

ORGANOMETALLIC PRECURSORS FOR
THE CHEMICAL VAPOR DEPOSITION OF LaB_6

By

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To my parents, Non, my family, and all my friends

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Abstract of Thesis Presented to the Graduate School
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LaB₆ has been used as an electron emissive source for field emitter arrays (FEAs). However, the synthesis of LaB₆ precursors and deposition of LaB₆ are challenging. This thesis describes the generation of known precursors and new precursors bearing hydrotris(pyrazolyl)borate for metal organic chemical vapor deposition (MOCVD) of LaB₆. Mass spectrometry was used for preliminary screening of the precursors, and some precursors were used for CVD. Material deposited by CVD was characterized by X-ray diffraction and Auger electron spectroscopy (AES).

CHAPTER 1 INTRODUCTION

Applications of Field Emitter Arrays

Field emitter arrays (FEAs) are used as high-intensity electron beam sources. Electron sources are used for vacuum electronics (e.g., the SPY1 cross-field amplifier system), high speed data communication (e.g., the HDR submarine SATCO transmitter), radars (e.g., SPS-73 radar), and electronic warfare systems.^{1,2}

In the past, traditional vacuum tubes have been used as electron emission sources. However, FEAs are an alternative for an electron emissive source. These FEA devices are reliable and have high performance aspects such as power efficiency, great compactness, and good response time compared to those traditional thermionic electron sources. FEAs can provide high anode current, instant turn on of a device, efficient frequency modulation, low power consumption, and low temperature operation.

The efficiency of FEAs in modulated power tubes is determined by emission current and current density. Efficiency of FEAs can be improved by increased current density at low operational voltages. Also, the capacitance and transconductance are important for the efficiency of FEAs. These parameters determine the emission currents of tip arrays. By intergrating some fabricated materials into the FEA tips, the performance of FEAs might be improved.

Pre-fabricated Field Emission Array Tips

The materials that provide low turn-on voltages of FEAs give high brightness electron beams. The emission current increases with gate voltage and a low turn-on voltage also enhances high emission current. With a constant average tip current, fabrication of large FEAs provides higher total emission current.

Many low work function materials are used for FEAs to increase the current density. Such materials such as carbides, borides, and nitrides which are used to fabricate Si tip arrays have a low work function of 2-3 eV. By integrating these materials into a high brightness electron source, the current density can be increased by a factor of 100. Some low work function materials, such as LaB₆, have been used on Si tips. The work function of sputtered LaB₆ thin film has a value of 2.78 eV.³ It has been suggested that integrating LaB₆ will enhance the current density of FEAs. The emission current at a 100 V gate voltage for a work function at 4 eV with the field enhancement from 4×10^5 to $6 \times 10^5 \text{ cm}^{-1}$ will result in an emission current density from 2×10^5 to $4 \times 10^6 \text{ A cm}^{-2}$. In comparison to plain Si tips, the emission current of fabricated Si tips is increased significantly. Fabricated FEAs show the enhancement of current density.⁴ With the growth of single crystalline coatings of LaB₆ on Si tips, the high emission current density might increase.

Properties of Lanthanum Hexaboride (LaB₆)

LaB₆ has been used as an electron emissive source for field emitter arrays (FEAs) due to its properties. LaB₆ is a low work function material having the work function value 2.8 eV.³ LaB₆ has a CsCl solid state structure with a cubic lattice unit with the lattice parameter 4.15 Å (Figure 1.1). LaB₆ has a high melting point of 2770 °C and

chemical stability at high temperature. Its properties are suitable for fabricated FEA tips as an emissive electron source.

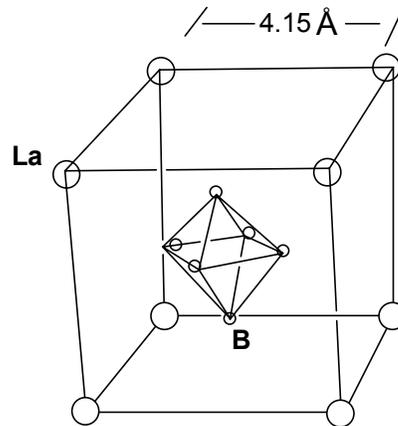


Figure 1.1 Structure of LaB₆

Coating Pre-fabricated Field Emission Array Tips

The deposition techniques for FEA tips should provide the following conditions for high efficiency: First, FEA tips must be sharp, and the coatings must have a good conformality as shown in Figure 1.2. Second, the thickness of tip arrays should be reproducible under suitable conditions. Last, the delivery system techniques should provide good control of the growth rate on the surface. Figure 1.3 shows field emission arrays.

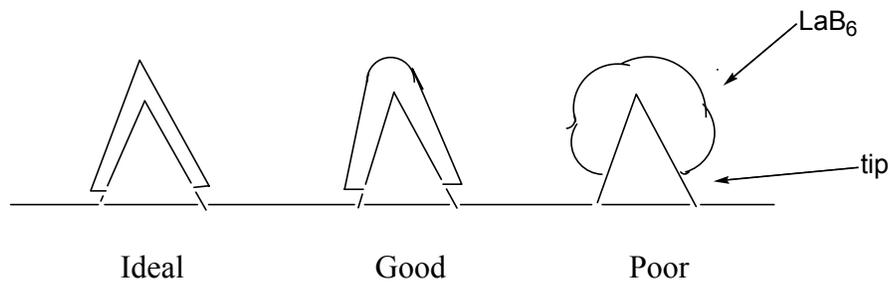


Figure 1.2 FEA tip coating conformality

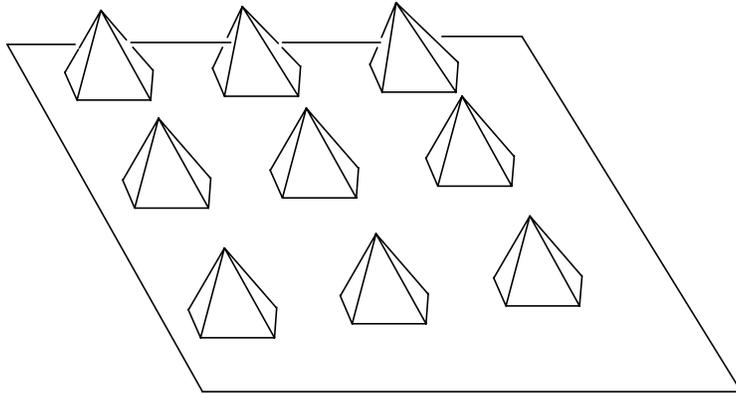


Figure 1.3 Example of field emission arrays

In the past, there have been difficulties with deposition of low work function materials. There are many coating techniques used for coating LaB_6 on to Si tips such as pulsed laser deposition, transfer mold deposition, or sputtering.⁵⁻⁸ Current deposition techniques have difficulties with controlling the thickness of thin films at suitable conditions. Moreover, some deposition techniques do not generate a uniform or sharp tip during the delivery process. Thus, the deposition techniques are a challenge for this FEA technology. Chemical vapor deposition is an alternative method for deposition of materials to give a LaB_6 layer on a Si substrate. The ultimate goal for this project is to fabricate gated Si tip-on-post FEAs using chemical vapor deposition of LaB_6 . Another strategy is to deposit a thick layer of the order of $2\ \mu\text{m}$ of single crystal LaB_6 on a Si substrate, and then produce tip arrays from the resulting materials.

