 3 H), 2.22 (s, 3 H), 2.19 (d, 1 H, $^2$J = 11.0 Hz), 0.96 (s, 3 H). $^{13}$C NMR (125.6 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 145.4, 142.2, 138.2, 137.9, 137.2, 136.8, 136.7, 136.6, 135.3, 134.9, 133.7, 132.2, 131.8, 129.7, 127.8, 127.5, 127.4, 127.0, 126.7, 124.5, 123.6, 122.3, 119.2, 80.1, 28.5, 21.7, 20.9, 20.8, 20.7, 20.1. $^{11}$B NMR (128 MHz, C$_6$D$_6$, 25 °C, ppm): 46.0 (broad).

To convert 6.1d to 6.1e, 20 mg of 6.1d was dissolved in 50 mL of toluene under nitrogen. The resulting solution was heated at 110°C overnight. To ensure full conversion of 6.1d to 6.1e, the solution could be heated for longer time. The solvent was then concentrated under vacuum. Crystals of 6.1e were isolated quantitatively. Anal. Calcd for C$_{31}$H$_{30}$BNS: C, 81.04; H, 6.58; N, 3.05; S, 6.98. Found: C, 81.44; H, 7.14; N, 2.95; S, 6.36. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 7.86 (m, 1 H), 7.43 (m, 2 H), 7.33 (m, 1 H), 7.14 (dd, 1 H, $^3$J = 8.0 Hz, $^4$J = 1.2 Hz), 7.00 (s, 1 H), 6.95 (s, 1 H), 6.90 (s, 1 H), 6.86 (t, 1 H, $^3$J = 7.6 Hz), 6.77 (s, 1 H), 6.73 (s, 1 H), 6.60 (t, 1 H, $^3$J = 7.2 Hz), 6.20 (d, 1 H, $^3$J = 8.4 Hz), 2.60 (d, 1 H, $^2$J = 16.0 Hz), 2.36 (s, 3 H), 2.32 (s, 3 H), 2.29 (s, 3 H), 2.23 (d, 1 H, $^2$J = 16.0 Hz), 2.21 (s, 3 H), 1.74 (s, 3 H). $^{13}$C NMR (125.6 MHz, CD$_2$Cl$_2$, 25 °C, ppm): 143.7, 139.5, 139.1, 138.9, 137.8, 137.1, 136.5, 136.4, 135.1, 134.6, 129.8, 128.4, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.3, 125.1, 123.4, 121.2, 115.2, 63.9, 34.2, 21.5, 20.9, 20.8, 20.3, 20.2. $^{11}$B NMR (128 MHz, C$_6$D$_6$, 25 °C, ppm): 48.0 (broad). (°The
coupling constant could not be obtained due to the complexity induced by second order coupling).

6.2.6 X-ray Diffraction Analysis

X-ray crystallography diffraction data collection protocols follow those described in Chapter 2.2.5. Compounds 6.2a and 6.3a belong to the monoclinic crystal space group P2₁/c and the orthorhombic space group P2₁2₁2₁, respectively. Compounds 6.1d and 6.1e belong to the monoclinic space group Cc and the triclinic space group p-1, respectively. All structures are solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated and their contributions in structural factors were included. The crystal structural data files of 6.2a, 6.3a, 6.1d and 6.1e have been deposited at the Cambridge Crystallographic Data Centre (CCDC 913143, 913142, 913141, and 913144, respectively).

6.2.7 DFT Calculations

Theoretical calculations were carried out at the CAM-B3LYP/SVP level of theory using Gaussian 09 software unless otherwise noted. Compared to B3LYP functional, test calculations demonstrated that CAM-B3LYP functional more accurately reproduced the experimentally determined UV-Vis spectrum of a reference compound in the same class as those considered here. The ground states of all reactants, products and intermediate structures were optimized without constrains, and characterized as minima on the potential energy surface through frequency calculations. The transition state structure was also optimized without constrains and contained only one imaginary frequency.

Calculated NMR spectra data. Chemical shifts were obtained by subtracting the calculated magnetic shielding for the nuclei of interest from the reference compound shielding [tetramethylsilane (TMS) for ¹H]. ¹H chemical shifts were calculated with optimized geometry
using the density functional theory–gauge including/invariant atomic orbitals (DFT – GIAO) approximation at the CAM-B3LYP/SVP level of theory.

6.3 Results and Discussion

6.3.1 Synthesis and Structural, Electronic Properties of 6.1a – 6.4a

Compounds 6.1a – 6.4a were synthesized in good yields by lithiation of the appropriate bromo-phenyl azole or phenyl-azole starting materials, followed by the addition of BMes₂F. They are fully characterized by NMR and elemental analyses. The crystal structures of 6.2a and 6.3a were determined by single-crystal X-ray diffraction analyses, with similar structural features to those of B(ppy)Mes₂ (1.32) and its derivatives.

Figure 6.4 Crystal structures of 6.2a and 6.3a with 50% thermal ellipsoids and labels for all atoms (hydrogen atoms are not shown for clarity).
Table 6-1 Selected bond length (Å) and angles (°) for 6.2a and 6.3a.

<table>
<thead>
<tr>
<th>Important bond lengths (Å) of 6.2a</th>
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<tbody>
<tr>
<td>C(11)-B(1) 1.642(6) B(1)-N(1) 1.615(5)</td>
<td>B(1)-C(20) 1.637(6)</td>
</tr>
<tr>
<td>B(1)-C(1) 1.643(6)</td>
<td></td>
</tr>
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<td></td>
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<tr>
<td>Important bond angles (°) of 6.2a</td>
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</tr>
<tr>
<td>N(1)-B(1)-C(20) 115.0(3)</td>
<td>N(1)-B(1)-C(11) 101.2(3)</td>
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<tr>
<td>C(20)-B(1)-C(1) 104.0(3)</td>
<td>C(11)-B(1)-C(1) 124.2(3)</td>
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<td>N(1)-B(1)-C(1) 95.0(3)</td>
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</table>

<table>
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<tr>
<th>Important bond lengths (Å) of 6.3a</th>
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</thead>
<tbody>
<tr>
<td>N(1)-B(1) 1.634(9) B(1)-C(14) 1.637(9)</td>
<td>B(1)-C(23) 1.656(9)</td>
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<tr>
<td>B(1)-C(1) 1.677(7)</td>
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<tr>
<td>Important bond angles (°) of 6.3a</td>
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<tr>
<td>N(1)-B(1)-C(14) 115.7(5)</td>
<td>N(1)-B(1)-C(23) 103.8(5)</td>
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<tr>
<td>N(1)-B(1)-C(1) 93.8(4)</td>
<td>C(14)-B(1)-C(1) 103.0(5)</td>
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<td></td>
<td>C(23)-B(1)-C(1) 125.4(5)</td>
</tr>
</tbody>
</table>

All four compounds 6.1a – 6.4a are either colorless or light yellow and are fluorescent with moderate quantum efficiencies of ~0.20. The absorption and emission spectra are shown in Figure 6.5. TD-DFT computational data indicates that the transition from the ground state to the first excited state of these compounds is dominated by the HOMO to LUMO transition, which is a charge transfer from the mesityl moiety to the π* orbital of the chelate backbone, similar to that of B(ppy)Mes₂ (1.32).

Figure 6.5 Absorption and emission spectra of 6.1a, 6.2a, 6.3a and 6.4a (5×10⁻⁵ M in CH₂Cl₂).
6.3.2 Photoisomerization of Isomers a to Isomers b

Since compounds 6.1a – 6.4a all exhibit similar structural and electronic features to those of 1.32, not surprisingly, all four compounds underwent photoisomerization upon irradiation at 350 nm in the same manner as B(ppy)Mes₂ (1.32) does, changing color to blue, deep blue or purple, as shown in Figure 6.6, forming isomers 6.1b – 6.4b quantitatively with moderate photoisomerization quantum efficiencies (0.46, 0.35, 0.25 and 0.38 for 6.1a – 6.4a, respectively). 

¹H, ¹¹B NMR data and DFT optimized structures confirmed that the structures of the dark isomers 6.1b – 6.4b are similar to that of the dark isomer of 1.32.

![Figure 6.6](image)

**Figure 6.6** Left: A scheme showing the photoisomerization from isomers a to isomers b. Right: The absorption spectra of dark isomers 6.1b – 6.4b in toluene (5×10⁻⁵ M). Inset: Photographs showing the colors of 6.1b – 6.4b in C₆D₆.

6.3.3 Further Isomerizations From Isomers b to c, then to d

Upon heating, the dark isomers 6.1b – 6.4b underwent further isomerization to isomers 6.1d – 6.4d, respectively, with isomers 6.1c – 6.4c as the corresponding intermediate (Figure 6.7). To illustrate this unusual and complex process, the discussion herein would focus on the transformation of 6.1b.