The Spencer group has investigated the deposition of LaB_6 on Si substrates by copolyolysis of lanthanum chloride with either nido-decaborane or pentaborane at $800\text{-}900^\circ\text{C}$.⁹ Films with a thickness of $1\text{-}2\ \mu\text{m}$ were reported. The characterization of the films was carried by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-

ray emission spectroscopy (XES). The films were very highly crystalline. The films prepared from LaCl_3 and nido-pentaborane at 815°C contained no impurities such as chloride by XRD. Both boron sources, nido-decaborane and pentaborane, gave similar results in the formation of lanthanum hexaboride thin films.

The deposition of LaB_6 by copyrolysis presented some difficulties. The films were contaminated with some free boron because boron can form covalent bonds on the thin film at lower temperature. The boron rich material can be identifying by bluish purple color of the film, and lanthanum rich can be identified by the reddish color.⁵

Pyrolysis of Boranes

Boron trichloride, BCl_3 is commonly used for CVD of metal borides. However, BCl_3 has a low boiling point of 12.5°C which has resulted in difficulties during the CVD processes. Pavel introduced other boranes with high boiling points such as BBr_3 (90°C), pentaborane (333°C), and decaborane (213°C).¹⁰ The copyrolysis of boranes has been investigated by several research groups.¹¹⁻¹⁶ Boranes investigated for CVD by copyrolysis include pentaborane and decaborane.^{17,18} B-B covalent bonds are formed at low temperature ($50\text{-}250^\circ\text{C}$), and the formation of BH_x solid occurred.⁹

At higher temperature, diborane dissociates and forms higher boranes such as pentaborane and decaborane. Therefore, the higher boranes are more stable as compared to diborane at high temperature. According to calculations on the basis of thermodynamic data, it was shown that with the deposition from boron hydrides, the CVD process should be done at low temperature for good efficiency of CVD.⁹

Chemical Vapor Deposition (CVD) and
Metal Organic Chemical Vapor Deposition (MOCVD)

In chemical vapor deposition, gaseous precursors are used to chemically deposit a solid thin film on a substrate. CVD is a result of a combination of surface reaction and mass transfer processes.¹⁹ The substrate is placed on a susceptor and heated. The deposition process occurs when the gaseous precursors are dissociated and deposited on the substrate as a thin film at an optimized condition. In metal-organic chemical vapor deposition (MOCVD), organometallic precursor molecules are thermally dissociated and react on the surface of the substrate.

MOCVD is the chemical vapor deposition that uses metal organic compounds as precursors. Such compounds contain a metal and organic ligands. When soluble and volatile compounds are required for CVD, such difficulties can be overcome using MOCVD. The major challenge for MOCVD is film contamination from the precursor ligands and solvent (when it is used).

The CVD process can be explained as a series of steps.¹⁹ First, gaseous precursors are transported to the CVD reactor. Second, the precursor gas dissociates homogeneously into many intermediate species. Third, these intermediate species diffuse to the substrate surface through a boundary layer. Fourth, reactive and nonreactive species are adsorbed on the substrate surface. Fifth, the heterogeneous chemical reactions occur for the reactive species, and the species diffuse onto the growing film. Sixth, the non-reactive species will not be adsorbed into the substrate, but will generate by-products. Seventh, the diffusion of reactive species from the film surface to the gas bulk through the boundary layer occurs. Finally, the non-reactive species, by-products,

and unreacted reactive species from the deposition pathway of the CVD reactor will be transported to the exhaust system.¹⁹

Aerosol -Assisted CVD

A precursor for conventional CVD must be volatile and chemically stable. The deposition of LaB_6 by conventional CVD would have a limited choice of precursors due to the need for volatility. However, aerosol-assisted CVD has been developed to allow the use of non-volatile precursors.²⁰ In this method, the precursor is transported to the substrate in form of an aerosol droplet from a solution in an appropriate solvent or co-solvents. Therefore, the precursor has to be stable in the selected solvent or co-solvents.

There are advantages and disadvantages of aerosol-assisted CVD. In terms of transporting precursors, the aerosol process provides simplicity, reproducibility, and high deposition rate. Precursors can be low of volatility and low thermal stability. However, contamination from the solvent can affect the quality of the film. Residual particles may remain after droplet evaporation during aerosol delivery of volatile precursors. Thus, the choice of solvent and precursor is a crucial issue for the film deposition. Figures 1.4 and 1.5 show the CVD system used for the aerosol-assisted CVD experiment described later.

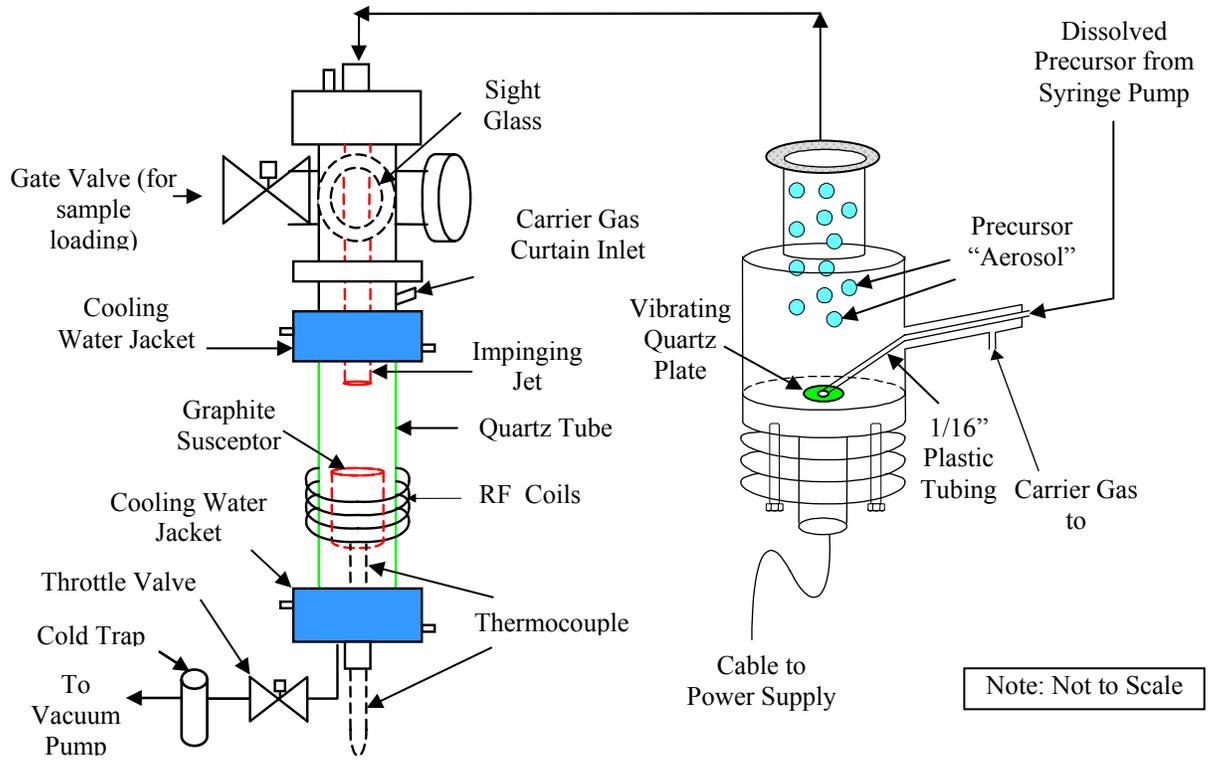


Figure 1.4 CVD ultrasonic nebulizing delivery system and reactor

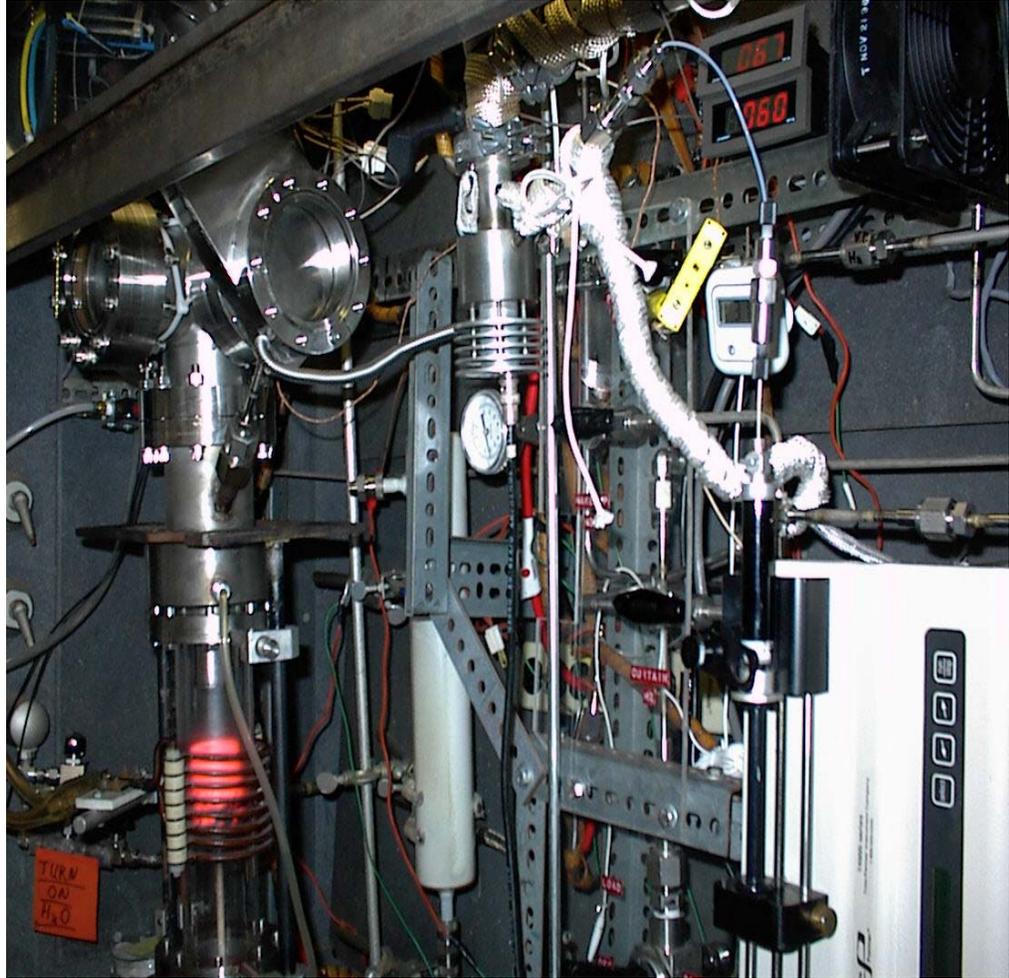


Figure 1.5 Picture of CVD system

CHAPTER 2 MOCVD PRECURSORS FOR LaB₆

Introduction

There are two types of precursor systems for CVD: single source precursors and two-component precursors used in co-reactant systems. The single source precursor is one that provides more than one element for the film. The two-component co-reactant systems use a separate compound for each element. Thus in a two component system for CVD of LaB₆, lanthanum complexes would be used for the source of La, and boron hydrides (e.g., B₂H₆ and BH₃ in solution of tetrahydrofuran) would be used for the source of B. This chapter discusses the chemistry of La complexes.

One aspect of this project is focused on the chemistry of tetrahydroborate with La complexes bearing bulky ligands (e.g., polypyrazolyl borates). Although these types of complexes would probably be poor precursors, lanthanum complexes with this type of ligand are good models to learn substitution chemistry of tetraborohydroborate at La because the bulkiness of the ligands provides control over the coordination sphere.

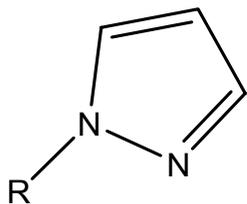
Poly(pyrazolyl)borate Ligands

Since the report of poly(pyrazolyl)borates by Trofimenko nearly thirty years ago,²¹ poly(pyrazolyl)borates have been studied widely in coordination chemistry.²²⁻²⁶ Poly(pyrazolyl)borate ligands can be easily prepared by reaction a pyrazole with a borohydride salt (e.q. 2.3). These ligands have been used as coordination-controlling environments for many transition metals. However, the coordination chemistry of the

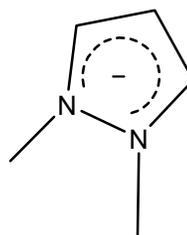
lanthanide series is more complex in comparison to the transition metals because of the larger size of the metal ions.²⁷ Coordination numbers in the lanthanide series can be up to 8 or 9 depending on the size of the metal and the size of ligands on a complex. Based on the results with transition metals, poly(pyrazolyl)borates are good candidate ligands for the study of coordination and substitution of tetrahydroborate on lanthanum.

Pyrazole and Pyrazolide Ion

Poly(pyrazolyl)borates are derivatives of pyrazole ligands. Substituents on the pyrazole rings determine the nucleophilicity and steric accessibility.²⁶



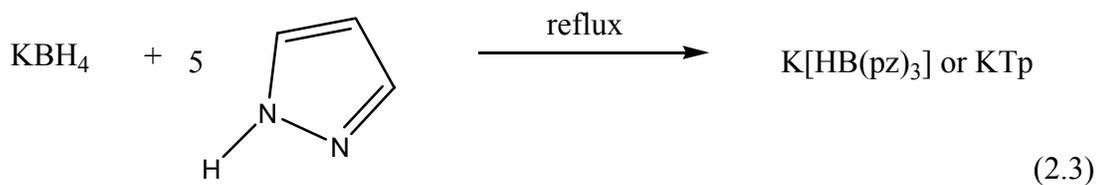
a pyrazole

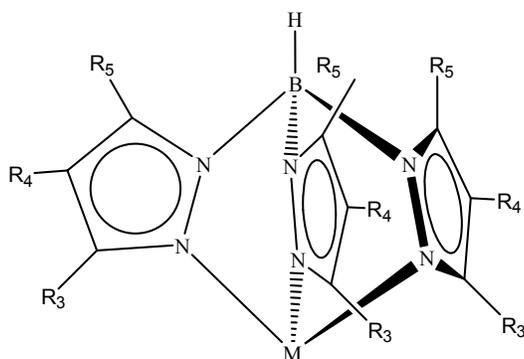


a pyrazolide ion

Abbreviations for Poly(pyrazolyl)borate Ligands

There are a variety of pyrazole substituents that have been used in preparation of poly(pyrazolyl)borates. The Tp and Tp' nomenclature refers to HB(pz)₃ and HB(3,5-Me₂pz)₃ respectively.²⁸ Other poly(pyrazolyl)borate ligands have common names based on the Tp abbreviation. For example, Tp^{tBu} is HB(3-Bu^tpz)₃.²² Table 1 shows a selection of abbreviations for tris(pyrazolyl) borate ligands.