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```
X = S (benzothiazolyl) 6.1a
X = S (5-Methylthiazolyl) 6.2a
X = O (benzoxazolyl) 6.3a
X = N (N-methylbenzimidazolyl) 6.4a

X = S (benzothiazolyl) 6.1b
X = S (5-Methylthiazolyl) 6.2b
X = O (benzoxazolyl) 6.3b
X = N (N-methylbenzimidazolyl) 6.4b
```
Figure 6.7 Transformation of isomers b to d upon heating.

Figure 6.8 $^1$H NMR spectra (aromatic and olefinic region) showing the sequential conversion of 6.1a (red)→6.1b (blue)→6.1c (green)→6.1d (purple) in C$_6$D$_6$. Key peaks are highlighted.

The $^1$H NMR spectral change of compound 6.1a upon irradiation and the subsequent change upon heating are shown in Figure 6.8. The dark isomer 6.1b transformed to the new species 6.1c in solution, slowly at ambient temperature and fast upon heating. The most distinct $^1$H NMR spectral features of 6.1c are the two singlet peaks from the olefinic protons of the cyclohexadienyl ring at 5.5 – 5.8 ppm, and the two singlet peaks, characteristic of a vinyl group at
4.5-5.0 ppm in C₆D₆. Surprisingly, the ¹H peaks belonging to 6.1c eventually all disappeared with prolonged heating, and then underwent further clean transformation to another distinct sets of ¹H peaks assigned to species 6.1d. Compound 6.1d could be readily crystallized out from its saturated toluene solution.

6.3.4 Characterizations of Isomer 6.1d

Compound 6.1d is stable under ambient air, and has been fully characterized by NMR, elemental and single-crystal X-ray diffraction analyses. In the ¹H NMR spectrum of 6.1d, distinct methylene peaks with an AB pattern and a two-proton coupling constant of 11 Hz were observed (Figure 6.13), indicating an asymmetric nature of the molecule. The ¹¹B NMR chemical shift (46.0 ppm) of 6.1d is downfield shifted by more than 50 ppm, relative to that of 6.1b, and is similar to those observed in Mes₂B=NR₂ and R₂B=NR’₂ compounds reported previously⁸ᵃ⁻⁸ᵉ, thus supporting the possible presence of a B=N bond. The crystal structure of 6.1d is shown in Figure 6.9, which confirms the NMR finding unequivocally.

![Crystal structure of 6.1d](image)

**Figure 6.9** The crystal structure of 6.1d.
Table 6-2 Selected bond length (Å) and angles (°) for 6.1d.

<table>
<thead>
<tr>
<th>Important bond lengths (Å) of 6.1d</th>
</tr>
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<td>B–N</td>
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<td>C(1)–C(2)</td>
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<td>1.492(7)</td>
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<tr>
<td>C(25)–C(26)</td>
</tr>
<tr>
<td>1.509(8)</td>
</tr>
<tr>
<td>S-C(25)</td>
</tr>
<tr>
<td>1.822(6)</td>
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<table>
<thead>
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<th>Important bond angles (°) of 6.1d</th>
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<tbody>
<tr>
<td>C(1)-B-C(10)</td>
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<tr>
<td>117.8(5)</td>
</tr>
<tr>
<td>C(1)-B-N</td>
</tr>
<tr>
<td>121.2(4)</td>
</tr>
<tr>
<td>C(10)-B-N</td>
</tr>
<tr>
<td>120.9(5)</td>
</tr>
<tr>
<td>B-C(1)–C(2)</td>
</tr>
<tr>
<td>102.4(5)</td>
</tr>
</tbody>
</table>

The C(25) atom of the thiazole ring transformed from a $sp^2$ carbon to a chiral $sp^3$ carbon atom while the methyl group bound to the aliphatic carbon atom in 6.1b became a methylene group (C(1)), forming a $\sigma$ bond with the boron atom. The B atom has a trigonal planar geometry, and a B=N bond with the bond length of 1.408(7) Å, comparable to some of the previously reported B=N bond lengths.\textsuperscript{8a,8d,8f} The thiazoline ring is considerably puckered with a mean deviation of 0.19 Å from the best least-square plane though the five atoms. The H(25) atom has a $syn$ conformation with respect to the adjacent phenyl C(26) – C(27) bond.

6.3.5 Determination of the Structure of Intermediate 6.1c

Due to the continuous conversion of 6.1c to 6.1d, it is impossible to get clean NMR spectra of 6.1c. With the structure of 6.1d obtained, an intermediate was located along the reaction coordinates between 6.1b and 6.1d by DFT calculations. The optimized structure of the intermediate is shown in Figure 6.10, and well explains the experimentally observed two sets of olefinic $^1$H peaks characteristic to 6.1c. During the 6.1b to 6.1c transformation, a hydrogen atom transferred from a methyl moiety to the C-2 atom of the thiazole ring, converting the thiazole to a
thiazoline, is significant and unusual, since the reduction/hydrogenation of azole compounds usually require catalysts or the use of highly reactive hydrides.\(^7\)

![Figure 6.10 DFT optimized structure of 6.1c.](image)

Further 2D NMR data and calculated \(^1\)H NMR spectrum of 6.1c all corroborated the proposed structure of 6.1c. The \(^1\)H-\(^{13}\)C HSQC spectrum of the 6.1b, 6.1c and 6.1d mixture was performed in d8-tol at 243K. As shown in Figure 6.11, the singlet at 6.59 ppm has a correlation peak with carbon \(^{13}\)C shift around 92.4 ppm, which is a clear indication of a quaternary carbon. The two singlet protons at 5.5-5.7 ppm have correlation peaks with carbons at different \(^{13}\)C chemical shifts. In contrast, the other two olefinic protons at 4.5-4.9 ppm have correlation peaks with carbon at the same \(^{13}\)C chemical shift, indicating that these two protons are bonded to the same carbon. Their appearance as two singlets is due to the germinal coupling in olefins. A comparison of calculated and experimental \(^1\)H NMR data for selected H atoms is shown in Table 6.3.
Figure 6.11 $^1H^{13}C$ HMQC spectrum of 6.1c in d$_8$-Tol at 243K.

Table 6-3 Calculated and experimental (298K in C$_6$D$_6$) chemical shift values for selected protons of 6.1c.

<table>
<thead>
<tr>
<th>H</th>
<th>Calc $\delta$ (ppm)</th>
<th>Expt $\delta$ (ppm)</th>
<th>H</th>
<th>Calc $\delta$ (ppm)</th>
<th>Expt $\delta$ (ppm)</th>
<th>H</th>
<th>Calc $\delta$ (ppm)</th>
<th>Expt $\delta$ (ppm)</th>
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<tbody>
<tr>
<td>33</td>
<td>6.73</td>
<td>6.63</td>
<td>26</td>
<td>6.08</td>
<td>5.69</td>
<td>27</td>
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<td>5.57</td>
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<tr>
<td>34</td>
<td>4.69</td>
<td>4.59</td>
<td>35</td>
<td>5.19</td>
<td>4.92</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With the structure of 6.1c elucidated, the formation of 6.1d can be considered as a consequence of a 1,3-sigmatropic shift by the boron atom in 6.1c, driven by re-aromatization of the cyclohexadienyl ring. This leads to a ring expansion of the 6-membered ring in 6.1c to the 8-membered ring in 6.1d. Although 1,2-sigmatropic migration of organoboron groups is well known, the 1,3-migration in 6.1c to 6.1d transformation is not common in organoboron compounds.
6.3.6 Diastereomers Interconversion Between Isomers d and e

To our surprise, upon heating at elevated temperature (90°C), 6.1d could be further quantitatively transformed to its diastereoisomer 6.1e, as shown in Figure 6.12. The $^1$H NMR spectral pattern of 6.1e is distinctly different from that of 6.1d (Figure 6.13). For example, the transferred hydrogen atom peak experiences a downfield shift from 6.1d to 6.1e. The germinal $^2$J$_{H-H}$ coupling constant of the CH$_2$ protons becomes much bigger (16 Hz in 6.1e vs 11 Hz in 6.1d).

![Figure 6.12](image)

**Figure 6.12** The interconversion between 6.1d and 6.1e.

![Figure 6.13](image)

**Figure 6.13** $^1$H NMR spectra (aromatic and aliphatic region) showing the inter-conversion of 6.1d and 6.1e in C$_6$D$_6$.

The crystal structure of 6.1e was determined by X-ray diffraction analysis and is shown in Figure 6.14. The key difference between 6.1d and 6.1e is the configuration inversion of the
chiral carbon atom, C(25). As a consequence, the H(25) atom becomes \textit{anti} and the S atom becomes \textit{syn} to the C(26) – C(27) bond in 6.1e. The H(27) atom forms an intramolecular H bond with the sulfur atom (H(27)·S = 2.89 Å), agreeing with the more than 1 ppm downfield shift of the H(27) peak in the NMR spectrum of 6.1e, compared to that of 6.1d (Figure 6.13). The C(2)-C(1)-B bond angle (124.17(18)°) in 6.1e is much greater than that (102.4(5)°) in 6.1d, consistent with the bigger $^{2}J_{H-H}$ coupling constant of the methylene protons.

![Figure 6.14 Crystal structure of 6.1e.](image)

**Table 6-4** Selected bond length (Å) and angles (°) for 6.1e.

<table>
<thead>
<tr>
<th>Important bond lengths (Å) of 6.1e</th>
<th></th>
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<tbody>
<tr>
<td>B–N</td>
<td>1.424(3)</td>
</tr>
<tr>
<td>B–C(1)</td>
<td>1.597(3)</td>
</tr>
<tr>
<td>B–C(10)</td>
<td>1.579(3)</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>1.513(3)</td>
</tr>
<tr>
<td>C(25)–C(26)</td>
<td>1.519(3)</td>
</tr>
<tr>
<td>S–C(25)</td>