**Table 1**

Abbreviation	Structure	R ₃	R ₄	R ₅
Tp	HB(pz) ₃	H	H	H
Tp ^{me2} or Tp [/]	HB(dmpz) ₃	Me	H	Me
Tp ^{Ph}	HB(3-phenylpyrazolyl) ₃	Ph	H	H

Characteristics of Poly(pyrazolyl)borate Ligands

Poly(pyrazolyl)borates are isoelectronic with cyclopentadienyl because they are six electron donors with one minus charge. Also, they bind to three coordination sites of a metal.²² Figure 2.1 shows the bonding modes of coordinated hydrotris(pyrazolyl)borate and cyclopentadienyl ligands. The geometry of poly(pyrazolyl)borates can be bidentate or tridentate, depending on the metals and the substituents on the pyrazoles.

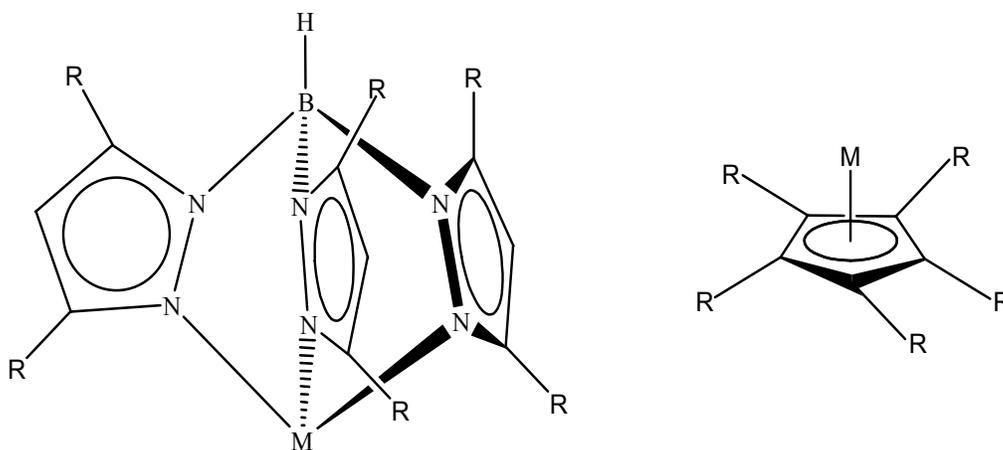


Figure 2.1 Bonding modes of hydrotris(pyrazolyl)borate and cyclopentadienyl ligands

Lanthanum Poly(pyrazolyl)borate Complexes

Lanthanum is the biggest metal in the lanthanide series and can have up to nine coordination sites. It generally has an oxidation number +3 in its complexes. With the large size and ionic bonding of lanthanum, the geometry and steric control in lanthanum complexes have been of interest. Bulky ligands such as poly(pyrazolyl)borates have been used to control the lanthanum coordination sphere.²⁹

There are several reports of synthesis of lanthanum complexes by the metathesis reaction of a lanthanum halide with the sodium or potassium salt of a poly(pyrazolyl)borate. Reaction of anhydrous LaCl_3 or lanthanum chloride hydrate with KTp or NaTp in THF afforded a good yield of LaTp_2Cl .³⁰

Substitution of the chloride ligand of Tp_2LaCl with an anionic bidentate ligand has been successfully reported. Anionic bidentate ligands such as β -diketonate, oxalates, and carboxylates can be accommodated due to the eight possible coordination sites on La. Some of these lanthanum complexes, such as are air stable and not moisture sensitive.³¹

Comparison of the Tp and Tp' Ligands

The preparation of Tp lanthanum complexes faces the problem of ligand redistribution. During higher temperature reactions, ligand redistribution of Tp on the lanthanum complexes becomes significant.³² The more sterically demanding ligand Tp' was found to suppress the ligand redistribution in the complexes.³³

Also, lanthanum complexes with Tp ligands have difficulties with solubility. The methyl groups on the 3' and 5' positions on the pyrazoles of Tp' tend to alleviate this problem. Moreover, with the steric crowding of Tp', its lanthanum complexes tend to be THF free, in contrast to related Tp lanthanum complexes, which have varying numbers of coordinated THF ligands.

Metathesis Reactions of Lanthanum Triflate

The synthesis of lanthanum poly(pyrazolyl)borate complexes was originally carried out by metathesis reactions of lanthanum halides with the poly(pyrazolyl)borate salt. Metathesis of lanthanum triflate has been subsequently investigated. Triflates were chosen as alternative starting materials because they contain a better leaving group relative to chlorides.³⁴ The lanthanum complexes containing a triflate ligand are good starting materials for further substitution chemistry.³⁵ This complex offers several advantages as compared to Tp_2LaCl . The Tp' ligand offers a more sterically demanding environment and suppresses ligand distribution. The triflate is a good leaving group which will be good for substitution reactions.

Lanthanum β -diketonate for MOCVD

β -diketonate complexes of metals have been used for the deposition of materials for electroluminescent devices (EL). Most thin films for EL devices require deposition

techniques such as CVD. The CVD requires volatile precursors that do not decompose at high temperature during the volatilization precursors. Lanthanum complexes that bear β -diketonate ligands have been used for MOCVD due to the volatility properties of the complexes.

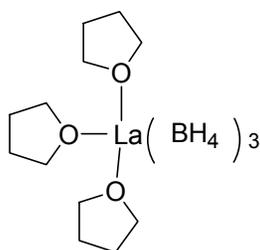
Lanthanum complexes containing β -diketonate ligands are volatile, anhydrous, unsolvated, and thermally stable.^{36,37} Fluorine substitution on the β -diketonate ligand increases the volatility of complexes.

Lanthanum Tris[bis(trimethylsilyl)amido] for MOCVD

Tris[bis(trimethylsilyl)amido]lanthanum has been used for MOCVD of lanthanum silicate thin films for semiconductor devices. The complex has been reported to be a volatile monomeric complex, which was used in the presence of oxygen for deposit of films over a wide range of temperature (350-600°C).³⁸ With the present of silicon on the complex, the silicon directly forms an lanthanum silicate film promoting the deposition. The content of Si did not vary with depth in these relatively thick of the films.

Chemistry of Lanthanum Borohydride Complexes

There have been reports of lanthanum tetrahydroborate complexes prepared by simple substitution of borohydride for halide ligands. For example, the tris(tetrahydrofuran) lanthanum tetrahydroborate complex **3** has been reported.³⁶ The complex is easily prepared by reacting anhydrous lanthanum chloride with an excess of sodium tetraborohydrate (e.q. 3.3). X-ray diffraction and ¹¹B NMR data for the complex have been reported.^{36,39}



Structure of Tetraborohydrate Complexes

The structure of metal tetrahydroborate complexes has been investigated. The structure of the complexes depends on the coordination environment and reaction conditions.⁴⁰ Marks and coworkers investigated the binding mode of the organolanthanide tetrahydroborate complexes using IR and Raman spectroscopy.⁴¹ The bonding of hydroborate and lanthanum is covalent.

Borohydride ligands can have four different modes depending on the environment of ligands around the metal (Figure 2.2). The binding mode of the tetrahedral BH_4^- ligand to a metal ion is an important structural feature of the complex. Only bidentate and tridentate binding modes are found in metal complexes as determined by IR. X-ray diffraction can also provide useful data for the binding modes. However, NMR does not yield meaningful structural information on tetrahydroborate metal complexes because they are fluxional on the NMR timescale.

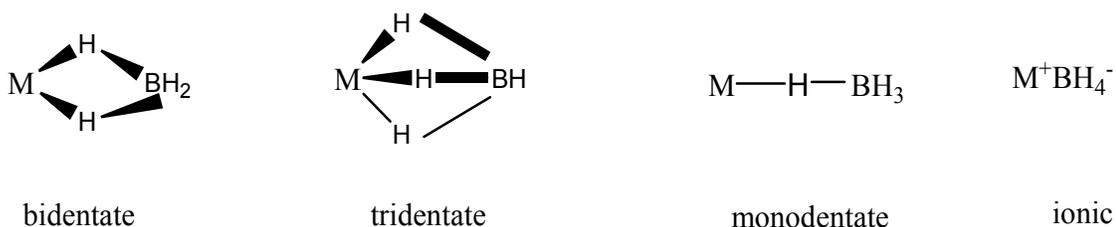


Figure 2.2 Binding Modes of Borohydride

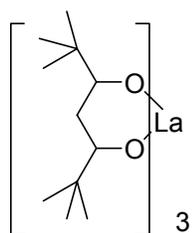
Conclusion

Lanthanum complexes bearing poly(pyrazolyl)borate ligands have been synthesized. Lanthanum complexes bearing such ligands are a good model to learn chemistry substitution of lanthanum complexes with borohydride anion. Lanthanum complexes used for the deposition of the CVD of LaB₆. The study of lanthanum complexes deposition allowed us to learn the optimized condition for the deposition of the CVD of LaB₆.

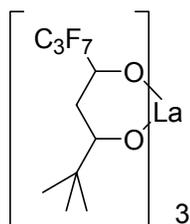
CHAPTER 3 EXPERIMENTAL RESULTS

Synthesis of MOCVD Precursors

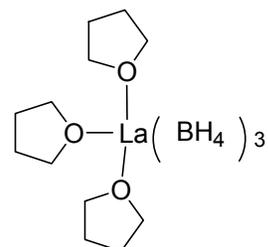
Complexes 1-4 have been tested as precursors for CVD as a source of lanthanum for LaB_6 . Each of these compounds has been synthesized following the literature procedure.^{31,42,43}



1



2



3

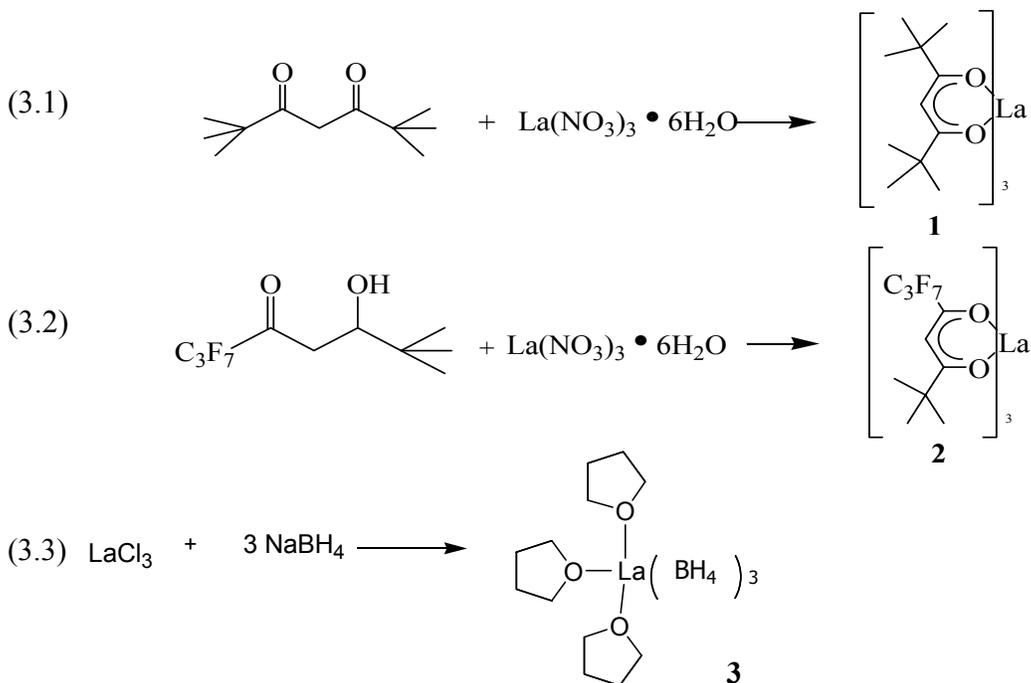


4

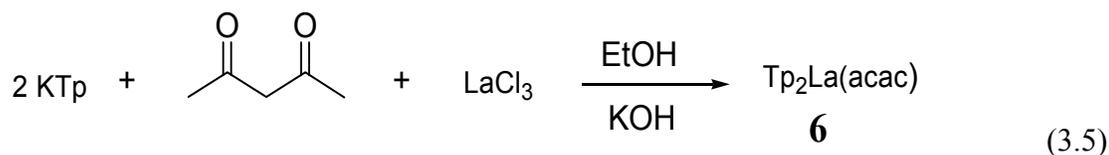
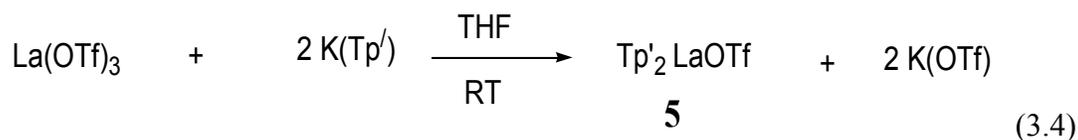
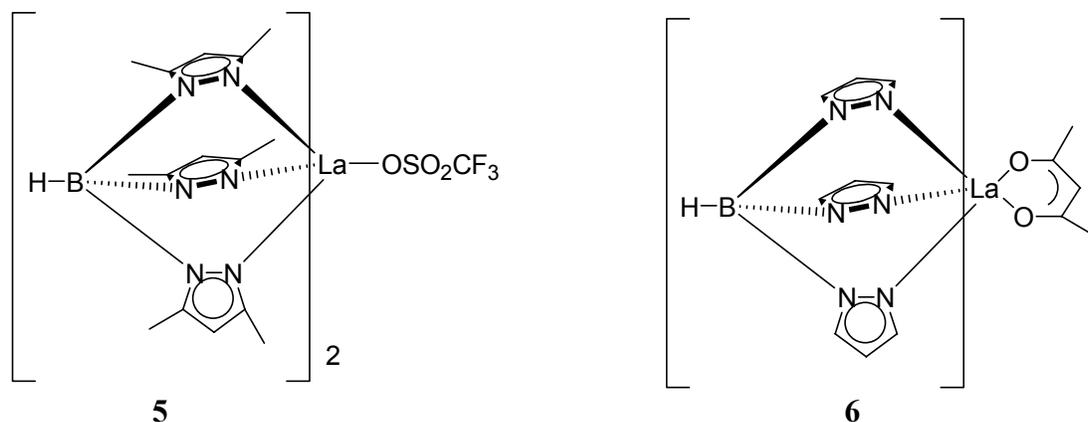
Lanthanum β -diketonate complexes such as **1** and **2** are good candidates for lanthanum precursors for MOCVD of LaB_6 . The bulky β -diketonate ligands promote volatility and inhibit association of the complexes during the deposition. Precursors **1** and **2** are easily prepared following the literature.^{36,37}