<td>1.831(2)</td>
</tr>
<tr>
<td>N–C(25)</td>
<td>1.499(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Important bond angles (°) of 6.1e</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-B-C(10)</td>
<td>113.90(8)</td>
</tr>
<tr>
<td>C(1)-B-N</td>
<td>123.5(2)</td>
</tr>
<tr>
<td>C(10)-B-N</td>
<td>122.50(19)</td>
</tr>
<tr>
<td>B–C(1)-C(2)</td>
<td>124.17(18).</td>
</tr>
</tbody>
</table>
The other key difference between 6.1d and 6.1e is that the benzothiazoline ring is no longer puckered but co-planar with the B, C(1) and C(10) atoms in 6.1e (the mean deviation from the plane defined by the benzothiazoline ring, B, C(1) and C(10) atoms is 0.052 Å), indicating the greater \(\pi\)-conjugation of the benzothiazoline and the boron atom in 6.1e than 6.1d. This is corroborated by the appearance of a distinct low energy absorption band at the 300 – 350 nm region in the UV-Vis absorption spectrum of 6.1e, which is much weaker and at a slightly higher energy in the spectrum of 6.1d (Figure 6.15).

![Figure 6.15](image.jpg)

**Figure 6.15** UV-Vis absorption spectra of 6.1d and 6.1e in THF (5 \(\times\) 10^{-5} M).

Most noteworthy is that fact that the two diastereomers 6.1d and 6.1e can be interconverted quantitatively. 6.1d is stable toward irradiation and can only be converted to 6.1e thermally. In contrast, compound 6.1e is thermally stable. Remarkably, 6.1e can be fully converted back to 6.1d on irradiation at 300 nm. The reversible diastereomer interconversion of 6.1d and 6.1e is a rare phenomenon, and illustrates the possibility of controlling the stereochemistry of azo-heterocyclic molecules with a boron unit.
6.3.7 Comparison of a→b→c→d→e Transformations in All Four Compounds

Figure 6.16 A summary of isomers a→b→c→d→e transformations.

The dark isomers 6.2b – 6.4b all underwent a similar multi-stage isomerization process as 6.1b did and a summary of these transformations is shown in Figure 6.16. To achieve appreciable thermal transformation of isomers b to d, higher temperatures were required for 6.2b (90°C) and 6.4b (130°C). Hence, not surprisingly, the intermediates 6.2c and 6.2c were not observed in the ^1H NMR spectra because of their rapid conversion to 6.2d and 6.4d, respectively. For 6.3b, it can isomerize to 6.3d at 50°C but much longer heating time (30 hrs) is needed to achieve the maximum conversion (~100%), compared to 6.1b that reaches the maximum
conversion (~82%) to \textbf{6.1d} at 50°C for 9 hrs. Qualitatively, the isomerisation reactivity of \textbf{b}→\textbf{d} follows the order of \textbf{6.1b} > \textbf{6.3b} > \textbf{6.2b} >> \textbf{6.4b}.

The formation of isomer \textbf{c} de-aromatizes the azole ring in isomer \textbf{b}. Thus, the much lower reactivity of \textbf{6.4b}, relative to \textbf{6.1b}, \textbf{6.2b} and \textbf{6.3b}, may be attributed to the higher aromaticity of the imidazolyl ring in \textbf{6.4b} than other types of azolyl rings in \textbf{6.1b}, \textbf{6.2b} and \textbf{6.3b}. The fact that the dark isomer of \text{B(ppy)Mes}_{2} (1.32a) does not undergo intramolecular H-atom transfer as the azole compounds do may also be explained by the well known high aromaticity of the pyridyl ring. Another important observation is that upon heating, besides isomerizing to the \textbf{d} isomers, the dark isomers \textbf{b} also thermally reversed back to the original isomers \textbf{6.1a} (~18%), \textbf{6.2a} (~13%), \textbf{6.3a} (~0%), and \textbf{6.4a} (~82%).

Isomers \textbf{6.2d}, \textbf{6.3d} and \textbf{6.4d} can be quantitatively converted to their diastereomers \textbf{6.2e}, \textbf{6.3e} and \textbf{6.4e}, at 110°C, 90°C and 130°C, respectively, in the same manner as \textbf{6.1d} does. Because of the high temperature used, \textbf{6.4e} was observed already in \textbf{6.4b}→\textbf{6.4d} conversion.

However, unlike \textbf{6.1e} that can be converted back quantitatively to \textbf{6.1d} by irradiation at 300 nm, compounds \textbf{6.2e} – \textbf{6.4e} can only be partially converted back to \textbf{6.2d} – \textbf{6.4d} by irradiation (max. ~60% for \textbf{6.2d}, ~20% for \textbf{6.3d}, and ~10% for \textbf{6.4d}). Prolonged irradiation of \textbf{6.2e} – \textbf{6.4e} did not increase the conversion yield, instead, unidentified products were observed that may be caused by either alternative photoisomerization pathways of \textbf{6.2e} – \textbf{6.4e} or the poor photo-stability of \textbf{6.2d} – \textbf{6.4d}.

### 6.3.8 Mechanistic Pathways Studied by DFT Calculations

To better understand the multi-stage isomerization process and the difference between the isomerization behaviors of \textbf{6.1a} – \textbf{6.4a}, the mechanistic pathways are investigated using DFT computational methods.\textsuperscript{10} The results for compound \textbf{6.1a} are shown in Figure 6.17. Compounds
6.2a – 6.4a are found to follow the same mechanistic pathways and the results can be found in Section 6.4.3.

**Figure 6.17** The relative energies and the structures of isomers, intermediates and transition states involved in the 6.1a → 6.1e transformation at the ground state. The relative excited state energies (S\textsubscript{1} or S\textsubscript{x}) of 6.1a, 6.1b, 6.1d and 6.1e are shown to illustrate the involvement of the excited state in the transformation process.

The transformation of 6.1a → 6.1b in the ground state follows the same isomerization pathways as established previously for B(ppy)Mes\textsubscript{2} and related compounds.\textsuperscript{6c} Based on the optimized geometry of 6.1b, the H atom of the methyl group on the BC\textsubscript{2} triangle is \textasciitilde2.46 Å away from the thiazole C-2 atom. In the transition state (TS3), the H atom is at midway between the
methylenic and the thiazole carbon atoms, and transferred directly to the thiazole, leading to the exclusive formation of the syn diastereoisomer 6.1c. The calculated thermal reversal barrier for 6.1b→6.1a is about 30 kJ mol⁻¹ higher than that of 6.1b→6.1c. This explains why 6.1b transforms predominantly to 6.1c thermally rather than reverse back to 6.1a. The activation barrier of 6.1c→6.1d is smaller than that of 6.1d→6.1c. Thus, once 6.1c is formed, it can readily convert to 6.1d via the transition state TS4, in which the B-C cyclohexadienyl bond is broken and the B atom is at about equal distances from this carbon atom and the two vinyl carbon atoms, supporting a concerted sigmatropic migration of the boron group.

![Diagram](image)

**Figure 6.18** The interconversion between 6.1d and 6.1e and the calculated transition state TS5 on the ground state potential energy surface.

The most important finding from the computational work is that the 6.1d → 6.1e conversion involves the transition state TS5, in which the C-S bond dissociates, a C=N bond forms, and the B=N bond becomes a B-N bond. The distance between the dissociated C-S atoms is determined to be 2.947 Å by DFT calculations. The structure of TS5 is reminiscent of the ring opened isomer of spiropyans and related species.⁴a,¹¹ As shown in Figure 6.18, the C-S bond dissociation is the key for the configuration inversion of the chiral carbon atom and the interconversion of the diastereoisomers of 6.1d and 6.1e. The ability of the boron center to
accommodate both B-N and B=N bonds likely also plays an important role in the reversible isomerization of $6.1d$ and $6.1e$. The barrier of $6.1d \rightarrow 6.1e$ is much greater than that of $6.1b \rightarrow 6.1c$, in agreement with the higher temperature needed for $6.1d \rightarrow 6.1e$ conversion.

The computational data also show that among the five isomers $6.1a - 6.1e$, the lowest energy benzothiazoline isomers are $6.1d$ and $6.1e$, among which the isomer $6.1e$ is about 27 kJ mol$^{-1}$ more stable than $6.1d$. Thus, the unusual multi-structural transformation process is thermodynamically favored.

*Photoisomerization of $6.1e$ to $6.1d$.* The $S_1$ state of $6.1e$ is below that of $6.1d$ and the HOMO$\rightarrow$LUMO transition dominates the $S_1$ state for both compounds. However, the oscillator strength for $6.1e$ is about 5 times greater than that of $6.1d$, agreeing with the UV-Vis spectrum shown in Figure 6.15. As a result, compound $6.1e$ needs to be excited above the $S_1$ state in order to convert effectively to $6.1d$ at the excited state. It is conceivable that a transition state similar to that of TS5 is involved in the excited state conversion of $6.1e \rightarrow 6.1d$, requiring the change of the B=N bond to a B-N bond and the breaking of the C-S bond. Thus, in order to achieve effective photoisomerization of $6.1e \rightarrow 6.1d$, the HOMO level should be localized on the B=N bond and the thiazoline unit, which is indeed the case for $1e$. In contrast, for $6.1d$, there is a large contribution from the dimethylbenzene ring (the C(2) ring in Figure 6.9) at the HOMO level, which may explain the inability of isomer $6.1d$ to photoisomerize to $6.1e$.

*Comparisons among the different the chelation backbones.* To further interpret the experimentally observed reactivity trend in Figure 6.16, the activation barriers and relative energies of isomers a – e at the ground state from DFT calculations are listed in Table 6.5 and 6.6.
Table 6-5 DFT calculated activation energies of in the “a→b→c→d→e” transformation.

<table>
<thead>
<tr>
<th>Compd</th>
<th>a→b/b→a</th>
<th>b→c/c→b</th>
<th>c→d/d→c</th>
<th>d→e/e→d</th>
</tr>
</thead>
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<tr>
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<td>239/153</td>
<td>124/144</td>
<td>102/227</td>
<td>206/233</td>
</tr>
<tr>
<td>6.2</td>
<td>261/175</td>
<td>135/129</td>
<td>108/232</td>
<td>147/184</td>
</tr>
<tr>
<td>6.3</td>
<td>254/182</td>
<td>133/138</td>
<td>104/222</td>
<td>182/228</td>
</tr>
<tr>
<td>6.4</td>
<td>279/180</td>
<td>141/117</td>
<td>103/236</td>
<td>260/306</td>
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</table>

Table 6-6 DFT calculated relative energy of all isomers.

<table>
<thead>
<tr>
<th>Compd</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
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<tr>
<td>6.1</td>
<td>-86</td>
<td>0</td>
<td>-20</td>
<td>-144</td>
<td>-171</td>
</tr>
<tr>
<td>6.2</td>
<td>-86</td>
<td>0</td>
<td>6</td>
<td>-118</td>
<td>-155</td>
</tr>
<tr>
<td>6.3</td>
<td>-72</td>
<td>0</td>
<td>-5</td>
<td>-123</td>
<td>-169</td>
</tr>
<tr>
<td>6.4</td>
<td>-99</td>
<td>0</td>
<td>25</td>
<td>-109</td>
<td>-156</td>
</tr>
</tbody>
</table>

The calculated barrier of b→c conversion follows the order of 6.1b < 6.3b = 6.2b < 6.4b, in consistent with the experimentally observed reactivity condition, for instance, the conversion of 6.4b→6.4c (Figure 6.16) required elevated temperature. The relative stability of the isomer c versus b (defined by the energy difference of the two isomers) follows the order of 6.1c (-20 kJmol⁻¹) > 6.3c (-6 kJmol⁻¹) > 6.2c (5 kJmol⁻¹) > 6.4c (25 kJmol⁻¹). Since the formations of isomers c de-aromatize the N-heterocycles, the b→c’s activation barriers and the stability of isomers c are closely related to the aromaticity of the N-heterocycles. The poor stability of 6.4c and high activation barrier of 6.4b→6.4c are in consistent with the high aromaticity of the benzimidazolyl ring, resulting in the low reactivity of 6.4b→6.4d. The greater activity of
6.1b→6.1d, compared to 6.3b→6.3d conversion, despite the somewhat lower aromaticity of the benzoxazole ring in 6.3b, may be caused by the weaker nitrogen donor in benzoxazole that is less effective in stabilizing the TS3 state, relative to that in 6.1b. Thus, the observed reactivity trend of b→d conversions is likely a consequence of both aromaticity and the nitrogen donor strength of the azole ring.

The activation barriers of the b→a thermal reversal follow the order of 1b < 2b < 3b = 4b, and the relative stability of a versus b follows the order of 4a > 1a = 2a > 3a, which, along with the b→c activity trend, are responsible for the observed relative distribution of isomers a and d (or e) in the thermal isomerization of b (Figure 6.16).

6.4 Supporting NMR and DFT Calculation Data

6.4.1 The a→e Conversions Monitored by 1H, 11B NMR Spectra

The time-lapsed a→e 1H NMR spectra for all four compounds are listed from Figure 6.19 to Figure 6.22, in which a: highlighted in yellow bar; b: highlighted in blue bar, 1c: highlighted in green bar; 1d: highlighted in red bar; 1e: highlighted in purple bar. The stacked a→e 11B NMR spectra for 6.1, 6.2 and 6.3 are listed from Figure 6.23 to Figure 6.24.
Figure 6.19 Time-lapsed $^1$H NMR spectra from 6.1a to 6.1e in C$_6$D$_6$, r.t.

Figure 6.20 Time-lapsed $^1$H NMR spectra from 6.2a to 6.2e in C$_6$D$_6$, r.t.
Figure 6.21 Time-lapsed $^1$H NMR spectra from 6.3a to 6.3e in C$_6$D$_6$, r.t.

Figure 6.22 Time-lapsed $^1$H NMR spectra from 6.4a to 6.4e in C$_6$D$_6$, r.t.
Figure 6.23 Stacked $^{11}$B NMR spectra of a→e isomers of 6.1 (left) and 6.2 (right) in C$_6$D$_6$ at r.t.

Figure 6.24 Stacked $^{11}$B NMR spectra of a→e isomers of 6.3 in C$_6$D$_6$ at r.t.

6.4.2 Isomers a→e NMR Spectra with Peak Assignments

Figure 6.25 Stacked $^{11}$H NMR spectra of 6.1a and 6.1b in C$_6$D$_6$ at r.t with peak assignments.
Figure 6.26 Stacked $^1$H NMR spectra of 6.1d and 6.1e in C$_6$D$_6$ at r.t with peak assignments.

Figure 6.27 Stacked $^1$H NMR spectra of 6.2a, 6.2b, 6.2d and 6.2e in C$_6$D$_6$ at r.t with peak assignments.
Figure 6.28 Stacked $^1$H NMR spectra of 6.3a and 6.3b in C$_6$D$_6$ at r.t with peak assignments.

Figure 6.29 Stacked $^1$H NMR spectra of 6.3d and 6.3e in C$_6$D$_6$ at r.t with peak assignments.

Since 82% of 6.4b went back to 6.4a upon heating, only 18% of 6.4b could be converted to final isomer 6.4e. By repeating the photo and thermal isomerization cycles of 6.4a$\rightarrow$6.4b$\rightarrow$6.4d$\rightarrow$6.4e, compound 6.4e can be obtained in reasonable good purity, as shown in the $^1$H NMR spectrum in Figure 6.30. The $^1$H$^1$H COSY, NOESY spectra of 6.4e are shown in Figure 6.31 and Figure 6.32 with important cross-peaks noted.
Figure 6.30 $^1$H NMR spectrum of 6.4e in C$_6$D$_6$ at r.t with peak assignments.

Figure 6.31 Excerpted region of the $^1$H$^1$H NOESY NMR spectrum of 6.4e in C$_6$D$_6$ at r.t.
Figure 6.32 Excerpted region of the $^1$H$^1$H COSY NMR spectrum of 6.4e in C$_6$D$_6$ at r.t.

6.4.3 DFT Calculated Energy Diagrams

Figure 6.33 The relative energies and the structures of isomers, intermediates and transition states involved in the 6.2a $\rightarrow$ 6.2e transformation at the ground state.
Figure 6.34 The relative energies and the structures of isomers, intermediates and transition states involved in the $6.3a \rightarrow 6.3e$ transformation.

Figure 6.35 The relative energies and the structures of isomers, intermediates and transition states involved in the $6.4a \rightarrow 6.4e$ transformation.
6.5 Conclusions

In summary, this chapter has demonstrated that azole-phenyl BMes$_2$ compounds undergo unprecedented multi-structural transformation when stimulated by heat or light. Mechanistic pathways for this remarkable phenomenon have been established. Because the formation of dark isomer $b$ is key to the subsequent structural transformation, this work demonstrates that light can be used as a convenient trigger or switch to turn on unusual and complex structural/chemical transformation of organoboron compounds. The intramolecular H atom transfer observed in this system is facilitated by the relatively low aromaticity of the azole rings. The ability of a BRR’ unit to accommodate both B=N and B-N bonds plays a key role in promoting the reversible switching of the two diastereomers $d$ and $e$, illustrating the potential use of organoboron chromophores in controlling stereoselective ring-opening/ring closing processes of azole heterocycles.
6.6 Notes and Referenes

The work described in this Chapter has been published as:


References:


Chapter 7

A Multitude of Organoborane Isomerism: Reversible Photo-thermal
Isomerization of Azaboratabisnorcaradiene to Azaborabenzotropilidene

7.1 Introduction

In recent years, various types of organoboranes have demonstrated distinct photochromic properties, among which a class of C,C or N,C-chelate BMes₂ organoboranes exhibit multi-stage photo- and thermal structural transformations, as shown in the work presented in Chapter 5 and Chapter 6. Although in many instances, the structural transformation of organoboranes is similar or parallel to their full carbon analogues, the incorporation of boron atom does introduce unique electronic, optical and chemical properties to a molecule, as exemplified by the following summarized work.

Photoirradiation of a four-coordinate 2-phenylpyridyl chelate BMes₂ compound resulted in its dark isomer (1.32a) involving a boratanorcaradiene moiety, similar to the product of the photoirradiation of tetraphenylborate. A careful scrutiny of the structure reveals that with the boron atom nesting in a 2-phenylpyridyl chelate environment, the photoisomerization produced boratanorcaradiene moiety is also fused with a second norcaradiene ring. More accurately, this dark isomer could also be viewed as a first example of boron-containing bisnorcaradienes, or azaboratabisnorcaradiene. Furthermore, the N donor can be replaced by a N-heterocyclic carbene
(NHC) C donor, which led to a different kind of azaborabisinorcaradiene (5.2a), which is the focus of Chapter 5.