Complexes such as **3** precursors are good candidates for a single source precursor for MOCVD of LaB_6 which contain La and B.

The complex is easily prepared by reacting anhydrous lanthanum chloride with an excess of sodium tetraborohydrate (e.q., 3.1).



Complex **4** prepared following the literature.⁴⁴ Complexes **5** and **6** were synthesized following the literature procedure for the simple metathesis reaction (eq.3.4-3.5).⁴⁵ Clark and coworkers investigated the reaction of the lanthanum complex **5** with other ligands such as acetonitrile, benzonitrile, amines, puridine, and nitrile.³⁸ Only acetonitrile bound to the lanthanum complex, forming $\text{Tp}'_2\text{La}(\text{MeCN})(\text{OTf})$. Also the addition of NaNO_3 to the solution of the complex in THF resulted in the formation of $\text{Tp}'_2\text{LaNO}_3$ in monodentate fashion.



Mass Spectrometry and Film Growth Study of Complexes 1 and 2

Mass spectrometry experiments were carried out with both **1** and **2**. These experiments have yielded information about the fragmentation characteristics of the complexes under gas phase ionization conditions. The utilization of mass spectral data predicts possible mechanisms for MOCVD processes, and MS data provide probable fragmentation patterns of the lanthanum complexes as CVD precursors.

The positive ion electron-impact ionization (EI) mass spectra of **1** and **2** yielded similar fragments. The molecular ion could be observed from both **1** and **2**. The base peak in the EI spectrum of **1** occurs at m/z 505 and is assigned to the $[\text{M} - \text{C}_{11}\text{H}_{19}\text{O}_2]^+$ fragment uses from loss of the β -diketonate ligand. The organic ion observed in the EI spectrum occurs at m/z 57, corresponding to the fragment $[\text{t-Bu}]^+$. Other mass envelopes are consistent with a loss of $[\text{t-Bu}]^+$ and the β -diketonate ligands.

The mass spectral analysis of **2** also yielded a similar pattern of fragments. The base peak in the EI spectrum of **2** occurs at m/z 729 and is assigned to the $[M - C_9H_9O_2F_7]^+$ fragment which arises from loss of the β -diketonate ligand. The organic ions observed in the EI spectrum occur at m/z 57 $[t\text{-Bu}]^+$ and 169 $[C_3F_7]^+$. Other mass envelopes are consistent with the loss of $[t\text{-Bu}]^+$ and $[C_3F_7]^+$

The mass spectral data collected for **1** and **2** offer some perspectives about their potential as MOCVD precursors. The cleavage of the β -diketonate moiety from the lanthanum complexes is necessary for the CVD process in forming LaB_6 films. However, the observation of the organic fragments may indicate potential problems with controlling contamination in films.

After the fragmentation analyses were carried out, precursors **1** and **2** were used to deposit thin films. The source of boron was used either $BH_3 \bullet THF$ 1 M or diborane (B_2H_6). Deposition tests required transport of the solid lanthanum precursor to the reactor in the vapor phase. Each precursor was dissolved in an appropriate solvent to a concentration of 12.6 mg/mL and volatilized using the nebulizing reactor described in Chapter 1. Film depositions were carried out by Omar Bchir.

The X-ray diffraction (XRD) results do not indicate any film crystallinity for growth from **1** or **2** except for SiO_2 formation on the substrate Si (100) and Si (111) at 600, 700, 800, and 900 °C. The film composition was characterized by Auger electron spectroscopy AES. AES results indicate deposition of B and a very small amount of La (less than 1%) from **1**. AES indicates deposition of La, B, C, O, and F from **2**. The concentration (atomic %) of La varied from 19%- 35 % at 600, 700, and 800 °C. However, at 900°C, the AES result indicates 10 % of La.

Mass Spectrometry and Film Growth Study of Complex 4

Mass spectrometry experiments were carried out with **4**. These experiments have yielded information about the fragmentation characteristics of the complexes under gas phase ionization conditions. The utilization of mass spectral data predicts possible mechanisms for MOCVD processes, and MS data provide possible fragmentation patterns of the lanthanum precursors under deposition conditions.

The positive ion electron-impact ionization (EI) mass spectrum of **4** was obtained. The molecular ion could be observed at m/z 619. The base peak in the EI spectrum of **4** occurs at m/z 160 and is assigned to the $[\text{N}(\text{SiMe}_3)_2]^+$ fragment. Another lanthanum-containing fragment was found at m/z 299 $[\text{M} - 2(\text{N}(\text{SiMe}_3)_2)]^+$. The mass spectral data collected for **4** offer some perspectives about these systems as MOCVD precursors. The cleavage of the trimethylsilylamido moiety from the lanthanum complexes is necessary for the CVD process in forming LaB_6 films.

After the fragmentation analyses were carried out, precursor **4** was used to deposit thin films. The source of boron was diborane (B_2H_6). Deposition tests required transport of the solid lanthanum precursor to the reactor in the vapor phase. The precursor was dissolved in benzonitrile to a concentration of 12.6 mg/mL and volatilized using the nebulizing reactor described in Chapter 1.

The X-ray diffraction (XRD) results indicate amorphous films were deposited on Si (100) and Si (111) from 300-800 °C. The film composition was characterized by AES. AES indicates deposition of B, C, O, and N during experiment with **4**. However, the AES data indicate that no La was deposited in the film.

Film Growth Study of 3

Precursor **3** was used to deposit thin film. The source of boron was used either $\text{BH}_3 \cdot \text{THF}$ 1 M or diborane (B_2H_6). Deposition tests required transport of the solid lanthanum precursor to the reactor in the vapor phase. The precursor was dissolved in benzonitrile to a concentration of 12.6 mg/mL and volatilized using the nebulizing described in chapter 1.