The azaborata-bisnorcaradiene derivatives display a multitude of photo- and thermal isomerism including 1,5-sigmatropic shift (b – b*) and intramolecular H atom transfer (b → e) [5d] / activation (b → d) as shown in Figure 7.1. The multiple competitive isomerization pathways displayed by this class of organoborane compounds appear to be governed by the σ-donor strength of the Y atom, the aromaticity of the heterocyclic aryl group and the electronic properties of the chelate backbone. In addition, the ability of the boron atom to switch between a four- and three-coordinate geometry also play a key role in accommodating such isomerism.

**Figure 7.1** A multitude photo- and thermal-isomerism of molecules containing azaborabisinorcaradienes moiety.

In contrast, bisnorcaradienes, without boron or nitrogen heteroatoms doping, display mainly the norcaradiene – tropilidene rearrangement. One extensively studied organic rearrangement system is the tropilidene (1,3,5-cycloheptatriene) – norcaradiene
(bicyclo[4.1.0]hepta-2,4-diene) isomerisation and walk rearrangement (Figure 7.2).\textsuperscript{1} The isoelectronic boron analogues, boratropolidene\textsuperscript{2} and boranorcaradiene,\textsuperscript{3} are known for several decades; and depending on the substituent groups, one isomer is usually greatly favored over the other and direct observation of interconversion between the two isomers is rare. A related isomerism is the bisnorcaradiene-benzotropolidene rearrangement shown in Figure 7.2.

![Figure 7.2](image)

**Figure 7.2** Selected isomers of norcaradiene, bisnorcaradines, benzotropolidenes and their boron and B,N-analogues.

As a continuing work to explore the photochromic organoboranes, this chapter focuses on a new isomerism phenomenon, namely the interconversion of azaboratabisnorcaradiene and azaborabenzotropolidene, based on a new class of N, C-chelated BMes\textsubscript{2} compounds (7.1a and 7.2a in Figure 7.3).

![Figure 7.3](image)

**Figure 7.3** Molecular structures of 7.1a and 7.2a.
7.2 Experimental

7.2.1 General Procedures

Experimental techniques for synthesis, the use of instrumentation and the collection of X-ray crystallography diffraction data are as described in Chapter 2.2.1.

7.2.2 Synthesis of 7.1a and 7.2a

t-BuLi (1.7 mL, 1.7M in hexane, 2.9 mmol) was added slowly to a solution of N-methyl-2-phenylimidazole (0.46g, 2.9 mmol) in diethyl ether (80 mL) at -78 °C. The resulting solution was stirred for about 1 hour at -78 °C, which was then followed by the addition of BMes₂F (0.86g, 3.2 mmol). The reaction mixture was kept -78 °C for another hour before slowly reaching up to ambient temperature overnight. Solvents were then removed under reduced pressure and the resulting solid was separated over silica gel by flash column chromatography using a CH₂Cl₂/hexane (1:1) mixture.

7.1a: 0.21g, 44% yield. ¹H NMR (600 MHz, CD₂Cl₂, 25 °C, ppm): 7.73 (d, 1 H, J = 7.8 Hz), 7.69 (d, 1 H, J = 7.8 Hz), 7.30 (t, 1 H, J = 7.2 Hz), 7.26 (t, 1 H, J =7.2 Hz), 7.16 (s, 1 H), 6.82 (b, 4 H), 6.58 (s, 4 H), 3.66 (s, 3 H), 2.30 (s, 6 H), 2.17 (s, 6 H), 2.00 (b, 12 H), 1.79 (s, 12 H). ¹³C NMR (150 MHz, CD₂Cl₂, 25°C, ppm): 156.6, 139.4, 138.0, 133.1, 132.6, 130.0, 129.2, 128.5, 127.6, 125.1, 121.2, 34.0, 24.8, 20.9, 20.4. ¹¹B NMR (128 MHz, C₆D₆, 25 °C, ppm): 2.8. The three-coordinate boron signal was not observed. Anal. Calcd for C₄₆H₅₂B₂N₂: C, 84.41; H, 8.01; N, 4.28. Found: C, 84.00; H, 8.22; N, 4.18.

7.2a: 0.1 g, 17% yield. ¹H NMR (600 MHz, CD₂Cl₂, 25 °C, ppm): 6.67 (m, 2 H), 7.25 (m, 2 H), 7.13 (d, J = 1.8 Hz, 1 H), 6.88 (d, J = 1.8 Hz, 1 H), 6.60 (s, 4 H), 4.01 (s, 3 H), 2.16 (s, 6 H), 1.82 (s, 12 H). ¹³C NMR (150 MHz, CD₂Cl₂, 25°C, ppm): 139.6, 133.1, 132.4, 129.2, 129.0, 128.1, 124.8, 123.8, 122.3, 119.8, 34.8, 24.7, 20.4. ¹¹B NMR (128 MHz, C₆D₆, 25 °C, ppm): 1.7.
Anal. Calcd for C$_{28}$H$_{31}$BN$_{2}$: C, 82.76; H, 7.69; N, 6.89. Found: C, 82.06; H, 7.84; N, 6.82.

7.2.3 General Procedures of Photolysis Study Monitored by NMR Spectra

The solutions for photo-isomerization study were all kept under nitrogen unless otherwise indicated. Photo-isomerization of 7.1a and 7.2a were monitored by NMR spectra in C$_6$D$_6$. NMR solvent C$_6$D$_6$ were purchased from Cambridge Isotopes and dried over molecular sieves in a glove box. ~1-2 mg of compounds 7.1a or 7.2a was dissolved in C$_6$D$_6$ under nitrogen inside a glove box. The solution was then irradiated inside an UV reactor at 350 nm. The thermally reversible reactions were done via placing the sealed NMR tube in a hot oil bath.

7.2.4 DFT Calculations

Theoretical calculations were carried out at the CAM-B3LYP/SVP level of theory using Gaussian 09 software unless otherwise noted. Compared to B3LYP functional, test calculations demonstrated that CAM-B3LYP functional more accurately reproduced the experimentally determined UV-Vis spectrum of a reference compound in the same class as those considered here. The ground states of all reactants, products and intermediate structures were optimized without constrains, and characterized as minima on the potential energy surface through frequency calculations. The transition state structure was also optimized without constrains and contained only one imaginary frequency.

**Calculated NMR chemical shifts**: NMR Chemical shifts were obtained by subtracting the calculated magnetic shielding for the nuclei of interest from the reference compound shielding [tetramethylsilane (TMS) for $^{13}$C and $^1$H]. $^1$H, $^{13}$C, $^{11}$B NMR chemical shifts were calculated with optimized geometry using the density functional theory–gauge including/invariant atomic orbitals (DFT – GIAO) approximation at the CAM-B3LYP/SVP level of theory. The $^1$H ($\delta = 31.38$), $^{13}$C ($\delta = 192.8$) NMR chemical shifts were referenced to tetramethylsilane (TMS). The $^{11}$B NMR...
chemical shifts were first computed with B$_2$H$_6$ as reference ($\delta = 94.8$), and then finally referenced to BF$_3$OEt$_2$. [\delta B$_2$H$_6$ (16.6) vs BF$_3$OEt$_2$].

**NICSs (Nucleus-Independent Chemical Shifts) calculation:** NICSs values were calculated via placing a ghost atom in the center of, 1Å above or 1Å below the imidazolyl five-membered ring, respectively. The NICSs calculations for 7.1b and 7.2b with basis set at B3LYP/6-31+G(d) were performed after their geometry optimizations at the same computational level using Gaussian 09 software package.

<table>
<thead>
<tr>
<th>Compd</th>
<th>NICS (0)</th>
<th>NICS(1)$^a$</th>
<th>NICS(-1)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1b</td>
<td>-9.46</td>
<td>-8.42</td>
<td>-7.91</td>
</tr>
</tbody>
</table>

$^aNICS$ (1), NICS(-1) denote that the ghost atom was placed 1Å above, 1Å below the five-member ring, respectively.

**Calculated UV-Vis absorption spectra:** For each isomer, upon the completion of geometry optimization at CAM-B3LYP/SVP level of theory, 30 lowest excited states were then computed via TD-DFT calculations at the same level of theory. The simulated UV-Vis absorption spectra were then plotted using the GaussSum software written by Noel O’Boyle.

### 7.3 Results and Discussion

#### 7.3.1 Synthesis

Compounds 7.1a and 7.2a were obtained in 44% and 17% yield, respectively, from a one-pot reaction that involves the lithiation of 2-phenyl-$N$-methylimidazole with t-butyllithium, followed by the addition of BMes$_2$F at -78 °C in diethyl ether, as shown in Figure 7.4. At this
reaction condition, the addition of \( t \)-butyllithium didn’t exhibit significant preference towards the deprotonation of \textit{ortho}-H on the substituted phenyl ring via N-directed \textit{ortho}-lithiation or the somewhat acidic 5-H of N-methylimidazolyl ring. As a result, 2-phenyl-5-BMes\(_2\)-N-methylimidazole was also obtained as a side product from the same reaction. Compounds 7.1a and 7.2a were separated by column chromatography and further purified by recrystallization.

![Figure 7.4](image)

**Figure 7.4** Synthetic routes to compounds 7.1a and 7.2a.

### 7.3.2 Photoisomerizations of 7.1a/7.2a \( \rightarrow \) 7.1b/7.2b

Compounds 7.1a and 7.2a exhibit similar structural features as the model compound 2-phenylpyridyl chelate BMes\(_2\), thus not surprisingly irradiation of the C\(_6\)D\(_6\) solution of 7.1a or 7.2a resulted in an olive greenish solution, and a dark reddish solution for 7.1a and 7.2a, respectively. The deep-colored solution of 7.1a and 7.2a were monitored by \textsuperscript{1}H and \textsuperscript{11}B NMR spectra. As shown in Figure 7.5, irradiation of the C\(_6\)D\(_6\) solution of 7.1a at 350 nm resulted in a new set of distinct olefinic proton peaks at \( \sim \)5.5 and 5.7 ppm in the \textsuperscript{1}H NMR spectrum, and the shift of the \textsuperscript{11}B NMR signal from 2.4 ppm (7.1a) to -11.8 ppm, which are assigned to isomer 7.1b, as shown in Figure 7.6.
Figure 7.5 Stacked $^1$H NMR spectra of the olefinic and aromatic region showing the conversion of $\text{7.1a} \rightarrow \text{7.1b} \rightarrow \text{7.1c}$ in C$_6$D$_6$. Upon irradiation or heating. The key peaks are highlighted by colour bars: blue, 7.1a; green, 7.1b; red, 7.1c.

Figure 7.6 Left: Photoisomerization of $\text{7.1a/7.2a} \rightarrow \text{7.1b/7.2b}$.

Further 2D $^1$H$^1$H COSY, $^1$H$^1$H NOESY, $^1$H$^{13}$C HMBC NMR data all unambiguously supported the molecular structure of 7.1b, which is an analogue of 2-phenylpyridyl BMes$_2$ dark isomer. Compound 7.2a displayed the same photoisomerization to 7.2b. This also further proved that the photoisomerization is a common phenomenon in biaryl N,C-chelate BMes$_2$ compounds.

The structure of 7.2b, determined by a single-crystal X-ray diffraction analysis, possesses similar features as those of our previously reported azaboratabisnorcaradiene analogues. As
shown in Figure 7.7, the azaborata-cyclohexadienyl ring and the cyclohexadienyl ring in 7.2b are approximately perpendicular to the shared borata-cyclopropyl ring.

![Crystal structure of 7.2b with 50% thermal ellipsoids.](image)

**Figure 7.7** Crystal structure of 7.2b with 50% thermal ellipsoids.

**Table 7-2** Selected bond lengths and angles of 7.2b.

<table>
<thead>
<tr>
<th>Selected bond lengths (Å) of 7.2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-C1</td>
</tr>
<tr>
<td>1.587(3)</td>
</tr>
<tr>
<td>C2-C3</td>
</tr>
<tr>
<td>1.488(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Selected bond angles (°) of 7.2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2-B1-C1 59.73(14)</td>
</tr>
</tbody>
</table>

### 7.3.3 Photochromism Between Isomers 7.1b/7.2b and 7.1c/7.2c

As shown in Figure 7.4, while monitoring the photolysis of 7.1a → 7.1b via $^1$H NMR spectroscopy, we noticed that besides the appearance of the characteristic $^1$H peaks belonging to isomer 7.1b, there was another set of $^1$H peaks gaining increasing intensity with prolonged irradiation. Eventually, the characteristic $^1$H peaks of 7.1b diminished, and were replaced by a new set of peaks assigned to 7.1c. Heating up the sample of 7.1c at 80 °C for a few hours could fully regenerate the original dark isomer 7.1b, while with UV irradiation restored, 7.1c could be
reproduced again from \textit{7.1b}. This phenomenon indicates a remarkable second-step photochromism between isomers \textit{7.1b} and \textit{7.1c}. As shown in Figure 7.8, the photochromism between \textit{7.2b} and \textit{7.2c} was also observed, though the photolysis of \textit{7.2b\rightarrow 7.2c} proceeded with much slower rate than that of \textit{7.1b\rightarrow 7.1c} and considerable degraded impurities after long-time irradiation.

\textbf{Figure 7.8} Stacked $^1$H NMR spectra of the olefinic and aromatic region showing the conversion of \textit{7.2a\rightarrow 7.2b\rightarrow 7.2c} in C$_6$D$_6$, upon irradiation or heating. The key peaks are highlighted by colour bars: blue, \textit{7.2a}; green, \textit{7.2b}; red, \textit{7.2c}.

\textbf{7.3.4 Determination of the Structures of Isomers 7.1c and 7.2c}

To elucidate the structure of the new isomers \textit{7.1c} and \textit{7.2c}, various 2D NMR ($^1$H$^1$H COSY, $^1$H$^1$H NOESY, $^1$H$^{13}$C HSQC, $^1$H$^{13}$C HMBC) data were acquired. The 2D $^1$H$^{13}$C HMBC NMR spectra of \textit{7.1c} and \textit{7.2c} showed that only one carbon atom around the boron center remains quaternary with chemical shift at 46 ppm, while in contrast compounds \textit{7.1b} and \textit{7.2b} have two characteristic quaternary carbon atoms (43.6 and 30.4 ppm for \textit{1b}, 42.4 and 27.4 ppm for \textit{2b}) in the cyclohexadienyl ring bound to the boron atom. The $^{11}$B NMR spectra of \textit{7.1c} and \textit{7.2c} exhibit
a broad peak at ~32 ppm, which is similar to those values reported previously for B=C double bond in [R₂C=BR’₂]⁺ and A₂C=BR(L) (A = SiR₃, SnR₃, L = a Lewis donor).⁶⁻⁹ These data led us to propose a structure for 7.1c and 7.2c, which contains a azaboratropilidene moiety fused with a cyclohexadienyl ring and shown in Figure 7.9. The photochromism phenomenon between isomers b and c can be viewed as an interconversion between azaboratabisnorcaradene and azaborabenzotropilidene derivatives.

The chemical shift of the carbon atom in the B=C bond in 7.1c and 7.2c was determined to be at ~122 ppm from ¹H¹³C HMBC spectra, which is much more downfield than those reported for A₂C=BR(L) (A = SiR₃, SnR₃, L = a nitrogen donor).⁷,⁸

Unfortunately, single crystals of 7.1c or 7.2c suitable for X-ray diffraction were not attained. Nonetheless, the proposed structures of 7.1c and 7.2c were then optimized by DFT calculations. To our delight, the calculated ¹H, ¹³C and ¹¹B NMR shifts match very well with the experimentally observed data. The proton nuclei’s via space correlations obtained from ¹H¹H NOESY spectra fit impeccably with the geometry of DFT optimized structures.

As shown by the calculated structure of 7.2c in Figure 7.10, the B=C bond is coplanar with the cyclohexadienyl unit and the 7-membered B, N-heterocycle is isoelectronic with tropilidene. The calculated B=C bond length for 7.2c is 1.47 Å, which is much longer than that of
methyleneborane derivatives (~1.37 Å), but comparable to those of [R₂C=BR’₂]⁺ or methyleneborane adducts with a Lewis base donor.⁶,⁸a

Figure 7.10 DFT optimized structure of 7.2c at CAM-B3LYP/SVP level of theory.

Table 7-3 Selected bond lengths, angles and torsion angles of the optimized structure of 7.2c.

<table>
<thead>
<tr>
<th>Selected bond lengths (Å) of 7.2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1-C2</td>
</tr>
<tr>
<td>1.468</td>
</tr>
<tr>
<td>C5-C6</td>
</tr>
<tr>
<td>1.339</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Selected bond angles (°) of 7.2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2-B1-N1</td>
</tr>
<tr>
<td>C2-B1-C20</td>
</tr>
<tr>
<td>N1-B1-C20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Torsion angles in 7.2c (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1C2C3C4: 173.6</td>
</tr>
<tr>
<td>C2B1N1C16: -32.5</td>
</tr>
<tr>
<td>N1C16C15C10: 43.8</td>
</tr>
<tr>
<td>C15C10C1C2: -69.5</td>
</tr>
</tbody>
</table>

7.3.5 Electronic Properties of Isomers b and c

As mentioned in Section 7.3.2, irradiation of colorless solution of 7.1a, 7.2a resulted in an olive greenish solution of 7.1b, and a reddish solution of 7.2b, respectively. The intense color is characteristic to this class of photo-transformed isomers from biaryl chelate BMes₂ compounds. As shown in Figure 7.11, 7.1b has a broad absorption band at λ_max = ~590 nm, while 7.2b has an intense absorption peak at λ_max = ~495 nm, which is characteristic to azaboratabisnorcaradienes.
DFT calculations suggest that for 7.1b and 7.2b, the HOMO is localized on the boranorcaradiene unit while the LUMO is localized on the ph-imidazolyl-(BMes₂) chelate backbone. The ~100 nm red shift of this absorption band by 7.1b, relative to that of 7.2b is caused by the BMes₂ unit in the backbone of 7.1b that is known to significantly lower the absorption energy through \(\pi\)-conjugation with the N,C-chelate backbone.\textsuperscript{10}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/fig7.11.png}
\caption{UV-Vis absorption spectra of 7.1b and 7.1c (left), 7.2b and 7.2c (right) in toluene (~1×10\(^{-4}\) M). Inset: photographs showing the colours of 7.1b, 7.1c, 7.2b, and 7.2c solutions.}
\end{figure}

The transformation of the b isomer to the c isomer is accompanied by a distinct color change from olive green to red for 7.1b to 7.1c, and red to reddish-brown for 7.2b to 7.2c. In contrast to 7.1b and 7.2b, the absorption bands of 7.1c and 7.2c move to lower energy at ~750 nm for 7.1c and ~580 nm for 7.2c. For 7.1c and 7.2c, the LUMO and LUMO+1 are localized on the ph-imidazolyl-(BMes₂) chelate backbone, with similar energy and compositions to those of 7.1b and 7.2b; the HOMO is, however, localized on the conjugated B=C double bond and the cyclohexadienyl moiety, and is destabilized by ~0.50 eV, relative to that of 7.1b and 7.2b (Figure 7.12 and Figure 7.13). TD-DFT computational studies assign the two lowest absorption bands in 7.1c and 7.2c to HOMO → LUMO, and HOMO → LUMO+1 charge-transfer transition. The
pattern of the calculated UV-Vis spectra of \textbf{7.1c} and \textbf{7.2c} match the experimental spectra very well, further validating the proposed structures for \textbf{7.1c} and \textbf{7.2c}.

\textbf{Figure 7.12} Molecular diagrams and calculated UV-Vis absorption spectra of \textbf{7.1b} and \textbf{7.1c}.

\textbf{Figure 7.13} Molecular diagrams and calculated UV-Vis absorption spectra of \textbf{7.2b} and \textbf{7.2c}.
7.3.6 Stability and Reactivity of Isomers c

Compounds 7.1c and 7.2c are rare examples of \( R_2C=BR(L) \) species. Previously reported examples that contain a B=C bond all require the stabilization/protection of bulky substituents (e.g. \( SiR_3 \) and \( SnR_3 \)) or extended conjugation with heteroatoms (e.g. boron).\(^6\text{-}^9\)