The X-ray diffraction (XRD) results indicate amorphous films were deposited on Si (100) and Si (111) at 300-800 °C. The film composition was characterized by AES. AES indicates deposition of B, C, and O during experiment with **3**. However, AES data indicate that no La was deposited in the films.

Conclusion

Several precursors were used to deposit on Si thin film at the optimized condition. The result showed that solvents and co-solvents might be the source the contamination. Mass spectrometry study showed the cleavage of ligands that were expected. La composition is less than 10 % on the film characterized by AES and XRD.

CHAPTER 4 EXPERIMENTAL PRECEDURES

General Methods

Standard inert atmosphere techniques were used throughout. Tetrahydrofuran and benzene were purified by passage through a MBRAUN MB-SP series purification system.

All chemicals used were purchased in reagent grade and used with no further purification. ^1H , ^{13}C , ^{11}B , and ^{19}F NMR spectra were recorded on Varian Gemini 300 and VXR 300 spectrometers. IR spectra were recorded on a Perkin-Elmer 1600 FTIR. High and low resolution mass spectrometry analyses were performed by the University of Florida analytical service.

Tris 2,2,6,6-tetramethyl-3,5-heptanedione lanthanum (III) (1)

2,2,6,6-Tetramethyl-3,5-heptanedione [H(thd)] (1.7 g, 9.3 mmol) was dissolved in 30 mL of 95% methanol. NaOH was dissolved in 50 mL of 50% aqueous methanol. The solution of NaOH (10 mL) was added into a solution of H(thd). Then the mixture was added to a solution of lanthanum (III) nitrate heptahydrate (1.3 g, 3.0 mmol) in 50% aqueous ethanol (30 mL). The mixture was allowed to stir for 2 hours. The solvent was removed until the volume was decreased by half, and distilled water (50 mL) was added to precipitate the product. The white solid was obtained by filtration and dried in vacuo to obtain **1** in 90 % yield. The product was characterized by comparison with literature data.³⁷ ^1H NMR (CDCl_3) δ 1.08 (s, 9 H), 5.68 (s, 1 H); ^{13}C NMR (CDCl_3) δ 28.88, 41.10,

93.26, 200.42 mp = 240 °C; LRMS (EI): m/z 688 $[M]^+$, 631 $[M - t-Bu]^+$, 505 $[M - C_{11}H_{19}O_2]^+$, 287 $[LaC_8H_{10}O_2]^+$, 127 $[C_7H_{10}O_2]^+$, 57 $[t-Bu]^+$.

Tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione) lanthanum (III) (2)

Lanthanum (III) nitrate heptahydrate (0.4 g, 1.0 mmole) was dissolved in the minimum amount of absolute methanol. The pH of the mixture was adjusted to pH 4-6 by adding the minimum amount of a solution of 4.12 M aqueous NaOH. A solution of 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (Hfod) (0.9 g, 3.3 mmole) in 20 mL of absolute ethanol was brought to pH 7 using 4.12 M sodium hydroxide solution. The mixture of Hfod and lanthanum (III) nitrate heptahydrate adjusted pH was allowed to stir while 40 mL distilled water was added. The resulting precipitate was collected and dried in vacuo. The product was obtained in 55% yield and characterized by comparison with literature data.⁴² 1H NMR ($CDCl_3$) δ 1.12 (s, 9 H), 6.02 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.59, 27.83, 42.42, 85.84; mp = 226°C; LRMS, (EI): m/z 1024 M^+ , 967 $[M - t-Bu]^+$, 855 $[M - C_3F_7]^+$, 169 $[C_3F_7]^+$, 57 $[t-Bu]^+$.

Tris(tetrahydrofuran) lanthanum tris(tetrahydroborate) (3)

A mixture of anhydrous lanthanum chloride (1.0 g, 4.1 mmole) and a 20 % excess of sodium borohydride (0.6 g, 15 mmole) in 30 mL dry THF was allowed to stir for 12 hours. The white precipitate of sodium chloride was removed by filtration and the liquid phase was collected. Then the solvent was removed by reduced pressure. The crude product was obtained as a white solid in 75 % yield. The crude product was recrystallized from a small amount of dry THF. The remaining sodium chloride was separated by filtration. The product was dried in vacuo and afforded **3** in 58% yield as a

white solid, which was characterized by comparison to literature data.³⁷ ¹¹B NMR (THF) δ -20.00 (q, 3 B).

Tris[bis(trimethylsilyl)amido]lanthanum(III) (4)

A mixture of anhydrous lanthanum chloride (2.0 g, 8.2 mmol) and LiN(SiMe₃)₂ (4.1 g, 25 mmol) was stirred in dry THF for 12 hours. The solvent was removed under reduced pressure to obtain a white solid which was washed with petroleum ether. Evaporation of the solvent afforded **4** in 80% yield. The product was characterized by comparison to literature data.^{43,46} ¹H NMR (C₆D₆) δ 0.10 (s, 54 H), ¹³C NMR (C₆D₆) δ 25.4, m.p. = 146-147°C; LRMS, (EI): *m/z* 619 [M]⁺, 618 [M - H]⁺, 299 [M-2(N(SiMe₃)₂)]⁺, 160 [N(SiMe₃)₂]⁺.

Potassium hydrotris (3,5 -dimethyl pyrazolyl)borate

A mixture of potassium borohydride (0.2 g, 0.04 mol) and 5 equivalents of 3,5-dimethylpyrazole (12 g, 0.2 mol) was heated with stirring until hydrogen gas was generated. The mixture was allowed to stir for 75 minutes. The mixture was then cooled, and toluene was immediately added to the solution. The resulting precipitate was filtered and air dried. The product was obtained as a white solid in 70% yield and characterized by comparison with literature data. ¹H NMR (acetone d₆) δ 2.01 (s, 9H), 2.17 (s, 9H), 5.53 (s, 6H).

Bis[hydro(3,5 -dimethyl pyrazolyl)borato]lanthanum (III) triflate (5)

A mixture of KTp¹ (3.90 g, 11.6 mmol) and lanthanum triflate (3.40 g, 5.80 mmol) was stirred in 100 mL THF at room temperature for 12 h. The solvent was removed under reduced pressure. The solid was extracted with toluene (2 X 100mL) and the combined toluene extracts were concentrated. The white solid was precipitated by cooling

overnight. The product was obtained in 85% yield by decanting off the mother liquor and drying under vacuum. The product was characterized by comparison to literature data.³⁵ ¹H NMR (CDCl₃) δ 1.83 (s, 18H), 2.38 (s, 18 H), 5.67 (s, 6H); ¹³C NMR (CDCl₃) δ 12.93, 13.5, 106.3, 145.7, 150.2; IR (KBr pellet, cm⁻¹) 2963 (sh), 2931 (sh), 2560 (sh) ν B-H, 2358 (s), 1550 (s), 1440 (s), 1410(s), 1352 (m), 1300 (m), 1204 (vs), 1034 (vs), 980 (m), 804 (s), 688 (m), 639 (m); LRMS (EI): *m/z* 882 [M]⁺, 813 [M- CF₃]⁺, 733 [M- OSO₂CF₃]⁺, 786 [M- (3,5-Me₂pz)]⁺, 329 [La(3,5-Me₂pz)₂]⁺, 96 [3,5-Me₂pz]⁺.