Compounds 7.1c and 7.2c rapidly decompose upon exposure to air. The destabilized HOMO level makes the molecule prone to oxidation by oxygen. 7.1c and 7.2c are highly reactive to water and alcohols, but stable to diethylamine. However, unlike the previously reported reactive \( A_2C=BR \) species,\(^8\) the B=C bond in compounds 7.1c and 7.2c did not show any \([2+2]\) cycloaddition reactivity with benzophenone, acetone or iminoborane \( tBuB=NTBu \). The reactivity study of c isomers (7.1c, 7.2c) substantiated the less polarized character of their B=C double bond. Several factors are believed to contribute to the stabilization and significant deshielding of the carbon atom (122 ppm) in the B=C bond of 7.1c and 7.2c, which include the bulky mesityl group on the boron atom, the strong imidazolyl \( \sigma \) donor, the extended \( \pi \)-conjugation of the B=C bond with the two C=C bonds in the cyclohexadienyl ring.

Notably, addition of a strong \( \sigma \) donor, 1,3-bis-methylimidazol-2-ylidene (IMe) to 7.1c formed the adduct 7.1c-IMe, as shown in Figure 7.14. All the methyl groups on the BMes\(_2\) group in 7.1c-IMe displayed well-resolved \(^1\)H chemical shifts. A new and sharp peak at -12 ppm in the \(^{11}\)B NMR spectrum of 7.1c-Me was observed, along with the broad peak at 32 ppm for the B=C bond, supporting the unexpected attachment of IMe to the sterically crowded BMes\(_2\)Ar unit,\(^11\text{-}^{12}\) rather than \([2+1]\) addition to the B=C double bond. Likewise, no reaction was observed between 7.1c and IMe.
Upon IMe addition, the HOMO and LUMO band gap of 7.1c-IMe significantly increased compared to that of 7.1c, as indicated by the hypsochromic shift of the lowest absorption band in its UV-Vis absorption spectrum shown in Figure 7.15. This further validates that IMe was added to the electron deficient ArBMes₂ center, and resulted in an increase of LUMO energy level.

**Figure 7.14** Formation of 7.1c with IMe adduct.

**Figure 7.15** UV-Vis absorption spectrum of 7.1c-IMe in toluene (5×10⁻⁵ M).

Compared to 7.1c and 7.2c that readily reverse back to their corresponding b isomers upon heating, the NHC adduct 7.1c-IMe exhibits much higher thermal stability. Unfortunately, the isolated crystals of 7.1c-IMe were very small and displaying multiple twining, numerous attempts to collect the X-ray diffraction data failed.
Nonetheless, despite the steric congestion around the newly formed four-coordinate boron center, adduct **7.1c-IMe** was found to be relatively fluxional in solution. As shown in the $^1$H NMR spectrum in Figure 7.16, there are two species of **7.1c-IMe** with the ratio of ~7:3 in the C$_6$D$_6$ solution at 280K. The 2D $^1$H$^1$H NOESY spectra recorded at 298 K and 280 K both indicate a dynamic exchange between these two species. The coexistence of two species is likely due to two rotamers from the B-C(imidazolyl) bond rotations at the four-coordinate boron center.

**Figure 7.16** $^1$H NMR spectra of **7.1c-IMe** in C$_6$D$_6$ at 280K. (Top: aromatic region. Bottom: aliphatic region). The peaks highlighted with red asterisks denotes the ~30% isomer of **7.1c-IMe** which coexists with **7.1c-IME** (~70%) in solution at 280K.

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The structures of the two rotamers were then optimized by DFT calculation and shown in Figure 7.17. Upon the IMe addition, there is significant B-C bond length elongation around the newly formed four-coordinate boron center and the calculated lengths of the B-C bonds surrounding the four-coordinate boron center in these two rotamers are in the range of ~1.67 – 1.69 Å. With the calculated total energy of the endo isomer (7.1c-IMe’, IMe syn to the quaternary carbon in the azaboratrotropilidene ring) being 8 kJ/mol lower than that of the exo isomer (7.1c-IMe”), the more dominate isomer observed in the equilibrium in C₆D₆ solution is believed to be the endo isomer (7.1c-IMe’, 70% at 280 K).

Figure 7.17 DFT optimized structure of 7.1c-IMe (left: endo isomer; right: exo isomer) with hydrogen atoms omitted for clarity (pink color: boron; blue color: nitrogen; grey color: carbon).

At elevated temperature, the B-C bonds rotations have greatly increased, as evidenced by the coalescence of peaks from the aryl/methyl protons on the mesityl rings in the ¹H NMR spectra shown in Figure 7.18. Moreover, along with elevated temperature, there was also increased amount of liberated free IMe from the adduct 7.1c-IMe observed.
Figure 7.18 Variable-temperature $^1$H NMR spectra of 7.1c-IMe in C$_6$D$_6$. The red asterisks denote the free IMe.

7.3.7 Conversion of Isomers b to a at Elevated Temperature

In contrast to compounds 7.1c and 7.2c that readily revert back to 7.1b and 7.2b, respectively, at 80 °C in C$_6$D$_6$, 7.1b and 7.2b retain much higher thermal stability and their solution in the C$_6$D$_6$ solution are thermally stable at 80 °C for a few days. Only at much elevated temperature (110 °C), isomers 7.1b and 7.2b can be fully converted back to their corresponding isomers a, thus completing the remarkable molecular journey of $a\rightarrow b\rightarrow c\rightarrow b\rightarrow a$ transformation, as shown in Figure 7.19.

Figure 7.19 Consecutive photochromism of compounds 7.1a and 7.2a.
7.3.8 Mechanism Pathway Studied by DFT Calculations

To understand the mechanism of this unusual isomerisation, the thermal pathway shown in Figure 7.20 was examined computationally using compound 7.2 as the model compound. The 7.2b – 7.2a isomerisation pathway follows the same pattern as established previously for the related N,C-chelated BMes$_2$ systems involving two transition states and an activation barrier of ~309 kJ/mol for 7.2a→7.2b and ~213 kJ/mol for 7.2b→7.2a. The calculated high activation barrier of ~213 kJ/mol for 7.2b→7.2a conversion is consistent with the experimentally observed reaction condition which required elevated temperature (110 °C) and long period of reaction time.

Figure 7.20 The isomerisation pathway between isomers 7.2a, 7.2b and 7.2c.

Two transition states and one intermediate (Int2) were located along the reaction coordinates of 7.2c – 7.2b (Figure 7.20). 7.2c to Int2 is an electrocyclic ring closing
rearrangement, similar to that of tropilidene to norcaradiene. Most significantly, \textbf{Int2} back to 7.2b could be described as a new type of walk rearrangement in which the walking unit is the cyclohexadienyl unit (type II’ in Figure 7.21). Sigmatropic shift in boranorcaradienes were observed before (type I in Figure 7.21). In addition, 1,5-sigmatropic shift was also observed for some azaboratabisnorcaradienes with the azaborata as the walking unit (type II in Figure 7.21, b – b* in Figure 7.1). It is worthwhile to point out that with stronger \( \sigma \) donors as imidazolyl, NHC, the b isomers retain higher thermal stability and don’t undergo the type II walk rearrangement, but exhibit photoreactivity, such as the work presented here and in Chapter 5.

![Diagram of walk rearrangements](image)

**Figure 7.21** The walk rearrangements of boratanorcaradiene and azaboratabisnorcaradiene.

The calculated transition states and the intermediate for the 7.2b→7.2c isomerism involve the change of the B-N bond order and the dearomatization of the imidazolyl ring (Figure 7.18). Weakening the aromaticity of the imidazolyl ring seems to be capable of expediting the photo-conversion process. The faster photo-conversion rate of 7.1b→7.1c relative to that of 7.2b→7.2c could be attributed to the BMes\(_2\) substituent that lowers the aromaticity of the imidazolyl ring (see section 7.2.4 for detailed calculations of the NICS values).
7.4 Conclusions

In summary, a new reversible photo-, thermal isomerisation phenomenon involving three organoborane species with distinct colours has been discovered, which further illustrates the multitude of isomerism displayed by azaboratabisnorcaradienes. The mechanism of the reversible isomerisation of azaboratabisnorcaradiene and azaborabenzotropilidene has been established to involve a walk rearrangement around an azaboratanorcaradiene ring and the electrocyclic closure/ring opening of azaboratropilidene. The σ donating strength and the aromaticity of the heterocycle bound to the boron atom are believed to play a key role in dictating the specific isomerisation pathway among the competing pathways.

7.5 Supporting NMR Data

7.5.1 $^{11}$B NMR data

![Figure 7.22 Stacked $^{11}$B NMR spectra of 7.1a, 7.1b and 7.1c(left); 7.2a, 7.2b and 7.2c (right) in C$_6$D$_8$.](image)
Figure 7.23 Left: $^{11}$B NMR of 7.1c-IME in C$_6$D$_6$ at 298K. Right: $^{11}$B NMR of 7.1c-IME in C$_6$D$_6$ at 350K (right). The small peak at -13.7 is from the adduct (7.1b+IME) generated at high temperature.

7.5.2 $^1$H NMR and 2D NMR data of 7.1b and 7.1c

Figure 7.24 $^1$H NMR spectra and peak assignments of 7.1b in C$_6$D$_6$ r.t.
Figure 7.25 $^1$H NMR spectra and peak assignments of 7.1c in C$_6$D$_6$ r.t.

Figure 7.26 $^1$H$^1$H NOESY spectra of 7.1c with important cross-peaks noted.
Figure 7.27 $^1$H$^{13}$C HMBC spectra of 7.1c. (the chemical shifts of C1 and C29 were also confirmed by the $^1$H$^{13}$C HSQC experiments)

7.5.3 $^1$H NMR and 2D NMR data of 7.2b and 7.2c

Figure 7.28 $^1$H NMR spectra and peak assignments of 7.2b in C$_6$D$_6$ at r.t (top: aliphatic region; bottom: aromatic region).
**Figure 7.29** $^1$H NMR spectra and peak assignments of 7.2c in C$_6$D$_6$ at r.t. (the green asterisks denote the side products from prolonged photo irradiation).

**Figure 7.30** $^1$H$^{13}$C HMBC spectra of 7.2c in C$_6$D$_6$, r.t.
7.5.4 $^1$H$^1$H NOESY NMR data of 7.1c-IME

Note: diagonal signals phased “up” (red color), conformational exchange cross peak phased “up” (red color), NOE cross peaks phased “down” (blue color).

**Figure 7.31** $^1$H$^1$H NOESY spectra (left: aromatic region; right: aliphatic region) showing the dynamic exchange between 7.1c-IME’ and 7.1c-IME” in C$_6$D$_6$ at 280K.

**Figure 7.32** Full $^1$H$^1$H NOESY spectrum of 7.1c-IME in C$_6$D$_6$ at 280K.
### Table 7-4 Summary of calculated and experimental 7.1c’s $^1$H NMR chemical shift values.

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Table 7-5 Summary of calculated and experimental 7.1c’s $^{13}$C NMR chemical shift values.

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7.5.6 Calculated NMR data of 7.2c

![Diagram of molecular structure]

$^{11}$B (51): observed: 31.7 ppm. Calculated: 32 ppm

Table 7-6 Summary of calculated and experimental 7.2c’s $^1$H NMR chemical shift values.

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215
Table 7-7 Summary of calculated and experimental $^{13}$C NMR chemical shift values.

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Table 7-7 Summary of calculated and experimental $^{13}$C NMR chemical shift values.

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Table 7-7 Summary of calculated and experimental $^{13}$C NMR chemical shift values.

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Table 7-7 Summary of calculated and experimental $^{13}$C NMR chemical shift values.

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Table 7-7 Summary of calculated and experimental $^{13}$C NMR chemical shift values.
7.6 Notes and References

The work presented in this chapter has been accepted for publication in Journal “Angewandte Chemie International Edition”, DOI: 10.1002/anie.201404435. This work is also selected as cover page article.

References:


Chapter 8

Conclusions and Future Work

The work presented in Chapter 2 and Chapter 3 has furthered the development of organoboranes for optoelectronics. A series of triarylboron functionalized Pt(II) complexes have been prepared and demonstrated superior performance in OLED devices. Incorporation of a bulky dimesitylboryl group on the Pt(II) chelation backbone offers these materials several beneficial characteristics: reduced intermolecular interactions, improved charge carrier balance and enhanced photo-luminescent efficiency. Moreover, the location of the dimesitylboryl functional group on the cyclometallating ligand has proven to have a crucial impact on the emission energy. In the case of the 2-phenylpyridyl ligand, with the dimesitylboryl group on the phenyl ring para to the Pt(II) center, the emission energy is significantly increased compared to that with dimesitylboryl group meta to the Pt(II) center. This could serve as a simple and effective strategy in the development of long sought blue phosphors.

N,C-chelate dimesityl organoboranes have exhibited interesting photoresponsive properties. These, however, could be problematic for their application as the charge carrier or emissive layers in OLEDs. To address this problem, the work outlined in Chapter 3 revealed that the incorporation a bisthiényl moiety with a lower energy transition state could successfully dissipate the excited state energy and prevent the N, C-chelate dimesitylboryl moiety from photo-degradation.

Following the discovery of the photochromic phenomenon based on phenylpyridine chelate dimesityl organoboranes in 2008, the work outlined in Chapter 4 to Chapter 7 has greatly expanded and enriched this area. In Chapter 4, a molecule, B(2-ferrocenyl-N-Me-
benzimidazolyl)Mes$_2$, with the photoactive dimesityl organoborane and redox active ferrocene moiety fused together was designed and synthesized, with the aim to regulate the photoreactivity of boron moiety via the oxidative state of iron center. Upon oxidation to ferrocenium state, the target molecule underwent quick decomposition in solution to some unidentifiable species with light irradiation. Though the blueprint of turn-on the photoreactivity via electrochemistry was unsuccessful, it was found that the N-B bond in the target molecule underwent dynamic disassociation/reassociation processes in solution, owing to the steric congestion and ring strain. Such B-N interaction could be viewed as labile Lewis pairs. In light of utilizing such Lewis pairs for small molecule activation and Lewis acid catalysis, future work could involve the replacement of the mesityl group with electron deficient group, such as 2,6-bis(trisfluoromethyl)phenyl.

From Chapter 5 to Chapter 7, a series of light and heat responsive properties of biaryl chelate dimesityl organoboranes has been disclosed. Chapter 5 unveiled a new type of biaryl chelate dimesitylborane with N-heterocyclic carbene as the $\sigma$ donor, which undergoes an efficient di-$\pi$-methane-like rearrangement as the 2-phenylpyridine chelate dimesitylborane does. The stronger $\sigma$ donating ability from NHC not only greatly stabilizes the photogenerated dark isomer on the ground state, but also bestows it further photoreactivity of a second-step photoisomerization to form a C-H insertion final product via “borylene” intermediate. This work demonstrates that light can be used to access and generate boron-related reactive species via an excited state, which opens up many possible reactivity pathways.

In Chapter 6, an entire cascade of rearrangement reactions based on benzoazolyl and thiazolyl $N,C$-chelate dimesityl organoboranes was presented, which includes photoisomerization, hydrogenation ofazole moiety via a hydrogen atom transfer, 1,3-shift of a
boron atom and a spiropyran-type ring-opening/closure process. Each reaction has the potential to be an important basis for finding a new reaction or photo functioning of organoboron compounds.

Chapter 7 is a spin-off work from Chapter 6. A simple variation of the nitrogen donor to imidazole was found to have a profound impact on the photo and thermal responsive properties of N,C-chelate dimesityl organoboranes. Imidazole is considered to have the strongest σ donating ability and highest aromaticity among all azole analogs. This class of imidazolyl N,C-chelate dimesityl organoboranes, firstly followed the classical photo-rearrangement conversion to its isomer containing an azaboratabisnorcaradiene moiety. It then underwent a second-step photochromic transformation to a new isomer with an azaborabenzotropilidene moiety, with each stage displaying distinctly different colors.

Such rich photo and thermal reactivity based on biarylchelate dimesitylboranes detailed above can be attributed to the following factors. First of all, the boron atom, being able to readily switch between a three and four-coordinate geometry, plays an indispensable role to fulfill the requirements in most transition states. Secondly, a chelation backbone offers sufficient freedom to allow the molecule to transform upon external stimuli in a certain systematic way, rather than an uncontrollable fashion, which is problematic to lots of boron containing materials. Lastly, the photo and thermal reactivity of the dark isomer generated from biaryl dimesitylborane is completely governed by the σ donating ability and aromaticity of the heteroaryl group. A stronger σ donor endows the dark isomer further photoreactivity because of its ability to stabilize the transient species on the excited state potential energy surface.

To further harvest the fruitful photo/thermal responsive properties of organoboranes, future research directions might consider the incorporation of such active boron units into peptides and conjugated polymers backbone or side chains. In the case of functionalized peptides,
the stimuli-responsive activity of the boron moiety might impact the peptide folding and function, which offers a way to study and mimic the biological system. The stimuli-responsive boryl functionalized conjugated polymer system has the potential to serve as a molecular switch or sensor, based on the working principle that in flexible organic electronics fabricated from conjugated polymers, an external stimulus can result in electronic and conformational changes in the polymers, which can then be transduced as an electric signal.