Potassium Hydrotris(pyrazol-1-yl)borate

A mixture of potassium borohydride (2.0 g, 37.0 mmol) and 5 equivalents of pyrazole (12.6 g, 186.0 mmol) was heated together with stirring until hydrogen gas was generated. The mixture was allowed to stir for 75 minutes. The mixture was cooled and toluene (200 mL) was added to the solution. The resulting precipitate was collected by filtration and air dried to obtain potassium hydrotris(pyrazol-1-yl)borate in 65% yield as a white solid. The product was characterized by comparison with literature data.

¹H NMR (C₆D₆) δ 6.10 (t, 3 H), 7.20 (d, 3 H), 7.35 (d, 3 H).

Acetylacetonatobis[hydrotris(pyrazol-1-yl)borato]lanthanum(III) (6)

Potassium hydrotris(pyrazol-1-yl)borate (0.5 g, 2.0 mmol), pentane-2,4-dione (0.1 g, 1.0 mmol), ethanol (10 mL), and 0.01 M aqueous KOH (10 mL) were mixed and added to a solution of LaCl₃ • 6H₂O (0.3 g, 1 mmol) in water (15 mL). The mixture was allowed to stir for 1 hour. The white solid precipitate was collected by filtration and dried in vacuo to obtain **6** (70 %yield). The product was characterized by comparison with literature data.³¹ ¹H NMR (CDCl₃) δ 7.67 (d, 6 H), 7.14 (d, 6 H), 6.03 (t, 6 H),

5.63 (s, 1 H), 2.00 (s, 6 H); ^{13}C NMR (CDCl_3) δ 23.3, 44.0, 50.6, 133.2, 129.2, 105.6; m.p. = 193°C.

Addition of sodium borohydride to $\text{Tp}'_2\text{LaOTf}$

A solution of sodium borohydride (0.05 g, 1.2 mmol) in 10 mL dry THF was added to a solution of $\text{Tp}'_2\text{LaOTf}$ (0.5 g, 0.6 mmol) in 25 mL dry THF. The reaction was allowed to stir at room temperature for one day. After the reaction, the mixture was extracted with toluene and evaporated to obtain the white solid in 55 % yield. ^1H NMR (CDCl_3) δ 0.57 (s), 1.33 (s), 1.39 (s), 1.56 (s), 1.97 (s), 2.18 (m), 2.37 (m), 5.46 (s), 5.66 (d), 5.64 (s); ^{11}B NMR (THF) δ -14.95 (broad).

Addition of potassium borohydride to $\text{Tp}'_2\text{LaOTf}$

A solution of potassium borohydride (0.04 g, 1.2 mmol) in 10 mL dry toluene was added to a solution of $\text{Tp}'_2\text{LaOTf}$ (0.5 g, 0.6 mmol) in 25 mL dry toluene. The reaction was allowed to stir at 60 °C for one day. After the reaction, the solvent was removed by reduced pressure to afford the white solid in 70% yield. ^1H NMR (CDCl_3) δ 0.63 (s), 1.27 (s), 1.33 (s), 1.51 (s), 1.70 (s), 2.08 (m), 2.27 (m), 5.20 (s), 5.48 (d), 5.61(s).

Addition of $\text{BH}_3 \cdot \text{THF}$ to $\text{Tp}'_2\text{LaOTf}$

A solution of 1 M $\text{BH}_3 \cdot \text{THF}$ (1 mL) was added to a solution of $\text{Tp}'_2\text{LaOTf}$ (0.5 g, 0.6 mmol) in 20 mL dried THF. The reaction was allowed to stir at room temperature for two days. Then, the mixture was extracted with 20 mL of dry toluene and the solution was vacuum filtered. The collected toluene solution was evaporated to obtain a white solid residue in 55 % yield. ^1H NMR (CDCl_3) δ 1.77 (s), 2.23 (m), 3.67 (s), 5.71 (s), 5.86 (s), 5.96 (d).

Addition of Potassium Hydrotris(3,5- dimethylpyrazolyl)borate to

La(BH₄)₃(THF)₃

A solution of KTp' (1.7 g, 5.0 mmole) in 30 mL dry THF was added to a solution of La(BH₄)₃(THF)₃ (1.0 g, 2.0 mmole) in a 5 mL dry THF. The reaction was allowed to stir at room temperature for two days. Then, the mixture was extracted with 20 mL of dry toluene and the solution was vacuum filtered. The collected toluene solution was evaporated to obtain a white solid residue in 60 % yield. ¹H NMR (CDCl₃) δ 0.59 (s), 1.27 (s), 1.34 (s), 1.40 (s), 1.58 (s), 2.02 (s), 2.17 (s), 2.34 (m), 5.48 (s), 5.62(d), 5.72 (s).

Preparation of Precursor 1 for LaB₆ Deposition

All syringes were prepared in a dry box. Compound 1 (0.12 g, 0.14 mmol) was dissolved in 9.5 mL of triglyme in a small vial. Then, the solution of BH₃ • THF 1 M (1.5 mL) was added into the small vial. After the compounds dissolved completely in the solution, a syringe was filled with the mixture.

For a deposition with diborane, compound 1 (0.12 g, 0.14 mmol) was dissolved in 10.0 mL of triglyme in a small vial. After the compounds dissolved completely in the solution, a syringe was filled with the mixture.

Preparation of Precursor 2 for LaB₆ Deposition

All syringes were prepared in a dry box. Compound 2 (0.18 g, 0.18 mmol) was dissolved in 9.5 mL of benzonitrile in a small vial. Then, the solution of BH₃ • THF 1 M (1.5 mL) was added into the small vial. After the compounds dissolved completely in the solution, a syringe was filled with the mixture.

For a deposition with diborane, compound **1** (0.18 g, 0.18 mmol) was dissolved in 10.0 mL of benzonitrile in a small vial. After the compounds dissolved completely in the solution, a syringe was filled with the mixture.

Preparation of Precursor **3** for LaB₆ Deposition

All syringes were prepared in a dry box. For a deposition with diborane, compound **3** (0.18 g, 0.18 mmol) was dissolved in 10.0 mL of benzonitrile in a small vial. After the compounds dissolved completely in the solution, a syringe was filled with the mixture.

Preparation of Precursor **4** for LaB₆ Deposition

All syringes were prepared in a dry box. For a deposition with diborane, compound **4** (0.18 g, 0.18 mmol) was dissolved in 10.0 mL of triglyme in a small vial. After the compounds dissolved completely in the solution, a syringe was filled with the mixture.

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BIOGRAPHICAL SKETCH

Chuleekorn Chotsuwan was born on May 3, 1979, at Nonthaburi, Thailand. She grew up in a rural area of Thailand. As a child, she always had an interest in science and experiments. In 1996, she got a scholarship from the Thai government to study chemistry in the U.S. She started her undergraduate degree at University of Colorado at Boulder. In 2001, she went to study in graduate school at the University of Florida and joined Professor Lisa McElwee White's group and started her LaB₆ MOCVD project. She obtained her Master of Science in chemistry in May 2004.